Elaboration de membranes poreuses à partir d’émulsions stabilisées par des nanoparticules 2D (h-BNNS)

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le 30 Octobre 2018

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“Don’t be afraid of hard work. Nothing worthwhile comes easily. Don’t let others discourage you or tell you that you can’t do it”

Gertrude Elion
ACKNOWLEDGMENTS

There are many people I would like to thank for their support throughout my PhD. First of all, I would like to express my gratitude and appreciation to my supervisor Prof. Philippe Miele who gave me the chance to work in his group, for his continuous support, encouragement and unwavering guidance during these three years of thesis. I would like to thank as well my co-supervisors Dr. Julien Cambedouzou and Dr. Céline Pochat for their invaluable guidance and advice throughout my project. Special thanks to Dr. Mikhael Bechelany, which has been a mentor to me, for having always encouraged me, for his insightful suggestions and for asking me every day when the articles will be ready. The financial support of Labex CheMISyst is also acknowledged.

I would also like to acknowledge and thank all the members of the jury: Pr. Valérie Ravaine, Dr. Ludovic Dumée, Dr. Florence Babonneau and Dr. Martin In who have kindly accepted and examined this manuscript.

During these three years of thesis, I had the great pleasure to meet incredible people from all over the world even if with some of them we just share a couple of moments. When I first arrived at the institute, I met some students doing a short stay in our lab, Ayben (from Turkey), Jielin (from China), Laks (from India), and Carlos (from Mexico). I also had the opportunity to meet Maryline (Lebanon), an amazing person and friend with whom I share not only the office during two years but scientific discussions and a lot of laughs and good moments. But not the only Lebanese girl, I spend good moments and eat delicious Lebanese food with Sara and Marlene. Also special thanks for the post-doc in our group, Sakthi for all the good moments at the lab and his helpful scientific discussions, and Matthieu who always was willing to help to improve our scientific writing and our presentations.
Acknowledgments

I also have met some nice French people during these three years, Thomas, Lucy, Cyril, Marine, Marianne, Matthieu, Clément, Julien...with whom I shared not only ‘lunchtime’ and ‘coffee breaks’ but also good ‘apéros’ and ‘soirées’. Thank you for all the great times!

I cannot forget to thank my lovely Spanish/Mexican friends, Quike, Sofia, Octavio and Carlos, making French people a bit ‘pissed off’ with our ‘loud’ Spanish conversations and for all our stories laughs and the great times together. And for sure thanks to Ana (my crazy Brazilian girl) the year she spends between us was great always laughing and with hundreds of histories about her travels. Thanks guys, these years wouldn’t have been the same without you!

Special words for a special person, Habib, it has been not only an office-mate but a friend. We have shared a lot of great moments in the office sitting next to me during these three years, with our talks in the morning drinking our coffee and our ‘little’ beers at after a hard working day at the lab. Traveling around Europe (Amsterdam, Brussels, Copenhagen, Dubrovnik, Hamburg, Helsinki, Oslo, Prague, Stockholm...What next?? Valencia?) with you I could appreciate the fantastic person you are! Thanks for all for all the amazing and unforgettable moments and funny experiences. I wish you all the best for your last year of thesis; I know you will do a great job!

Lastly, I would like to thank the most important people in my life, my parents, who always support me in my decision to go abroad to do a PhD and encourage me to strive for the best and for bringing me up to know the value of hard work and perseverance. I would also like to thanks Pierre, for supporting me throughout this journey and sharing with me the best and the most complicated moments.
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Annex I  
Pickering emulsions (PE) stabilized by two dimensional (2D) materials: a comparative study

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Scientific Contributions
ABSTRACT

Emulsions stabilized through the adsorption of colloidal particles at the liquid-liquid interface have been of interest in a wide variety of applications, ranging from pharmaceutical or food products to templates for the preparation of new materials.

In this thesis, oil-in-water (O/W) and water-in-oil (W/O) emulsions are efficiently stabilized using colloidal inorganic particles (graphene oxide (GO) and hexagonal boron nitride nanosheets (h-BNNS)). The adsorption of particles to the oil-water interface is induced by adjusting the particle wetting behavior in the liquid media. Two types of emulsions, O/W and W/O are formed by using two-dimensional materials possessing different hydrophilic behaviors. The conditions required to reach the most stable emulsion using two different types of particles at different formulations are investigated. The final microstructure of the mixtures is tailored by adjusting the initial composition of emulsion. The use of high concentration of particles leads to enhanced stability of particle-stabilized emulsions. h-BNNS based emulsions were reported in this work for the first time and their behavior was deeply investigated. Furthermore, a novel green approach to obtain polyvinyl alcohol (PVA)-based porous membranes was reported. In this case, the addition of PVA to the emulsion increases its long term stability and allows its shaping using conventional technologies such as casting. The polymer composites obtained from emulsions stabilized with inorganic particles exhibit microporosity, showing typical pore dimensions of $0.19 \pm 0.03 \, \mu m$ or $1.1 \pm 0.3 \, \mu m$ depending on the curing time. These obtained porous membranes display good performance in water permeability and particle rejection. Membranes displaying a pore size of about $1.1 \, \mu m$ showed water permeability about $2 \, 000 \, L/h \, m^2 \, bar$, and a rejection rate of $86\%$ with particles of the same size as the pores.
RESUME

De nos jours, les émulsions stabilisées par adsorption de particules colloïdales à l'interface liquide-liquide (émulsions de Pickering) présentent un intérêt pour une grande variété d'applications allant des produits pharmaceutiques ou alimentaires aux modèles pour la préparation de nouveaux matériaux.

Dans cette thèse, des émulsions huile-dans-eau (H/E) et eau-dans-huile (E/H) ont été efficacement stabilisées grâce à des particules inorganiques colloïdales (oxyde de graphène (GO) et nanofeuilllets de nitrure de bore (h-BNNS)). L'adsorption de particules à l'interface huile-eau est induite par l'ajustement de la mouillabilité des particules dans les milieux liquides. Deux types d'émulsions, H/E et E/H, sont formées en utilisant des matériaux bidimensionnels qui possèdent des comportements hydrophiles différents. Les conditions requises pour atteindre l'émulsion la plus stable sont étudiées en variant la formulation de l'émulsion pour chaque type de particules. Les microstructures finales des émulsions peuvent être modifiées en ajustant leur composition initiale. L'utilisation d'une concentration élevée de particules améliore la stabilité des émulsions. Des émulsions à base de h-BNNS ont été rapportées dans ce travail pour la première fois et leur comportement a été profondément étudié. De plus, une nouvelle approche verte pour obtenir des membranes poreuses à base d'alcool polyvinylque (PVA) a été rapportée. Dans ce cas, l'ajout de PVA à l'émulsion augmente sa stabilité à long terme et permet sa mise en forme à l'aide de technologies conventionnelles telles que l’étalement. Les composites polymères obtenus à partir d'émulsions Pickering présentent une microporosité de $0,19 \pm 0,03 \mu m$ ou $1,1 \pm 0,3 \mu m$ en fonction du temps de séchage.
Les membranes poreuses obtenues présentent de bonnes performances en matière de perméabilité à l'eau et de rejet des particules. Pour des membranes ayant une taille de pores d'environ 1,1 µm et une perméabilité à l'eau d'environ 2000 L/h/m², un taux de rejection de 86% a été mesuré avec des particules de la même taille que les pores.
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GENERAL INTRODUCTION
General Introduction

Emulsions are defined as a mixture of one liquid dispersed in another immiscible liquid in the form of droplets, and stabilized by an emulsifying agent. Conventional emulsions stabilized by surfactants or polymers, find numerous applications in industrial and daily life. Emulsions are commonly classified into two types: (1) oil-in-water (O/W) emulsions, in which oil droplets are dispersed in an aqueous medium; (2) water-in-oil (W/O) emulsions, in which water droplets are dispersed in an oil medium. About a century ago, Pickering discovered that fine solid particles could be used to stabilize emulsions instead of surfactants. These solid-stabilized emulsions, are also known as Pickering emulsions.¹ Recently, there has been a growing interest in this kind of emulsions as they are often encountered in the recovery, separation, and cleaning of crude oil, wastewater treatment, food industry, etc. Compared to classical surfactants as emulsifiers, particles often achieve better emulsion stability. The adsorption of particles at the oil-water interface is accomplished by adjusting the wetting of the particles by the two immiscible liquids. In addition, different types of emulsions can be obtained by varying this parameter. The final microstructure of oil-water mixtures are tailored by adjusting the initial composition of emulsions. The use of high concentration of particles leads to enhanced stability of particle-stabilized emulsions. The rheological properties of Pickering emulsions have a direct dependence on the initial formulation of the emulsions, factors such as the particle concentration and dispersed phase volume fraction are playing a role on final properties.² Moreover, these emulsions have become popular as precursors and templates for the assembly of novel materials.³ A special type of Pickering emulsions stabilized by 2D materials has become popular due to they provide better features and behaviors to stabilize the emulsions such as high atomic efficiency or barrier properties.⁴
The primary propose of this research was to provide a better understanding and to gain insights about the effect of two-dimensional materials stabilized Pickering emulsions. The second objective was to further investigate the use of these Pickering emulsions for the preparation of porous materials, in particular polymer porous membranes for water purification. The aim is to find an easy, low-cost and environmentally friendly method for the development of porous membranes with high flux, good selectivity and anti-fouling properties. This thesis is divided into 6 chapters:

❖ **Chapter 1:** In this chapter we introduce the concept of Pickering emulsions, the advantages of using 2D materials for their preparation and the application of these emulsions to produce porous materials. This chapter is divided in three main sections. The first section is based on a literature review concerning Pickering emulsions stabilized with different types of particles and their destabilization methods. The second part contains an overview of the different approaches, bottom-up and top-down, for the production of two-dimensional hexagonal boron nitride nanosheets which will be used to stabilize the Pickering emulsions. The last section will be dedicated to the application of these Pickering emulsions for the production of porous materials. The different methods described in the literature for obtaining these types of materials and in particular porous polymer materials will be as well discussed.

❖ **Chapter 2:** This chapter will be dedicated to detail the different materials and methods used to carry out the exfoliation of hexagonal boron nitride (h-BN), the preparation of graphene oxide (GO) and h-BN nanosheets (h-BNNS) based emulsions and the development of porous membranes through the as-prepared emulsions. The different techniques used to characterize the obtained materials will be also described in detail.
Chapter 3: In this chapter the exfoliation of hexagonal boron nitride (h-BN) in liquid phase by ion intercalation was investigated. A green approach to prepare exfoliated h-BNNS from commercially available pristine h-BN involving a two-steps procedure was developed.

Chapter 4: In this chapter the formation of inverse Pickering emulsions using exfoliated h-BN as an effective particulate stabilizer without using any surfactants is reported. The stability and the type of h-BNNS emulsion were deeply investigated. Different aspects such as the surface coverage and the rheological properties depending on the dispersed phase volume fraction were here addressed.

Chapter 5: In this chapter the development of novel hexagonal boron nitride nanosheets/polyvinyl alcohol (h-BNNS/PVA) porous membranes via Pickering emulsion templating was investigated. Nowadays, membrane technology for water separation and purification is growing in importance compared to other technologies owing to its energy efficiency. Among different materials for the preparation of membranes, polymers are the best candidates for the development of porous membranes because of their well-defined nanostructures and functionally. PVA has promising properties such as biodegradability, biocompatibility, non-toxicity; and furthermore it is a hydrophilic polymer. The templating method gives the advantage over other methods (sintering, phase inversion, coating or electrospinning) to control the porosity in the final obtained material by tuning the concentration of the different species (stabilizer, polymer and volume fractions ratios).
Annex I: In this annex a comparative study of Pickering emulsions stabilized by two-dimensional materials was carried out. Graphene oxide (GO) and hexagonal boron nitride nanosheets (h-BNNS) were used as emulsion stabilizers. GO nanoparticles were prepared through the oxidation of graphene by Hummer’s method. The exfoliation of hexagonal boron nitride (h-BN) was carried out in liquid phase through ion intercalation. The emulsions were prepared through sonication of a mixture containing water, oil and the above cited nanoparticles. It was found through confocal laser microscopy characterization that each type of particles could stabilize two kinds of emulsions depending on their hydrophilic behavior. GO due to its hydrophilic behavior stabilize O/W emulsions while h-BNNS with hydrophobic behavior stabilize W/O emulsions. The droplet size and their microstructure depend strongly on the initial particle concentration. The rheological behavior of both GO and h-BNNS based emulsion was investigated.
REFERENCES

Chapter 1

INTRODUCTION
Pickering emulsions can be described as emulsions stabilized by solid particles. They play an important role in many applications such as food technology, oil recovery, surfactant-free cosmetics and skin care products. More recently, they have become popular as templates for the synthesis of novel materials \textit{via} a self-assembly process, including microcapsules, foams or membrane composites. In comparison to classical surfactants, particles provide better features as emulsifiers.

The aim of this chapter is to give some background information on the different types of Pickering emulsions stabilized with particles of different shapes. In particular, we will focus our attention in a special type of two-dimensional material, hexagonal boron nitride nanosheets. We will discuss their features and our interest to use this type of particles as stabilizers, and furthermore we will give an overview of their different synthesis routes. To conclude this chapter, the procedures for obtaining porous materials \textit{via} soft templating method routes will be presented.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{flowchart.png}
\caption{Flowchart of the different sections presented in this chapter}
\end{figure}
1.1 Conventional Emulsions

1.1.1 Introduction

An emulsion is a colloidal dispersion of two or more immiscible liquids, typically oil and water, formed when an energy input is provided through shaking, stirring, homogenizing or applying power ultrasound. The emulsions are usually composed of one phase (called dispersed phase) dispersed in a second phase (called continuous phase) with a liquid-liquid interface formed by the droplet surfaces. Emulsions are thermodynamically unstable mixtures; this concept can be understood by considering the change in Gibbs free energy during the emulsification process, given by $^{1}$:

$$\Delta G = \gamma \Delta A - T \Delta S$$  \hspace{1cm} \textbf{Equation 1.1}

where $\Delta G$ = Change in Gibbs free energy (J); $\gamma$ = Surface or interfacial tension (N/m or J/m$^2$); $\Delta A$ = Increment of area (m$^2$); $T$ = Temperature (K); and $\Delta S$ = Change in entropy (J/K)

In order to minimize the interfacial free energy, the emulsion droplets tend to coalesce over time, thus reducing the interfacial area of two phases, until complete phase separation is achieved. This process can be slowed down dramatically, however, in the presence of emulsion stabilizers such as surfactants or colloidal particles. The adsorption of surfactants at interface induces a decrease of the interfacial tension and therefore lowers the free energy of the liquid-liquid interface. In contrast, the adsorbed particles acts as emulsifier to lower the free energy primarily by reducing the interfacial tension between two phases. $^{2}$
In conventional emulsions, surfactants, polymers or a mixture of both are used as the emulsifying agent. Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic (lipophilic) groups (their “tails”) and hydrophilic groups (their “heads”). Therefore, a surfactant contains both a water-insoluble (or oil-soluble) component and a water-soluble (or oil-insoluble) component. In conventional emulsions, surfactants will diffuse in water and adsorb at interfaces between air and water or at the interface between oil and water, in the case where water is mixed with oil. The water-insoluble hydrophobic group may extend out of the bulk water phase, into the air or into the oil phase, while the water-soluble head group remains in the water phase. The adsorption of the surfactant molecules reduces the interfacial tension and the thermodynamic instability caused by the increase in interfacial surface area. This distribution forms a barrier shifting the system towards a lower energy and more stable state and thereby prevents droplet-droplet coalescence.3

Figure 1.2 Schematic illustration of conventional emulsion with surfactants or polymers assembled at the interface
1.1.2 Emulsion type

The emulsions can be categorized depending on the nature of the emulsifier, on the nature of dispersed phase, or on the droplet size.

According to the size of their droplets, three types of emulsions can be distinguished:

1. Macroemulsions: the most well-known type, with droplets size from 1.5 – 100 µm
2. Miniemulsions: with droplets size from 50 – 500 nm
3. Microemulsions: with droplets size < 50 nm

Depending upon the nature of the dispersed phase, the emulsions are classified as:

1. Oil in water (O/W, or “direct” emulsions): the emulsion in which oil is present as the dispersed phase and water as the dispersion medium (continuous phase)
2. Water in oil (W/O, or “inverse” emulsion): the emulsion in which water forms the dispersed phase and oil acts as the dispersion medium
3. Double and multiple emulsions: water-in-oil-in-water (W/O/W) and oil-in-water-in-oil (O/W/O). In these systems both oil in water and water in oil emulsion exist simultaneously, they are considered as emulsions-of-emulsions.

Figure 1.3 Scheme of the different types of emulsions: a) oil in water, b) water in oil, c) water-in-oil-in-water and d) oil-in-water-in-oil.
The type (O/W or W/O) of emulsion that forms is dependent on various parameters. These include the nature of the emulsifier, the volume ratio of each phase, the miscibility of the two phases and the rate and order of mixing the components in the emulsion system. Generally the Bancroft’s rule is applied to predict the type of emulsion that may form. The rule states that the phase in which an emulsifier is more soluble constitutes the continuous phase.\cite{4} For surfactant-stabilized emulsions, consistently with the Bancroft’s rule, more oil-soluble surfactants tend to stabilize water-in-oil emulsions, and more water-soluble surfactants tend to stabilize oil-in-water emulsions. There is a parameter, the so-called Hydrophilic-Lipophilic Balance (HBL) value, that is used to determine whether for practical purposes, a surfactant or a surfactant mixture may be considered more lipophilic (oil-soluble) or more hydrophilic (water-soluble). The HBL values can be estimated based on calculating the mass ratio of hydrophilic part over the total mass of surfactant molecules.\cite{5}

For particle-stabilized emulsions, the emulsion type depends on the particle wettability. This parameter can be quantified by measuring the contact angle between the particle and at least one of the phases. This part will be described in more details in the next section, which will be dedicated to Pickering emulsions.

To summarize, this section introduced some basic concepts of conventional emulsions, the different types of emulsions and the most important parameters for their stabilization. The following section discusses the details of emulsions stabilized by solid particles and related concepts.
1.2  Pickering emulsions

1.2.1  Introduction

Pickering emulsions or solid-stabilized emulsions were defined at the beginning of the 20th century in pioneering works of Ramsden\textsuperscript{6} and Pickering.\textsuperscript{7} They are described as colloidal suspensions stabilized only by solid particles instead of organic surfactants or polymers. These solid particles are adsorbed at the liquid-liquid interface and are expected to form a barrier to prevent the droplet-droplet coalescence. As classical emulsions, they can be simply categorized based on the particle wettability: on the one hand, emulsions formed with hydrophilic particles normally stabilized Oil-in-Water (O/W) emulsions; on the other hand, those prepared with hydrophobic particles more probably form Water-in-Oil (W/O) emulsions.

![Schematic Illustrations of Two Types of Pickering Emulsion Droplet Depending on the Dispersed Phase Stabilized by Solid Particles](image)

**Figure 1.4** Schematic illustrations of two types of Pickering emulsion droplet depending on the dispersed phase stabilized by solid particles.
Despite the advantages of particles over surfactant based emulsions, such as higher stability and lower toxicity, research in Pickering emulsions have stalled for a long period after their first disclosure. Recently, there has been an increasing interest in this kind of emulsions because they open a highway for potential new applications. Pickering emulsions have so far been used widely in many industrial applications such as food technology,\(^8\) cosmetic products,\(^9\) oil recovery,\(^10\) and more recently, in drug delivery.\(^11\) Many types of solid particles, organic or inorganic, have been reported as Pickering emulsifiers. Here we listed the more important types of particles, and how different researches have used them to stabilize emulsions.

### 1.2.1.1 Spherical particles

The most extensively studied particle emulsifiers during last decades have been silica particles. Binks \textit{et al.} have used silica particles to investigate various aspects of oil-water emulsions such as phase inversion,\(^12,13\) solid wettability,\(^14,15\) and thermo- and pH-responses.\(^16\) In other studies, Arditty \textit{et al.} have investigated the coalescence aspects\(^17\) of emulsions stabilized by silica particles and their rheological properties.\(^18\) Calcium carbonate has been used as stabilizer for O/W emulsions, the particles also acted as nucleation sites for the subsequent crystallization of \(\text{CaCO}_3\) with the addition of \(\text{CaCl}_2\) and \(\text{CO}_2\) gas as precursors.\(^19,20\) Teixeira \textit{et al.}\(^21\) have studied the different mechanistic aspects of the Pickering emulsion polymerization process using laponite clay as stabilizer with a variety of monomer mixtures. Another kind of particles studied by Binks \textit{et al.} is polystyrene latex particles. They prepared emulsions with different types of oils using latex particles with different wettability. They found that the type of emulsion formed depended on the wettability of the particles and that as the particle diameter increased, the emulsion droplet diameter increased and the stability of emulsions decreased.\(^22,23\)
1.2.1.2 Two-dimensional particles

Recent research has established the ability of two dimensional (2D) materials such as graphene oxide (GO) to stabilize Pickering emulsions. Kim et al.\textsuperscript{24} first reported GO-stabilized liquid-liquid emulsions, and He et al. recently reported the effects of pH, ionic strength, sonication time, and GO concentration on their behavior and effectiveness.\textsuperscript{25} Moreover, our group has demonstrated the ability of other kinds of 2D materials, i.e. hexagonal boron nitride (h-BN) to stabilize Pickering emulsions.\textsuperscript{26}

Although the phenomenon of emulsification was discovered more than one century ago and despite the significant increase in the use of Pickering emulsions in different fields, the underlying fundamental mechanisms of emulsion stabilization by solid particles are still unclear and lack in general harmony. Various factors play important roles in Pickering emulsions stabilization and the following section discusses more in detail some of the mechanisms.

1.2.2 Emulsion stability and destabilization mechanisms

What does “stability of an emulsion” means? The term ‘emulsion stability’ refers to the ability of an emulsion to keep its properties unchanged over a certain period of time. However, if an emulsion is thermodynamically unstable, it means changes in its properties will occur; the more slowly the properties change, the more stable the emulsion is. The lack of thermodynamic stability is caused by the large interfacial W/O area upon emulsification and the corresponding increase in the interfacial Gibbs free energy (see Equation 1). The positive free energy of forming this interface always outweighs the negative contribution from particles attachment. Although attached particles are not at equilibrium, they are irreversibly attached, giving emulsions kinetic stability. Several mechanisms have been proposed to explain emulsion destabilization.
In general, the destabilization of Pickering emulsion can involve several mechanisms that can lead to macroscopic phase separation of an emulsion; they are illustrated in the Figure 1.5. Two or more of these instability phenomena may occur at the same time. Here below we will describe more in detail the different phenomena:

**Sedimentation/Creaming**: These phenomena are mainly determined by the density difference ($\Delta \rho$) between the continuous and the disperse phases, the droplets size ($D$) and the viscosity ($\eta$). Due to gravity, droplets tend to move up or down through the continuous phase.\textsuperscript{27,28} If droplets have a higher density, they tend to move down to form a layer at the bottom of the emulsion. This phenomenon is known as sedimentation. On the contrary, if the droplets have a lower density than the continuous phase, they tend to move up to form a layer droplet on top of the emulsion. This phenomenon is known as creaming. Generally, if the density of oil is lower than the density of water, thus droplets of O/W emulsions tend to cream, while those of W/O emulsions tend to settle. The creaming rate of a single droplet that is not subject to deformation is given by Stokes’ law\textsuperscript{29} (Equation 1.2).

\[
v = \frac{2gr^2\Delta \rho}{9\eta_{\text{cont}}}
\]

**Equation 1.2**

where: $g$ is the acceleration due to gravity, $r$ is the radius of the droplet, $\Delta \rho$ is the density difference between the droplet and the continuous phase and $\eta_{\text{cont}}$ is the viscosity of the continuous phase.
There are different ways to reduce the creaming rate: one way is to minimize the density between the two phases, another way is to reduce the interfacial tension. The creaming rate can also be reduced by increasing the continuous phase viscosity to decrease the velocity at which the droplet moves down, or by increasing the droplet concentration, which leads to a closely droplet packing preventing their movement.

**Flocculation:** It is the process whereby two or more particles or droplets associate with each other maintaining the primary droplets size into larger units. Flocculation occurs when there is not sufficient repulsion to keep the droplets apart to distances where the van der Waals attraction is weak. Depending on the attractive energy input, the flocculation may be reversible (weak flocculation) or irreversible (strong flocculation). The formation of droplets flocs in the emulsion has an influence on the creaming rate.\(^{30,31}\) In diluted emulsions, flocs, which do not or hardly interact between each other, tend to increase the creaming rate, since larger particles are more subject to gravitational effect. On the other hand, the presence of flocs tends to increase the emulsion viscosity, which can slow down the creaming. The colloidal stability or the flocculation stability is of great importance for the synthesis of advanced materials from Pickering emulsions droplets.

**Ostwald ripening:** It is a process of gradual growth of the smaller droplets into larger ones due to mass transport of soluble dispersed phase through the continuous phase. The solubility of the oil phase increases with decreasing the droplet radius. In polydispersed emulsions, the smaller droplets exhibit a greater solubility than larger ones due to curvature effects. Over time, the smaller droplets shrink (and will eventually disappear) and the larger droplets expand as molecules of smaller droplets diffuse into large droplets. This phenomenon will be suppressed when the disperse phase has low solubility in the continuous phase.
In our work, the used oil phase is ethyl benzoate, a non-polar oil with low solubility in water (0.72 mg/mL at 25°C), and thus Ostwald ripening will not play an important role in the evolution towards phase separation. Ostwald ripening may be prevented if particles are densely packed at water-oil interfaces, even in systems with water-soluble-oil.\textsuperscript{32}

**Coalescence:** It is the process in which two droplets merge together to form a larger single droplet due to the thinning and rupture of the film separating the two phases. The new drop has a reduced specific surface area. Two limiting situations have been explored experimentally. For poorly stabilized drops, the characteristic time separating two coalescence events is limited either by Brownian diffusion\textsuperscript{33} (in diluted emulsions) or film drainage\textsuperscript{34} (in concentrated emulsions). When droplets move close to each other, they may be deformed and the surface of the droplets may be flattened.\textsuperscript{35} This deformation leads to a larger surface of exchange between the droplets and thus to the coalescence. The rate at which the thin film between the two phases break has a great interest to predict coalescence.\textsuperscript{36} The film rupture mechanisms are largely dependent on the properties in the continuous phase of emulsifiers adsorbed on the droplets. One should also take into account that droplets are moving constantly, so collision time may be short. However, if this time is long compared to the time required for the film to break, coalescence is likely to occur.\textsuperscript{27}

Initially, the interfacial particle coverage is insufficient to halt droplets coalescence. As droplets grow in size, the degree of particle coverage increases until a dense interfacial particle layer is formed that inhibits further coalescence. This process is known as limited coalescence and generates kinetically stable emulsions with relatively narrow droplets size distributions.\textsuperscript{17,37}
In a unique case, particles protruding from a droplet can simultaneously adsorb to another interface, bridging two droplets with a shared particle monolayer; this configuration allows the equilibrium contact angle to be satisfied on both sides of the bridging particle and thus prevents the coalescence phenomenon.\textsuperscript{38}

\textbf{Figure 1.5} Flowchart of breakdown processes in emulsions
1.2.3 Pickering emulsion type

In particles-stabilized emulsions, the type of emulsion is governed by the particle wettability, which can be quantified by measuring the water contact angle. In this case, the Bancroft rule can be interpreted as saying that hydrophilic particles – those with contact angle smaller than 90° measured through water phase – prefer to stabilize oil-in-water emulsions, whereas particles with a contact angle greater than 90° are hydrophobic and tend to stabilize water-in-oil emulsions (Figure 1.6). If the particles are completely wetted by water and oil, they remain dispersed in either phase and no stable emulsions are formed. 39

The preferred formed emulsion according to Bancroft rule upon mixing equal volumes of oil and water phase is those with the potential for high long term stability. The type of emulsion formed can be altered by changing the volume ratio of the two phases. If the volume of the dispersed phase increases dramatically over the continuous phase, it will lead to the so-called “catastrophic phase inversion” 12,13 and they will be unstable against coalescence since they are non-preferred emulsions following the Bancroft rule. 40

Figure 1.6 Scheme for the relation between the particle contact angle and the emulsion type
The particle wettability can be altered by surface modification. Binks et al. investigated the influence of the wettability of spherical nanometer-sized silica particles on the type and stability of emulsions formulated with water and toluene. They found that emulsions can be catastrophically inverted from W/O to O/W on increasing the volume fraction of water, $\varphi_w$. The value of $\varphi_w$ required for inversion increases with particle hydrophobicity.\textsuperscript{41} Colloidal silica particles, functionalized with hydrophilic and hydrophobic groups, have also been studied for utilization in particle-stabilized emulsions by Björkegren et al. and they found that colloidal silica functionalized with hydrophobic groups produced emulsions with smaller droplets compared to using unmodified silica (Figure 1.7).\textsuperscript{42}

### 1.2.4 Morphology of solid particles and packing density

A crucial aspect of droplet stability is the packing density and structure of the particle layer. In the case of spherical particles, the most commonly reported particle configurations are dense, hexagonally close-packed particles. This packing model predicts larger drops for increasing values of the volume fractions of the drops. If the drops can adsorb more colloidal particles,\textsuperscript{43} the surface tensions values decreases and on average larger drops will be formed. The volume fraction of the drops is an important factor to determine the packing. In a monodisperse emulsion, the maximum volume fraction ($\phi_m$) to which drops are hexagonally close packed without being distorted is 74%. If the volume fraction increases up to a certain critical value ($\phi_c$), the drops will coalesce together.\textsuperscript{44}
Figure 1.7 Emulsion-based spherical particles via interfacial assembly of particles at the oil–water interface of a droplet (Reproduced from reference 43)

In the case of anisotropic particles, other orientations and packing densities are possible. However, anisotropic particles that have been used to study the Pickering-type stabilization of fluid interfaces are often polydisperse.\textsuperscript{45,46}

A limited number of systems exploiting the interfacial self-assembly of monodisperse, anisotropic particles have been investigated, including millimeter-scale objects with complex shapes.\textsuperscript{47} In the case of sharp-tipped ellipsoids, they can be assembled into dense structures, with micellar or side-side arrangement. These self-assembled networks, formed by capillary effects and tailored by wetting and surface charge, could hence be of relevance to stabilize interfaces against deformation.\textsuperscript{48,49} In the case of cylinders, they can be oriented and assembled with high reliability to form end-to-end chains in dilute surfaces or dense rectangular lattices in crowded surfaces owing to capillary interactions\textsuperscript{50,51} that may induce also long-range attractive capillary interactions.

Recently, other anisotropic particles such as cubes and peanut-shape microparticles were investigated.\textsuperscript{52} Cubes were assembled at the interface in monolayers with a packing intermediate between hexagonal and cubic, with average densities of up to 90\% and local densities higher than the densest sphere packings, reducing the energy penalty.
associated with the area of the residual oil–water interface to a minimum. Moreover, cubes were exclusively oriented parallel with one of their flat sides at the oil water/interface. Peanut-shaped microparticles organized locally in interdigitating stacks, oriented with their long axes parallel to the interface (Figure 1.8). Despite their anisotropic particle shape, indications for long-range capillary interactions were not observed for interfacial cubes and peanuts.\textsuperscript{52}

![Figure 1.8 Sketch of the parallel orientation of a cube and peanut particle attached to the oil–water interface (Reproduced from reference 53)](image)

In our study, the shape of the particles is different from all the forms mentioned above. Two-dimensional (2D) materials are used in this study to stabilize the emulsions. Even if the ability of some 2D materials, such as GO\textsuperscript{25} or h-BN\textsuperscript{26} has been established for the preparation of Pickering emulsions, the interfacial behavior and emulsifying performance of this large class of 2D materials such as GO, h-BN or exfoliate diversions of lamellar chalcogenides or oxides is largely unexplored. A thermodynamic model for ultrathin plate-like Pickering stabilizers has been developed by Creighton \textit{et al.}\textsuperscript{54} they hypothesized that atomically thin plate-like solids, such as GO, would exhibit unique features and behaviors as Pickering emulsions stabilizers (Figure 1.9), including:
(i) high atom efficiency, in which every atom lies at liquid-liquid interface and participates directly in the stabilization;

(ii) multilayer tiling for enhanced interfacial coverage and passivation;

(iii) barrier properties;

(iv) van der Waals transparency, which related to the phenomenon of wetting transparency for GO on solid substrates;

(v) elasticity and conformation to curved interfaces

(vi) templating for the creation of new structures.

Figure 1.9 Schematic overview of two-dimensional features emulsion stabilizing
(Reproduced from reference 54)

The authors used this model to identify the optimal material surface chemistry and geometry and examined several of the potentially unique aspects of emulsions stabilized by 2D materials using graphene-based materials as examples to test the model predictions. In the case of 2D materials, two possible deposition pathways were hypothesized using the model: (i) an ordered layer-by-layer deposition (sequential close packing) and (ii) a random ballistic deposition in which the center point of each disk has an equal probability of residing on any surface patch.
1.2.5  Factors influencing Pickering emulsions

The effectiveness of solid particles to act as emulsifiers depends mainly on various particles factors such as wettability, size and concentration. Further critical parameters are the nature of the oil, the phase volume fraction, the sonication time and power, and last but not least, the order of addition during processing. We discuss below the different factors more in detail.

Wettability

As mentioned earlier, the strength at which particle is adsorbed at the oil-water interface depends on its hydrophobicity, which is directly related to the contact angle that the particles experience at the oil-water interface. Whether oil-in-water (O/W) or water-in-oil (W/O) Pickering emulsions can be formed is determined by the wettability of solid particles at the oil–water interface: if one of the liquids wets solid particles more than the other one, the better wetting liquid becomes the continuous phase and the other becomes the dispersed phase. It is generally accepted nowadays that particles with a contact angle between 60° and 80° stabilize O/W emulsions while those with a contact angle between 100° and 130° stabilize W/O emulsions. The wettability of particles can be tailored by surface functionalization. Briggs et al. investigated the influence of surface functional groups on multi-walled carbon nanotubes (MWNT). They found that the oxidation of MWNT with nitric acid modifies the inherent hydrophobicity of the nanotubes to hydrophilic behavior. Thus, hydrophilic MWNT will stabilize O/W emulsions while non-functionalized MWNT will stabilize W/O emulsions.54
Particle concentration

Particle concentration is another important factor in the formation of Pickering emulsions, and it has a remarkable influence on the emulsion stability and on the average of droplet size.\textsuperscript{40} It is widely known that solid particles have to be adsorbed at the oil-water interface to act as emulsifiers. Therefore, it may be intuitive to expect that emulsion stability would increase with the increase of particle concentration. This fact was verified by Gelot \textit{et al.}, who observed that when the particles concentration was increased, the emulsion were stable against coalescence for longer times since more particles were able to go to the interface, thereby improving the emulsion stability.\textsuperscript{55} Tambe and Sharma showed that droplets must be covered by closely packed layer of particles in order to prevent coalescence.\textsuperscript{56} Frelichowska \textit{et al.} investigated the effect of silica particle concentration on the stability of O/W emulsions. They found that emulsions are not stable at low silica concentrations, while the stability of the emulsion was enhanced when the silica content increases. Furthermore, they showed that droplet size could be tuned by adjusting the particle concentration.\textsuperscript{57}

Many authors have investigated the effect of solid particle content on droplets size,\textsuperscript{17,25,58} they all showed that droplets size decreases by increasing the particles concentration. Disrupted small droplets have a higher surface area that has to be covered in order to prevent coalescence of these droplets. By increasing the particle concentration, more particles are available in the system to adsorb at the newly formed droplets surface. In case where the solid particles adsorb as a dense monolayer, the total oil–water interfacial area is set by the amount of solid particles.
Chapter 1

Under such conditions, simple geometrical considerations (Equation 1.3) give a relationship between the droplet diameter and the mass ratio of dispersed phase to the solid particles with spherical morphology. We have use this formula as well for our 2D nanoparticles even due to no model for these particles is described in literature.

\[
\text{Droplet diameter} = \frac{6 \rho_{\text{oil}} a_{\text{solid}}}{M(\text{oil}) M(\text{solid})}
\]

Equation 1.3

where \(\rho_{\text{oil}}\) is the density of oil and \(a_{\text{solid}}\) is the interfacial area covered per mass of solid particles. Such a relationship has often been observed in experiments.\(^{18}\)

![Diagram of nanoparticles and nanosheets](image)

**Figure 1.10** Schematic outlines for the droplet coverage with nanoparticles and nanosheets

In case of low amount of solid particles, only a small interfacial area can be stabilized, so that very large droplets should be obtained. A mild emulsification process (hand shaking) allows for the formation of stable but coarse emulsions.\(^{17,59}\) A high energy emulsification process breaks the droplets into small droplets that undergo coalescence once the power is switched off. Coalescence may stop when the interfacial area reaches the area corresponding to full coverage by the particles (Figure 1.10).\(^{37}\) A high amount of solid particles should allow the preparation of very fine emulsions, however an efficient emulsification process is required.
Oil type and volume fraction

The type of oil used to prepare the emulsion and also the ratio of the dispersed phase and continuous phase are other important factors that affect the emulsion stability and sometimes even the emulsion type. The type of oil phase is also important as it determines the interfacial tension of the oil-water interface and it plays a role in the interactions undergone by the particles. He et al. used several aromatic and non-aromatic solvents as oil phase to prepare GO stabilized Pickering emulsions. They showed that all the emulsions were of the O/W type, and the stabilizing ability of GO for aromatic solvents was much greater than that for nonaromatic solvents.\textsuperscript{25} Thickett et al. presented a theoretical description of O/W emulsions stabilized by GO sheets where the polarity of the oil phase was considered in detail. They verified that GO-stabilized emulsions were successfully prepared for hydrophobic and aromatic oil phases (e.g. styrene), but not for polar oil phases.\textsuperscript{60}

The volume fraction of the dispersed phase plays an important role on the emulsion stability and type. By varying the oil/water ratio at constant particle wettability, it leads to a catastrophic inversion. The inversion could occur also by traditional way when the particle wettability changes progressively. Binks et al. demonstrate that for emulsions stabilized by hydrophilic silica particles, phase inversion from O/W to W/O occurs at the dispersed phase volume fraction around 0.7.\textsuperscript{13} In the case of GO stabilized emulsions, He et al. showed that when benzyl chloride-in-water emulsions are prepared at different oil volume fractions, there is a remarkable variation in the emulsion stability as the oil/water ratio changes. When the oil/water ratio is higher than 0.5, the stable emulsion fraction increases as the oil/water ratio increases, however if the oil/water ratio is lower than 0.5 the stable emulsion fraction notably decreases.\textsuperscript{25}
Sonication conditions

The sonication conditions either the sonication time or the energy input can affect the morphology of the emulsion. As the sonication time increases, the average size of the emulsion droplets becomes smaller with a more uniform size distribution, and the stable emulsion volume increases slightly. There is a time limit beyond which the size of the emulsion droplets does not change anymore.

pH and ionic strength

The stabilization of Pickering emulsions, as we discussed above, is affected by the surface wettability of the particles. Hence, nanoparticles with switchable partial surface wettability offer a scope for the preparation of both O/W or W/O emulsions. Varying the pH changes the hydrophobicity and hence the wettability of the particles that possess ionizable surface groups. Therefore, the adsorption behavior of the particles at the interface and sometimes the emulsion type can be controlled by varying the pH.\textsuperscript{16,25}

In this section, it has been established that Pickering emulsions are distinctly different from conventional surfactant-stabilized emulsions, with unique properties, advantages, and applications. In addition, the destabilization mechanisms of emulsions were described as well as the different types of existing particles used as stabilizers. Furthermore, the factors influencing the emulsion stabilization were discussed. In the next section, we will focus our attention in the synthesis of a special type of two-dimensional materials, i.e. hexagonal boron nitride nanosheets, which we will further use for the preparation of Pickering emulsions in the following chapters.
1.3 Two-dimensional materials

Two-dimensional (2D) materials have attracted tremendous research interest since the breakthrough of graphene in 2004.\(^6^1\) Their atomic thickness and huge exposed surface even make them highly designable and manipulable, leading to extensive application potentials. In this section, we will discuss the structure and advantages of two-dimensional materials compared to bulk materials and their use as emulsifiers.

1.3.1 Generalities

What is a 2D material? It is a material, in which the atomic organization and bond strength along two-dimensions are similar and much stronger than along the third dimension. These materials possess reduced dimensionality. They have attracted scientists attention due to their extraordinary physical\(^{62,63}\) and outstanding electrical properties. They possess strong in-plane chemical bonds but weak coupling van der Waals interaction between the layers, thus they offer the opportunity for the bulk counterparts to be cleaved into individual freestanding atomic layers. The process that changes the pristine bulky materials to nano-scale thin films is known as exfoliation. After exfoliation, the newly obtained material will not possess all the original properties of the bulk crystal. However, some new and interesting properties will come up, making the nanosheets so unique for their potential applications in various fields. Nowadays a large range of 2D nanomaterials exists such as graphene (G), hexagonal boron nitride, metal chalcogenides and metal oxides. Some examples are illustrated in Figure 1.11. These nanostructures present great futures such as large surface areas, ultralow weight, and high strength. In this work, we will focus our attention especially on hexagonal boron nitride as 2D material. In the next sections, we will discuss about its structure, its advantages over another 2D nanomaterials as well as its methods of synthesis.
Figure 1.11 Structure of the most common 2D nanomaterials

1.3.2 Hexagonal boron nitride nanosheets (h-BNNS)

In the past few years, an enormous attention has been paid to 2D hexagonal boron nitride (h-BN). The h-BN nanosheets are sp²-hybridized 2D insulators and possess a structure analogue to graphene with a honeycomb configuration made up of an equal number of boron and nitrogen atoms alternatingly arranged. The B-N bonds display 1.45 Å in length and the distance between the centers of neighboring rings is 2.50 Å. Hexagonal boron nitride nanosheets (h-BNNS) are formed by multiple basal planes stacked on top of each other and bonded with each other by van der Waals forces at a distance of 0.333 nm. The B-N bonds within h-BNNS planes are covalent and highly polarized.
Due to its structure and its large band gap (5-6 eV), h-BNNS possess outstanding mechanical, thermal and dielectric properties, as well as excellent chemical stability, therefore this material have great potential applications such as advanced composites, transparent films, protective coatings and electronic devices.

The strategies for synthesizing h-BNNS can be generally classified into two approaches: bottom-up and top-down. In the bottom-up strategy, the 2D nanosheets are generated via assembly of atomic or molecular species, as well as from their precursors, into complex structures. Sol-gel processing, plasma, laser pyrolysis, atomic or molecular condensation are examples of methods based on this strategy. For h-BNNS elaboration, the chemical vapor deposition (CVD) technique is the most used approach in this type of strategy. However, this synthetic route requires a substrate and extreme reaction conditions making it less desirable.

### Table 1.1 Summary of h-BNNS characteristics exfoliated using different methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Lateral size</th>
<th>Layers</th>
<th>Yield (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mechanical cleavage</strong></td>
<td>2 – 3 nm</td>
<td>2-3</td>
<td>18</td>
<td>79</td>
</tr>
<tr>
<td><strong>Hummer’s method</strong></td>
<td>4 µm</td>
<td>2 - 3</td>
<td>0.0065</td>
<td>82</td>
</tr>
<tr>
<td><strong>Fluorination</strong></td>
<td>4 µm</td>
<td>3 - 4</td>
<td>-</td>
<td>83</td>
</tr>
<tr>
<td><strong>Lewis bases</strong></td>
<td>300 nm</td>
<td>3 - 20</td>
<td>10 – 20*</td>
<td>84</td>
</tr>
<tr>
<td><strong>Chlorosulfonic acid</strong></td>
<td>0.5 µm</td>
<td>5</td>
<td>25*</td>
<td>85</td>
</tr>
<tr>
<td><strong>Surface modification</strong></td>
<td>0.5 µm</td>
<td>9 - 10</td>
<td>-</td>
<td>86</td>
</tr>
</tbody>
</table>

*Authors calculated the yield including the functionalized groups
In contrast, top-down approach produces 2D nanosheets starting form bulk materials. Due to the nature of layered structure of bulk materials, which are constituted of strong in-plane covalent bonds between B and N, and weak van der Waals interaction between atomic layers, it is possible to obtain the 2D nanosheets by extracting the atomic layers from their 3D crystals, which is the origin of the exfoliation. This approach mainly includes mechanical or chemical exfoliation of h-BN nanosheets from bulk. Diverse synthesis routes are briefly discussed herein following this strategy, and the main characteristics are summarized in Table 1.1. Micromechanical cleavage technique is the pioneering procedure to obtain atomic sheets of layered materials. Geim and Novoselov were the first to discover graphene multilayers by peeling off repeatedly further layers of graphite from its block until they get down to flakes of only few atoms thickness using the adhesive force of a tape. Pacilé et al., performed the exfoliation of h-BN particles by the Scotch tape method getting around 10 layers flakes. Apart from mechanical peeling by adhesive tapes, there are other approaches that use shear forces to exfoliate bulk materials in order to obtain two-dimensional nanosheets, such as ball or jet milling. During the mechanical cleavage, the shear force can easily break the weak van der Waals interactions between h-BN layers, and leave the strongly sp² bonded in-plane structure intact. The mechanical exfoliation can sometimes be helped by molten hydroxide addition (Figure 1.12).
Although these methods produce relatively high quality BNNS, the low yield and high cost have significantly limited their scalability. In contrast, BNNS made from bulk BN powder by solution processed exfoliation exhibit three important advantages: (i) as raw material, bulk BN powder is abundant and cost-effective, (ii) a relatively high yield can be obtained due to its simple process and (iii) functional groups found on BNNS after solution processes facilitate the use of BNNS in various fields. All these advantages are essential to the large-scale preparation and application of BNNS.

Chemical exfoliation of nanosheets from their bulk materials have been successfully carried out and some of the methods possess worldwide recognition, such as Hummer’s method for the exfoliation of graphene from graphite flakes.\textsuperscript{77} Compared with the methods developed for graphite exfoliation, the exfoliation methods to produce h-BNNS from h-BN were not as effective.
Du et al. reported the exfoliation of h-BN via Hummer’s method. This is considered as a low cost method, but it uses large amount of acids during the procedure. The production of h-BNNSs involves two aspects, the insertion of $\text{H}^+$ and $\text{MnO}_2$ nanoparticles and the generation of $\text{O}_2$ (Figure 1.13a). h-BNNS were produced at low quantity (yield $\sim 0.0065\%$) with microscale lateral size and 2-3 layer thickness.\textsuperscript{78}

Another exfoliation mechanism was proposed by Du et al., in which a one-step route was used to exfoliate and fluorinate the BNNSs with ammonium fluoride (NH$_4$F, Figure 1.13b).\textsuperscript{79}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure13.pdf}
\caption{Scheme of h-BNNS exfoliation via a) Hummer’s method and b) Fluorination with NH$_4$F (Reproduced from reference 82 and 83)}
\end{figure}
Lin et al. proposed a method involving lipophilic and hydrophilic amino molecules to exfoliate and functionalize at the same time the h-BN. In practice, two Lewis bases were used to functionalize the bulk h-BN. Further interactions between the h-BN surface and the Lewis agents were found. The obtained h-BNNS could be homogeneously dispersed in water and organic solvents such as tetrahydrofuran (THF).

Okamoto et al. produced highly soluble NF-h-BNNS with yields up to 25% from bulk h-BN trough bath sonication in presence of chlorosulfonic acid (CSA). They demonstrated that the CSA was physically adsorbed on the h-BNNS surfaces due to interactions between \( \text{SO}_3\text{Cl} \) anions of CSA and electron deficient B atoms of BN surfaces (Figure 1.14).

The obtained NF-h-BNNS showed high solubility in organic solvents such as isopropanol, acetone and hexafluoro-2-propanol (HFIP).

![Figure 1.14 Scheme of CSA-promoted exfoliation of h-BNs into NF-BNNSs](Reproduced form reference 85)
Wang et al. fabricated h-BNNS by liquid phase exfoliation of pristine h-BN in mixed solvents (isopropanol/deionized water ~ 3:2). This procedure leads to the production of h-BNNS in mixed solvents at a concentration of 3 mg mL$^{-1}$. Furthermore, the exfoliated h-BNNS were functionalized by polydopamine (PDA), and the obtained h-BNNS were therefore dispersible in water (Figure 1.15).\cite{82}

**Figure 1.15** Schematic illustration of the exfoliation and surface modification of h-BNNS by dopamine chemistry (Reproduced from reference 86)

Recently, h-BNNSs have been found to have some advantages over existing technologies for organic pollutant adsorption and clean-up of oil spillage due to the polarity of B-N bonds, their high surface area, and the nanosheet structure.\cite{83}

In this section, different exfoliation methods for the synthesis of h-BNNS were described and the characteristics of the obtained h-BNNS were highlighted. From previous sections, we discussed the potential of Pickering emulsions to be used as template for the preparation of new porous materials. The next section will give an overview of different methods for the preparation of porous materials; in particular we will focus our interest in emulsion templating methods.
1.4 Porous materials

1.4.1 Porous materials

Since the discovery of the porosity in stibnite in 18th century by Cronstedt, porous materials have attracted scientific and technological interest in many areas. In the recent years, scientists focused their attention in using porous materials for different applications such as microelectronics substrates,\textsuperscript{84} scaffolds for tissue engineering,\textsuperscript{85} supports for catalysis,\textsuperscript{86} membranes for separation processes\textsuperscript{87} and as templates for the production of inorganic materials.\textsuperscript{88} Porous materials can be classified in three different classes depending on their pore size. Materials with a pore diameter smaller than 2 nm are called as microporous, those with a pore diameter between 2 and 50 nm are denoted as mesoporous, and those with pore size above 50 nm are classified as macroporous (Figure 1.16). The distribution size, shape and volume of the void spaces in porous materials directly relates with their ability to perform the desired function in particular applications. Over the recent years there is a need to create uniformity within the pore size, shape and volume because it can lead to superior application properties.

![Image of IUPAC classification of porous materials depending on the pore size](image)

**Figure 1.16** IUPAC classification of porous materials depending on the pore size
Templating is one of the most widely used methods to synthesize materials with a defined structure. The templates themselves can come in a great variety of forms including molecules, supramolecular assemblies, colloids, nanoparticles or even biological species such as viruses. In general, there are various methods to synthesize mesoporous materials (Figure 1.17). These methods can be classified as hard-templating, soft-templating or template-free approaches.

On one hand, the soft templating route (Figure 1.17a) is a procedure where organic molecules or supramolecular aggregates are used as structuring agents to promote the formation of different kinds of porous solids. After removal of the template, ordered mesoporous materials with open pores can be obtained. On the other hand, the hard templating route (Figure 1.17b) also known as nanocasting, uses a ‘host’ in which ‘guest’ molecules will be directly intercalated or grafted through surface modification, resulting in an inverse replica of the ‘host’. The hard template can be formed in-situ due to a transformation of chemical precursor (Figure 1.17d). The combination of hard and soft templating routes can produce hierarchical porous materials with particular properties (Figure 1.17c). Besides these templating routes, the template-free method (Figure 1.17e) is also used in the synthesis of porous materials. In this route, the mesopores stem is formed by the aggregation of nanoscale building blocks by nucleation from precursors. Reticular chemistry can be used to prepare mesoporous materials with crystalline walls using molecular building blocks (Figure 1.17f). Selecting the right template is the key to ensure the formation of the desired nanostructure framework, which can be later removed without damaging the formed structure.
Over the past decades, mesoporous materials have been used in a broad range of applications such catalysis, sensing, energy storage and optoelectronics. However, these mesoporous materials can also be shaped into thin films or membranes in order to participate in separation technology. Porous membranes are very important for water treatment, secondary battery technologies and gas purification.
1.4.2 Porous membranes

A membrane could be defined as a semi-permeable barrier that allows the separation of components between two phases. Membranes are favored over other technologies for water treatment, such as disinfection, distillation, or media filtration. In particular, pressure-driven membrane processes are the most widely used in this type of applications. Typically, pressure-driven membranes are classified according to their characteristic pore size or their intended applications (Table 1.2). Membranes with a pore size above 50 nm are microfiltration membranes, those with pores between 2 and 50 nm are denoted as ultrafiltration membranes and if the pores are between 0.2 and 2 nm, the membranes are adapted for nanofiltration, reverse osmosis (RO) or forward osmosis (FO).

Table 1.2 Membrane characterizations by pore type and target species

<table>
<thead>
<tr>
<th>Pore type (nm)</th>
<th>Membrane type</th>
<th>Species</th>
<th>Dimensions (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macropores (&gt; 50)</td>
<td>Microfiltration</td>
<td>Yeast &amp; fungi</td>
<td>1000 – 10 000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bacteria</td>
<td>300 – 10 000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Oil emulsions</td>
<td>100 – 10 000</td>
</tr>
<tr>
<td>Mesopores (2-50)</td>
<td>Ultrafiltration</td>
<td>Colloidal solids</td>
<td>100 – 1000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Viruses</td>
<td>30 – 300</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Proteins</td>
<td>3 – 10</td>
</tr>
<tr>
<td>Micropores (0.2 – 2)</td>
<td>Reverse osmosis</td>
<td>Nanofiltration</td>
<td>Antibiotics</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Organic antibiotics</td>
<td>0.3 – 0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Forward osmosis</td>
<td>Inorganic ions</td>
</tr>
</tbody>
</table>
In terms of materials, the membranes can be classified in polymeric or organic membranes and ceramic or inorganic membranes. Organic membranes are usually made up of various polymers, among which the typical one are cellulose acetate (CA), polyamide (PA), polysulfone (PS), polyvinyl fluoride (PVDF) and polypropylene (PP). Polymeric membranes are relatively cheap, easy to manufacture, available in a wide range of pore sizes, and they have been widely used in various industries. These membranes consist often in an asymmetric structure consisting of an open porous support layer beneath a less porous thin skin layer of the same material (Figure 1.18b). In the next section, we will discuss deeply the advantages and the preparation methods of organic membranes. Besides, inorganic membranes were developed in the early 1940’s for the enrichment of uranium, but it was not until the 70s that these membranes start to be commercialized and used in industrial applications. Generally, ceramic membranes display an asymmetric structure with a dense top layer (Figure 1.18a). The materials supports include alumina, silica, zirconia, mullite, oxide mixtures and sintered metals.

Figure 1.18 Conceptual cross-section of a) asymmetric structure of an inorganic membrane and b) asymmetric structure of an organic membrane (Reproduced from reference 96)
1.4.3 Porous polymer materials

Porous polymers have the advantages to generate monoliths, films, and beads, often with well-defined porosities and high specific surface areas. The high level of interest in the research and development of porous polymer systems is a recent phenomenon (Figure 1.19).^99

![Figure 1.19](image)

**Figure 1.19** The number of publications per year (1989–2016) resulting from a search for: (left-hand y-axis) both “porous” and “polymer”; (right-hand y-axis) “polyHIPE” (Reproduced from reference 97)

There are different approaches described in literature to generate porous polymer including, macromolecular frameworks or rigid structures with inherent microporosity; porogen incorporation; and last but not least templating. Our interest is focused in the development of porous polymer-based materials using emulsion templating methods. In this section, we will discuss the different existing scenarios to create porosity from emulsions and we will focus our discussion especially in the use of Pickering emulsions as templates to create the desired porous polymer-based material, in particular porous polymer-based membranes.
We saw in the above paragraph that a template is a form, mold or pattern used as a sacrificial agent to prepare materials with a defined shape. In a typical colloidal templating scenario, a biphasic system is generated, and then a polymer is added to one of the phases (usually the continuous phase). The colloidal entities serve to create porosity in the final polymeric material. Depending on the employed system (emulsions, microemulsions or solid particles), the material pore size can range from a few nanometers to hundreds of micrometers.

1.4.3.1 High internal phase emulsions

The most studied route to fabricate porous emulsion-templated polymeric materials is high internal phase emulsions (HIPE). HIPEs are highly viscous emulsions, in which the major, or ‘internal’ phase, is in most of the cases constituted with more than 74 % of the volume dispersed within the continuous or ‘external’ phase. A polyHIPE is produced when the monomers are present in the external phase surrounding the dispersed droplets of the internal phase (Figure 1.20). SEM images of such polyHIPEs can be found in Figure 1.21. However, the materials synthesized from polyHIPE have poor mechanical properties and low gas permeability due to the rather small pore and throat size. Menner et al. found that the mechanical properties of these macroporous polymers could be improved by increasing the material density; however, that requires a reduction of the internal phase volume. They reported the preparation of materials with interconnected porosity from medium internal phase emulsions (MIPEs) containing only 60 vol. % of dispersed phase, and low internal phase emulsions (LIPEs) containing down to 25 vol. % of dispersed phase. The mechanical properties of the macroporous polymers obtained from emulsion templates with a reduced internal phase volume were improved and they were still permeable to some gases.
A drawback of these methods is the use of significant amounts, between 5 and 50 % in volume, of surfactants to stabilize the emulsions. The presence of surfactants within the polyHIPEs has a downside effect on the properties of the final material. In addition, the surfactants used to prepare polyHIPE can be relatively expensive and costly to remove. Alternatively to classical surfactants, particles are proposed as emulsions stabilizers.
1.4.3.2 Pickering emulsions templating

One of the advantages of using the particles as emulsifiers rather than surfactants includes the low concentration of particles required to stabilize the emulsion. Particles tend to be adsorbed at the liquid-liquid interface, and thus they form a thin layer, which prevents the emulsion coalescence.41 Recently, it has been demonstrated that a range of different particles such as silica, titania or block copolymers can be used to stabilize W/O HIPEs (Figure 1.22). Menner et al. reported the stabilization of Pickering W/O HIPEs with an internal phase up to 80 vol % by using titania nanoparticles, which have been previously hydrophobized by adsorption of oleic acid. The void size distribution could be tuned with the internal phase volume fraction and with the nanoparticles content.105 The same group also reported the preparation of HIPEs emulsion with oleic acid functionalized silica nanoparticles with an internal volume of about 92 %.106 Koning et al. prepared styrene/divinylbenzene based polyHIPE single-walled carbon nanotubes (SWCNTs) composites foams with an internal phase volume ranging from 70-80 %.107 Carbon nanotubes (CNTs) have been used to produce carbon-based foams through MIPEs method with an internal phase up to 60 %. The produced foam displays a porosity of about 70 %.108 Ikem et al. reported the preparation of Pickering-MIPEs with 70 vol. % of internal phase stabilized with 1 wt. % of modified titania nanoparticles with oleic acid.109
Figure 1.22 SEM images for Pickering-polyHIPEs stabilized with a) titania nanoparticles, b) silica nanoparticles and c) SWCNTs (Reproduced from references 102, 103 and 104)

There is a growing interest for preparing these porous polymer materials in special shape, such as membranes, to take benefit of their pores for separation and filtration applications. Next section will be dedicated to this special class of materials, we will discuss the existing methods to produce porous polymer membranes and the advantages of preparing these porous polymer-based membranes through Pickering emulsion templating.
1.4.4 Porous polymeric membranes

1.4.4.1 Phase inversion

Phase inversion (PI) method is a well-known method for the preparation of porous asymmetric membranes. It consists in inducing phase separation in a homogeneous polymer solution to get two phases: a polymer rich-phase, which will give the membrane matrix, and a polymer poor-phase (consisting in a lower quality solvent for the polymer with low amount of polymer), which will lead to the porous structure of the membrane.

Different kinds of techniques can be used to provoke the demixing of the initial homogenous polymer solution (Figure 1.23), such as non-solvent induced phase separation (NIPS), thermally induced phase separation (TIPS), vapor induced phase separation (VIPS) and evaporation induced phase separation (SIPS). NIPS consists of immersing the polymer solution into a bad solvent, so called non-solvent, but offering good miscibility with the solvent. The fast mass transfers induce phase separation and the solvent extraction leads then to the polymer precipitation, structuring the membrane matrix. The VIPS method includes the exposure of the polymer solution to non-solvent vapors instead of direct immersion as in the NIPS process. The phenomena are similar but membrane morphology is different because of the slower mass transfers. In the TIPS method, the temperature of the solution is reduced and thanks to the adequate choice of polymer/solvent binary system, phase separation is induced by a decrease in solubility of polymer at low temperature. Finally, in SIPS, the solvent evaporates either in atmospheric air or at high temperature. The change in composition of the polymer solution induces the demixing of the system.
Figure 1.23 Summary of different phase separation methods

The porous membrane usually prepared by phase separation methods concerns most of the time hydrophobic polymers such as polyethylene sulfone (PES)\textsuperscript{110}, polyacrylonitrile (PAN)\textsuperscript{111} or polyvinyl fluoride (PVDF)\textsuperscript{112}. One of the drawbacks of these polymeric membranes is the fouling due to the adsorption of macromolecules or proteins during filtration tests. One way to reduce the fouling is to increase the hydrophilicity of membrane surface. Thus in membrane science, the development of a new route to produce porous membranes with high flux, good selectivity and with anti-fouling properties is still a challenge.
1.4.4.2 Electrospun methods

Electrospun is a straightforward method for the preparation of fibrous membranes with complex architectures, owning high porosity and interconnected open pore structure. In an electrospinning process, a polymer solution is stored in a reservoir, normally a capillary tube or a syringe. Then, the polymer is faced to an electric field and free charges are created on the solution surface. The increased intensity of the electric field will make the surface solution at the tip of the syringe deform in a conical shape known as a Taylor cone. When the electric field reaches a typical value, at which the applied electric voltage overcomes the surface tension force, the polymer solution is ejected towards the collector. The polymer fibers are randomly laid on the collector forming a fibrous membrane. Zhang et al. prepared hybrid polyvinyl alcohol/polypropylene (PVA/PP) composites membrane using the electrospun method; the obtained membranes display an average pore size about 15.6 µm, these membranes could reject 96 % of the 0.5 µm particles with a water flux about 32.2 L h⁻¹ m⁻².¹¹³

The inconvenient with the electrospun method is the lack of control on the porosity; it is possible to control the fibers size but not the porosity created within the internal structure. For these reasons, we focus our attention on the development of porous materials through the emulsion templating method.
1.4.4.3 Pickering emulsion based membranes

Our interest resides in the preparation of membranes using the emulsion templating method. The literature based on the development of membranes using this method is scarce. Our group has already reported the preparation of gelatin membranes based on graphene oxide Pickering emulsion (Figure 1.24). The GO is able to stabilize the emulsion due to its amphoteric nature. The membrane prepared with 3 g L\(^{-1}\) of GO displays a pore size about 1.6 ± 0.5 µm and a pure water permeability about 5.8 ± 1.3 L h\(^{-1}\) bar\(^{-1}\) m\(^{-2}\) \(^{114}\).

![Scheme for the preparation of gelatin/GO Pickering emulsion membranes and gelatin porous membrane with 3 wt. % GO (Reproduced from reference 107)](image)

**Figure 1.24** Scheme for the preparation of gelatin/GO Pickering emulsion membranes and gelatin porous membrane with 3 wt. % GO (Reproduced from reference 107)

The preparation of porous polymer membranes using Pickering emulsion as template is advantageous because we can tailor the polymer properties depending on the potential application. In addition, this method allows as well to easily tune the pore size on the final materials by controlling the conditions (stabilizer and polymer concentration, volume phases ratio, crosslinking and curing time) during the membrane preparation.
1.5 Conclusions

The present chapter has introduced at first the definition of Pickering emulsions, their destabilization mechanisms, the different type of particles described in the literature that can be used for their preparation and the factors affecting their stability. Then, the generalities on two-dimensional materials were presented, based on our choice to consider Pickering emulsions. In particular, the properties of hexagonal boron nitride and the current techniques used to synthesize these 2D nanostructures through different strategies based on the top-down approach have been discussed. Finally, some of the most used techniques for the preparation of porous polymer materials were addressed. Among all techniques, emulsion templating was described in more detail, as well as the different routes (HIPE, MIPE and LIPE) for the preparation of porous materials employing surfactants and the improvements of the technique using particles as stabilizers. Membranes prepared using emulsion templating method are limited, therefore our interest focused on the development of porous polymer membranes using h-BNNS as emulsion stabilizers.

Hence, it would be of scientific and technological interest to assemble h-BNNS and a polymer, such as PVA, into composite membranes for filtration purposes by a facile and sustainable one-pot method, which would preserve the exceptional properties of h-BNNSs, with improved durability, stability, water permeability, and low pressure requirements while offering easy pore size tailoring and excellent anti-fouling properties.
1.6 Research aim

The aim of the present work is to develop a new method for the preparation of porous PVA-based membranes via the Pickering emulsion method using two-dimensional materials as stabilizers. Our research will focus first on the elaboration and characterization of two-dimensional materials that we will further use for the preparation of Pickering emulsions. Then, the properties of the obtained two-dimensional materials-based emulsions will be studied. At last, the development of porous polymer membranes using the as-prepared Pickering emulsion as soft template and their potential application in water purification will be investigated.
REFERENCES


Introduction

81 Morishita, T. & Okamoto, H. Facile exfoliation and noncovalent superacid functionalization of boron nitride nanosheets and their use for highly thermally conductive and electrically insulating polymer nanocomposites. ACS applied materials & interfaces 8, 27064-27073 (2016).
Chapter 2

Materials and methods
2.1 Introduction

This chapter will be split in three main sections corresponding roughly to the chapters we will find among this thesis. In each section the materials, the experimental methods as well as the characterization techniques used will be fully described.

In the first section the preparation and the characterization of two-dimensional (2D) materials will be discussed. In the second part, we will discuss about the preparation of emulsions using these 2D materials as stabilizing agents, as well as the techniques applied to the characterizations of emulsions. In the last section, the preparation of porous membranes and the techniques used to characterize them will be described.

2.2 Two-dimensional materials

2.2.1 Graphene Oxide

Graphene oxide (GO) is formed by heavily oxidizing graphite to chemically exfoliate the flakes of the graphitic stack into mono- and few-layer sheets, depending on the degree of oxidation and post-processing. Graphite oxide was first prepared by Brodie in 1859, though many commercially implemented methods today rely on modifications to Hummers’ method. The structure of GO is notoriously difficult to characterize and define broadly because of its inherently nonstoichiometric structure and dependence on production parameters. According to existing direct imaging evidence, GO is largely considered to have long-range order in \(sp^2\) lattice.
The graphene oxide used in all the experiments was synthetized by modified Hummers method from graphite flakes. Graphite powder (CAS n° 7782-42-5, < 20 µm, ≥ 99.95 % trace metal basis), hydrochloric acid (CAS n° 8647-01-0, ACS reagent, 37 %), sulfuric acid (CAS n° 7664-93-9, 99.99 %), phosphoric acid (CAS n° 7664-38-2, 85%, 99.99 % trace metal basis), potassium permanganate (CAS n° 7722-64-7, ACS reagent, ≥ 99.0 %) and hydrogen peroxide (CAS n° 7722-84-1, ≥ 30%) were purchased from Sigma Aldrich. 3g of graphite were dispersed in concentrated H$_2$SO$_4$:H$_3$PO$_4$ (9:1, 400 mL) solution. Then, 18 g of KMnO$_4$ were added gradually to the mixture with stirring for 12 h. Later on, the mixture was cooled down to room temperature and then H$_2$O$_2$ (3 mL) was added. A brown precipitate was observed, showing the exfoliation of graphene oxide from graphite. After one hour of stirring, GO was separated by centrifugation at 6000 rpm (2697 G) for 10 minutes and the supernatant was decanted away. The resultant precipitate was washed several times with 30% hydrochloric acid and absolute ethanol. Finally, the obtained powder was dried at 50°C for 24 h to obtain the graphene oxide.

2.2.2 Hexagonal Boron Nitride

Hexagonal Boron Nitride (h-BN) is a lattice alternately arranged by B and N atoms in a two-dimensional plane by hexagonal lattice formation, displaying a honeycomb structure. The N and B atoms are combined by a sp$^2$ orbital to form a strong σ bond combined by weak interlayer Van der Waals forces. Hexagonal boron nitride (h-BN) is very attractive for many applications, particularly, as protective coating, dielectric substrates, transparent membranes, or deep ultraviolet emitters.
The h-BN used in all the experiments was PHPP325B COMBAT® powder purchased from Saint Gobain. The material appearance is a white powder with particle size around 3µm. It possesses a specific surface area of 60 m²/g and an apparent density of 2.2.

### 2.2.3 Exfoliation method

Ultrasonic acoustic cavitation has been extensively used for exfoliation and dispersion of nanomaterials because it can concentrate the acoustic energy in small volumes. In particular, acoustic cavitation has been used in the production of 2D nanosheets such as graphene, transition metal dichalcogenides or boron nitride from bulk layered materials in liquid solutions. The acoustic cavitation concerns physical effects of high energy including the formation, growth and implosive collapse of bubbles at high ultrasonic intensities in a liquid medium. However, the high speed jets and intense shock waves can diminish the size of the nanosheets or generates defects on the surfaces.\textsuperscript{3-5}

An ultrasonic homogenizer consists essentially of three components: the high-frequency (HF) generator, the ultrasonic converter (UW), and the functioning tip. The HF-generator first transforms the alternating supply voltage from 50-60 Hz into a HF-voltage of 20 kHz. If this voltage is applied to a suitable oscillator inside the ultrasonic converter, it is possible to transform electric oscillations into mechanical oscillations of same frequency. The mechanical oscillation is transmitted by the ultrasonic converter through sonotrodes and is transmitted into the sample through the horns connected in between. The working intensity transmitted into the medium increases in inverse proportion with the diameter of the sonotrode area. The smallest tips transmit the largest power per measure of area in maximum oscillation amplitudes of several tenths of a millimeter.
**Generator:** The generator converts mains voltage to high frequency of 20 kHz electrical energy (most likely, although other frequencies are also available)

**Ultrasound converter:** Converter transforms electrical energy into mechanical vibrations of fixed frequency.

**Standards and booster horns:** Horns increase sonication amplitude.

**Probes:** Probes transmit ultrasonic energy into the sample.

**Figure 2.1** Schema of ultrasonic device with its different parts

h-BN nanosheets (h-BNNS) were fabricated using liquid phase exfoliation with the assistance of an ultrasounds device (model SONOPPLUS HD 3100, 100W, 20 kHz) with a microtip of diameter 3 mm (MS73). 1.0 g of pristine h-BN was added to 100 mL of water. The solution was heated up to 80 °C, then 20 g of gelatin from porcine skin (gel strength 300, Type A) were added, the mixture was kept under stirring at the same temperature until the complete dissolution of the gelatin. After, different concentrations of zinc chloride (ZnCl₂, CAS n° 7646-85-7, 99.99 % trace metal basis) and potassium chloride (KCl, CAS n° 7447-40-7, ≥ 99 %) were added to the mixture. These ionic species are expected to intercalate between the h-BN layered structure, increasing the layer spacing, weakening the interlayer adhesion and reducing the energy barrier to exfoliation.
The dispersion was kept in a bath at 50 °C to avoid the gelatin solidification and it was sonicated for 3 hours at 65 % amplitude with pulse off/on 0.5 – 1 s. After the sonication, the yellowish suspension was subjected to two centrifugation steps. In a first step, the solution was centrifuged at 3000 rpm for 30 min. Then, the supernatant was collected and subjected to a second centrifugation step at 6000 rpm for 30 min. The speed during the centrifugation also plays an important role in the obtained h-BNNS lateral size, because the large nanosheets will be separated from the thinner ones during this centrifugation steps. The supernatant, where are the lightest nanosheets, was collected and dried at 60 °C overnight. The resultant material was heated up to 600 °C under air atmosphere to remove the gelatin. Then, the obtained powders were heated up to 1000° under Ar atmosphere with a flux of 200 mL/min, to improve the h-BNNS crystallinity. The obtained h-BNNS were washed several times with water and ethanol to remove any remaining impurity.

2.2.4 Characterization techniques

2.2.4.1 Transmission electron microscopy

Transmission electron microscopy (TEM) is a technique in which a beam of electrons is transmitted through a specimen to form an image. The specimen should be an ultrathin section of less than 100 nm thick or a suspension on a grid. In TEM, the beam of electrons from the electron gun is focused through the condenser lens into a small beam. This beam is restricted by the condenser aperture, which excludes high angle electrons. The beam then strikes the specimen and parts of it are transmitted depending upon the thickness and electron transparency of the specimen. This transmitted portion is focused
by the objective lens into an image on phosphor screen or a charge coupled device (CCD) camera.

In a so-called “bright field” experiment, the darker areas of the image represent the areas of the sample where fewer electrons are transmitted, while the lighter areas of the image represent the areas of the sample where more electrons were transmitted.

Figure 2.2 Schematic of a basic transmission electron microscopy (TEM) (Reproduced from Wikimedia Commons)

TEM was used to determine the morphology, the thickness and the lateral size of the as-synthesized h-BNNS by ion intercalation method. TEM experiments were performed using a JEOL 2200 FS-200 kV equipped with a STEM module (Scanning Transmission Electron Microscopy), a Bright Field (BF) detector and a CCD Gatan USC 4092 x 4092 px$^2$ camera.
2.2.4.2 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a rapid analytical technique, which gives a robust image of the crystallographic structure and chemical composition. X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate the beam and directed toward the sample. The measurement of the intensity of the scattered X-ray is plotted as a function of the angle $2\theta$ between incident and scattered radiation. The distance between scattering planes $d$ can be expressed according to Bragg’s law:

$$n\lambda = 2d \sin \theta$$ \hspace{1cm} \textbf{Equation 2.1}

where $n$ is an integer, $\lambda$ is the wavelength and $\theta$ is the half-angle between the incident and scattered beam. X-rays of the incident beam can interact elastically with the electron cloud of the atoms of a material. These elastically diffracted waves from different atoms interfere either constructively or destructively resulting in a diffraction pattern, in which the intensities and position are directly related to atomic distribution and atom-atom distances.

XRD was used to determine the interlayer spacing and the crystallite size of h-BNNS. The XRD patterns of used materials were recorded using a PANalytical Xpert powder XRD system with Cu K\textalpha radiation, a scan speed of 2° min$^{-1}$, a 2\theta range between 10 and 70°, and a step rate of 0.02° per second.
2.2.4.3 Raman spectroscopy

Raman spectroscopy is a technique based on inelastic scattering of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. This technique is used to observe vibrational, rotational, and other low-frequency modes in a system. In chemistry, it is commonly used to provide a structural fingerprint, according to which molecular units can be identified. Typically, the sample is illuminated by a laser, and then the incident light interacts with the molecule and distorts the cloud of electrons to form a “virtual state”. This state is not stable and the photon is immediately re-radiated as scattered light. A peak appearing in the Raman spectrum will be derived from a specific molecular vibration or lattice vibration. Peak position shows the specific vibrational mode of each molecular functional group included in the material. The shape of a Raman peak is important, not just its position. The width of the peak gives also information about size-effects. Any residual stress inside the crystal can also be evaluated from the direction and amount of any shift of the Raman peak.

Raman spectroscopy was used to characterize changes in the h-BN structure before and after exfoliation by the ion intercalation method. The spectra have been obtained from a Horiba xplora, using a wavelength $\lambda = 659$ nm. The samples were deposited onto a glass slide to perform the analysis. The data were treated with the Labspec software.
2.2.4.4 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is a technique providing an infrared spectrum of absorption or emission of a specimen. The molecular vibrational spectrum can be divided into three regions: the far infrared (400 cm\textsuperscript{-1} to 0 cm\textsuperscript{-1}), the mid infrared (4000 cm\textsuperscript{-1} to 400 cm\textsuperscript{-1}, the most common used region due to the fact that most organic and inorganic compounds absorb within it), and the near infrared (> 4000 cm\textsuperscript{-1}). When exposed to infrared radiation, molecules selectively absorb radiations of specific wavelengths, which causes a change in their dipolar momentum. Consequently, the vibrational energy levels of sample molecules transfer from their ground state to an excited state. The frequency of the absorption peak is determined by the vibrational energy gap. The number of absorption peaks is related to the number of vibrational degrees of freedom of the molecule. The intensity of the absorption peaks is related to the change of dipole moment and to the possibility of the transition of energy levels.

The FTIR analyses were performed on h-BN and exfoliated h-BNNS in order to follow the structural changes before and after the exfoliation. The FTIR spectra were obtained using the attenuated total reflection (ATR) technique (Figure 2.4) with a ThermoNicolet Nexus 710 FTIR spectrometer. The spectra were obtained from 4000 to 600 cm\textsuperscript{-1} with 34 scans and 4 cm\textsuperscript{-1} resolution.

![Figure 2.3: Schema of a Fourier transform infrared spectroscopy (FTIR) ](image-url)
2.3 Pickering emulsions

In this section, we will describe the preparation and characterization of graphene oxide (GO) and hexagonal boron nitride (h-BN) emulsions. It will also focus on the preparation of hexagonal boron nitride nanosheets/polyvinyl alcohol (h-BNNS/PVA) based emulsions, which will be used to prepare the membranes.

2.3.1 Ethyl Benzoate

Ethyl benzoate, C₆H₅O₂C₂H₅, with purity ≥ 99 % was purchase from Sigma Aldrich (CAS n° 93-89-0). This structure is an ester formed by the condensation of benzoic acid and ethanol. It is a colorless liquid that is almost insoluble in water (720 mg L⁻¹ at 25°C)⁶, but miscible with most organic solvents. As many volatile esters, ethyl benzoate has a pleasant odor described as sweet, wintergreen, fruity, medicinal, cherry, and grape.

![Ethyl Benzoate structure](image)

Figure 2.4 Ethyl benzoate structure

This solvent was chosen as oil phase for the preparation of Pickering emulsions. It possesses low toxicity in comparison to other aromatic solvent, such as benzene, chlorobenzene or toluene. The aromatic ring in ethyl benzoate can easily interact with the residual conjugate domains in the GO and h-BN through π-π interactions.⁷
2.3.2 Pickering emulsion preparation

Pickering emulsions were prepared in two steps using power ultrasounds device (model SONOPLUS HD 3100, Germany) with a microtip of diameter 3 mm (MS73). In the first step, the nanoparticles (GO or h-BN) were suspended in water and sonicated for 1 h at 65 % amplitude with pulse off/on 0.5 – 1 s. This step ensures the well dispersion of the nanoparticles in the water and it also allows the exfoliation of boron nitride, due to the weak Van der Waals interactions between h-BN layers. The sonication procedure is able to break these interactions leading to mono- or few-layered material. The second step leads to the emulsion formation with the addition of the ethyl benzoate followed by the same sonication procedure than in the first step. The schematic of the emulsion preparation is represented in Figure 2.5.

In this study, the stability of the emulsions was investigated. In order to do that, different factors such as the BN concentration, the oil/ water ratio ($R_{O/W}$), and the sonication procedure were varied.

![Figure 2.5 Schematic illustration of emulsion preparation using nanoparticles (NPs) as stabilizing agent.](image)
Table 2.1 Oil and water emulsion composition and oil/water ratios

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Oil (mL)</th>
<th>Water (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>5.00</td>
<td>5.00</td>
</tr>
<tr>
<td>0.8</td>
<td>4.45</td>
<td>5.55</td>
</tr>
<tr>
<td>0.6</td>
<td>3.75</td>
<td>6.25</td>
</tr>
<tr>
<td>0.4</td>
<td>2.90</td>
<td>7.10</td>
</tr>
<tr>
<td>0.2</td>
<td>1.70</td>
<td>8.30</td>
</tr>
</tbody>
</table>

Table 2.2 Emulsion composition

<table>
<thead>
<tr>
<th>BN (w/v %)</th>
<th>Ratio O/W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emulsion formulation</td>
<td>0.5, 1.0, 1.5 and 2.0</td>
</tr>
</tbody>
</table>

The influence of different parameters, such as the amplitude (20, 40, 60 and 80 %) and power (20, 40, 60 and 75W), were varied to investigate their influence in the stability and droplet size of h-BNNS based emulsions.
2.3.3 Pickering emulsion characterization

2.3.3.1 Small Angle X-ray Scattering (SAXS)

Small Angle X-ray Scattering (SAXS) can be used to determine nanoparticle size distributions, resolve the size and shape of macromolecules, determine pore sizes, and characteristic distances of partially ordered materials. This is achieved by analyzing the elastic scattering behavior of X-rays when travelling through the material, recording their scattering at small angles (typically 0.1 - 10°). Depending on the angular range in which a clear scattering signal can be recorded, SAXS is capable of delivering structural information for a typical length range between 0.3 and 150 nm.

SAXS of the h-BNNS emulsions was performed in a laboratory setup involving a molybdenum source, which delivers a 1 mm large squared beam of 17.4 keV energy. Monochromatization was applied using a “Fox3D” multi-shell mirror, and collimation of the beam was achieved using two sets of scatterless slits. The diffraction patterns were recorded using a mar345 two-dimensional imaging plate with typical duration of 1 h. The measurements were performed in transmission geometry, and the emulsions were held in 2 mm large glass capillaries. This set-up allows probing typical distances up to 30 nm.
2.3.3.2 Optical Microscopy

Optical microscopy is a technique employed to observe closely a sample through the magnification of one or a series of lenses with visible light. The emulsions microstructure and type were characterized using a optical microscope (Olympus BX41, Japan) at 5x magnification, equipped with a digital camera (U-TV1X-2, Olympus, Japan).

To investigate the emulsion droplet size, a droplet of emulsion was deposited onto a glass slide and covered with a coverslip. The software used to take the images was Replay® and Image J was used to determine the droplet diameter form the pictures. Mean diameter was calculated from 50 determinations.

Figure 2.6 Schema of small angle X-ray scattering system (Reproduced from Saga Light Source website, Kyushu Synchrotron Research Center)
Figure 2.7 Schematic image of optical path microscopy system (Reproduced from Edmund optics website)

2.3.3.3 Confocal Laser Scanning Microscopy

Confocal laser scanning microscopy (CLSM) is an optical imaging technique for increasing optical resolution and contrast of a micrograph by means of using spatial pinhole to block out-of-focus light in image formation. The optics behind this type of imaging is a laser emitted from the light source that becomes a parallel beam of expanded diameter when it passes through the pinhole aperture, encounters the dichromatic mirror, and is reflected onto the objective lens. The light beam is reflected at 90° when it hits the dichromatic mirror, and is focused onto the desired focal plane on the sample when it passes through the objective lens. The sample fluoresces in all directions under excitation from the laser. Part of the fluorescence becomes focused at the focal point of the objective once it passes through the objective lens, dichromatic mirror, and focusing lens.
The fluorescent light passes through a pinhole at the focal point and can then be picked up by the detector. When a laser scans the sample point-by-point, the photomultiplier tube behind the pinhole receives the corresponding point-by-point confocal optical image.

The emulsion type was determined using a laser microdissection microscope (LEICA, LMD 6500) with a 10x objective. The dispersed phase (oil or water) of the emulsion was labeled with a dye during the emulsification process to be able to obtain the images by fluorescence. The water phase was identified by the addition of fluorescein sodium; this dye has the ability to solubilize in water but not in ethyl benzoate. Methyl red was selected as a dye for ethyl benzoate to allow us to identify the oil phase. Thus, when light source irradiates the sample, the phase which has been labeled will be excited and emit the light back while the other will not be excited.

Figure 2.8 Schematic image of confocal laser scanning microscopy
2.3.3.4 Rheology

Rheology is the science that describes, explains and quantifies the phenomena appearing while bodies or liquids are deformed or flowing under the effect of an applied force. Deformation in this case means the change of shape and size of a body due to applied forces (external and internal forces). This deformation can be reversible or irreversible. In the first case, when the force acting upon the body ends, the shape reverts to its original state and the deformation work is recovered, it is known as well as elasticity. Otherwise, the shape does not revert to its original state and the deformation energy cannot be recovered; in this case the deformation is irreversible. To characterize the flow behavior of substances, the latter are subjected to defined forces and the resulting deformations are described in detail in function of different parameters. Depending on the direction of the affecting force, the relevant characteristics for rheometry are distinguished: elongation, compression strain and shear strain.

The simplest model to illustrate rheological properties is the parallel plate model (Figure 2.10). The top plate, which has a surface area $A \ [m^2]$, is moved by a force $F \ [N = \text{kg} \ m/s^2]$ at a speed $v \ [m/s]$. The bottom plate remains at rest. The distance between the plates, to which material adheres, is described by $h \ [m]$. Now, the thinnest elements of the liquid will be displaced between the plates. This laminar flow is of fundamental important for rheological investigations. Turbulent flow, which increases the flow resistance and thus showing false rheological properties, must be avoided.
Figure 2.9 Parallel plates model

To better understand the system, it is necessary to introduce some equations explaining the behavior of the system.

Shear stress ($\tau$) is known as the force (F) acting on an area (A) to generate a movement in the liquid element between the two plates. The velocity of the movement at a given force is controlled by the internal forces of the material.

$$\tau = \frac{F}{A} \text{ (Pa)}$$  \hspace{1cm} \text{Equation 2.2}

Shear rate ($\dot{\gamma}$) is the laminar shear flow generated between the two plates when applying a shear stress. The lowermost layer remains at rest while the uppermost layer moves at the maximum velocity $v_{\text{max}}$. The shear rate is defined as:

$$\dot{\gamma} = \frac{dv}{dh}$$  \hspace{1cm} \text{Equation 2.3}

where $dv$ is the differential velocity between adjacent velocity layers and $dh$ is the differential thickness of the flow layers.
In a laminar flux, the differential velocity between adjacent layers is constant (\(dv = \text{const.}, \; dh = \text{const.}\)). Then the differential can thus be approximated as follows:

\[
\dot{\gamma} = \frac{\text{Velocity } v}{\text{Distance } h} \; (s^{-1})
\]

Equation 2.4

Viscosity (\(\eta\)) is also an important parameter. The flow behavior of an ideal liquid is described by the dynamic viscosity law:

\[
\eta = \frac{\tau}{\dot{\gamma}} \; (\text{Pa} \cdot \text{s})
\]

Equation 2.5

where \(\eta\) is the viscosity (Pa·s), \(\tau\) shear stress (Pa) and \(\dot{\gamma}\) is the shear rate (s\(^{-1}\))

The viscosity could be also described as the measurement of resistance against the flow. Depending on this resistance, the fluids can be classified in two types: Newtonian or non-Newtonian liquids. In the first case, the shear rate is linearly proportional to shear stress, so the viscosity is constant. The material behaves as an ideal plastic body, but in practice only a few materials have an ideal flow behavior. In the case of non-Newtonian liquids, the relation between shear stress and shear rate is not linear so viscosity varies with the shear:

\[
\eta = f(\tau) \quad \text{or} \quad \eta = f(\dot{\gamma})
\]

The flow and strain behavior of a material may be affected by a number of external factors. The most important parameters are:
- Substance: the viscosity of a material depends on its physical and chemical properties
- Temperature: it has a major effect on the viscosity
- Time: the viscosity depends on the strain history of a material, in particular on previous loads.
- Shear rate: If the shear rate changes during an application, the internal structure of the sample will change and the change in stress or viscosity can then be seen.

The applied forces can also induce structural changes in the material and therefore in its viscosity. Depending on the material response, two different behaviors can be defined. On one hand, the shear thinning behavior, where the molecules or particles suffer an arrangement when the system starts to flow. On the other hand, the shear-thickening behavior, this is characterized by the disorder of the particles or molecules when the system starts flowing.

![Diagram](image)

**Figure 2.10** Schematic illustrations of the two different behaviors, a) Shear thinning behavior and b) Shear thickening behavior
Materials and methods

To analyze our GO and h-BNNS systems, 0.8 mL of sample was deposited on the module. The rheometer (Anton Paar MCR 302) temperature was fixed at 20°C for all the experiments. The experiment was carried out using cone-plate geometry; with 50 mm diameter and a gap set at the center of the cone of 101 μm. The viscosity evolution is followed over the time varying the shear rate between 1 and 100 rad s⁻¹. Silicon oil was placed around the geometry to avoid a possible evaporation during the experiment.

Figure 2.11 Rheometer image and measuring principle design
2.4 Membranes development

In this section, we will discuss the preparation of emulsions formulated with h-BNNS and PVA, and the elaboration and characterization of the as-prepared porous membranes via Pickering emulsion templating.

2.4.1 Polyvinyl alcohol

Polyvinyl Alcohol (PVA) is an environmental friendly and water-soluble synthetic polymer with excellent film forming and emulsifying properties, and outstanding resistance to oil, grease, and solvents. All these properties make PVA suitable for many applications. PVA is commonly used in the textile industry, for paper products manufacturing, in the food packaging industry, and for medical devices.

PVA is used as an industrial and commercial product due to its low environmental impact, which includes its high chemical resistance, aqueous solubility, and biodegradability. It has been extensively used in adhesive, in textile warp sizing and finishing, in paper size and coating, in the manufacturing of poly (vinyl acetate) (PVAc) emulsion, in the suspension polymerization of polyvinyl chloride PVC, and as binder for ceramics, foundry cores and in several pigments.

PVA is a synthetic copolymer obtained by radical polymerization of vinyl acetate monomer to poly PVAc followed by hydrolysis of PVAc to PVA. Since the hydrolysis reaction does not go to completion, PVA is always a copolymer of PVA and PVAc. Figure 2.12 shows the chemical reaction for producing PVA.
The PVA properties depend on the different parameters used during its synthesis such as, the reaction time, the polymerization temperature, the monomer ratio, the solvent concentration, the thermic initiator and also the hydrolysis reaction. Thus, the PVA will be characterized by:

- The degree of polymerization (DP): represents the average number of monomer units present in a molecule. The parameters $n$ and $m$ represent the number of vinyl alcohol units and vinyl acetate per polymer chain. It is directly related to the molecular mass of the polymer. It depends mainly on the operating conditions applied during the synthesis of PVAc used as precursor of PVA. The DP can be determined by steric exclusion chromatography (SEC), which separates and detects the molecules in function of the chain sizes.

$$DP = n + m$$  

Equation 2.6
- **The degree of hydrolysis (DH):** represents the fraction of vinyl alcohol in the polymer. It depends on the conversion method and the operating conditions. This usually ranges from 70% for PVA with low hydrolysis degree to 99% for fully hydrolyzed PVA.

\[
DH = 100 \frac{n}{n+m} \tag{Equation 2.7}
\]

- **The polydispersity index (PDI):** it refers to the ratio of the weight average molecular weight (\(M_w\)) to the number average (\(M_n\)), and is sometimes also called as molecular weight distribution. The PDI is used to indicate the distribution of polymer chain molecular weights in a given polymer. This can be obtained by various means such as gas phase chromatography (GPC), rheology or solution viscosity.

PVA films are highly resistant to organic solvents and oils. The resistance tends to increase with increasing the degree of hydrolysis, but no difference appears in the solvent resistance of low, medium and high degree of polymerization, within the same hydrolysis degree.\(^9\) We have chosen PVA 98 % with a low molecular weight (Mowiol 4-98, CAS n° 9002-89-5, \(M_w = 27000\) g/mol) purchased from Sigma Aldrich to carry out the experiments.
2.4.2 h-BNNS/PVA emulsions preparation

Pickering emulsions stabilized with exfoliated h-BNNS/PVA were prepared following a simple two-step sonication protocol similar to the one described for the preparation of GO and h-BNNS emulsions (Section 2.3.3). First, h-BN (2 wt%) powder was suspended in water and sonicated for 1 h at 65 % amplitude with pulse off/on 0.5 – 1 s using ultrasounds device (model SONOPLUS HD 3100, 100W, 20 kHz) with a microtip of diameter 3 mm (MS73). This step ensures the exfoliation of boron nitride. Due to the weak Van der Waals interactions between h-BN layers, the sonication procedure is able to break these interactions leading to mono- or few-layered materials.\(^\text{10}\)

Then, 15 wt% of PVA was dissolved in the exfoliated h-BNNS aqueous suspension under magnetic stirring at 80 °C for 4 h. Later, ethyl benzoate was added to the as-prepared h-BNNS/PVA suspension with different oil/water ratios. The emulsion was obtained after sonication with the same equipment for 15 min at 65 % amplitude and pulse off/on 0.5 – 1 s.

**Figure 2.13** Schematic illustration of h-BNNS/PVA Pickering emulsion preparation
2.4.3 Development of h-BNNS/PVA membranes

All the membranes were prepared using the doctor blade technique. Doctor blade (or tape casting) is one of the widely used techniques for producing thin films with large areas onto glass supports at room temperature. In this process, well-mixed slurry containing a suspension of particles along other additives is placed on a substrate; in our case, we used a glass support. The slurry is spread on the substrate, forming a thin film when a constant relative movement is established between the blade and the substrate. The doctor blading can operate at speed up to several meters per minute and is suitable to coat substrate with a very wide range of wet film thicknesses ranging from 20 to several hundred microns.¹¹

In our case, the h-BNNS/PVA emulsion was slowly deposited onto the glass support. Then a speed of 40 cm s⁻¹ was applied to cast the emulsion with a 500 µm thickness. After casting, a homogeneous white film was obtained. Two different approaches can be used to obtain crosslinked PVA membranes. The crosslinking reaction can be carried out in an indirect or direct way. The first one consists of crosslinking the membrane after its elaboration, when its structure is already fixed (indirect crosslinking). Otherwise, the crosslinking can be initiated before the membrane elaboration by direct addition of the crosslinker to the emulsion solution (direct crosslinking).
**Figure 2.14** Schema of the casting technique used for the membrane preparation

### 2.4.4 Crosslinker

The PVA is a hydro-soluble polymer, thus a crosslinking step is necessary to make the membranes insoluble to be used in filtration applications concerning aqueous solutions. This consists in the creation of a physical or chemical network between the different polymer chains to limit their mobility and thus to make the membrane insoluble in aqueous media. In the literature, there are different methods described to crosslink the PVA in order to obtain hydrogels or membranes.\(^{12,13}\)

Chemical crosslinkers allow the connection between two PVA chains by a chemical reaction of PVA with the crosslinker. In this study, glutaraldehyde (GTA) was used as crosslinker agent. The GTA is a dialdehyde commonly used for the polymers crosslinking, its reaction with PVA has been widely studied in the literature. The reaction mainly consists in the creation of acetal groups in acid media between an aldehyde from the GTA and two hydroxyl groups from the same or different PVA chains. Kim et al. have detailed the reaction mechanism between GTA and PVA in acid media.\(^{14}\) The crosslinking reaction initiates by the reaction between the GTA and the acid catalyst.
This reaction allows the protonation of GTA, which will be able to react with the PVA chains (Figure 2.16). The acid used during all the study to ensure the acidity of the media was the hydrochloric acid (HCl).

![Chemical structure](image)

**Figure 2.15** Crosslinking reaction of PVA with GTA catalyzed in acidic media

In the indirect crosslinking, the membranes were cured at room temperature for different durations (1, 3 and 24 h). This step will define the membrane structure, as during the curing time, water and ethyl benzoate evaporate, leading to higher polymer concentration. Thus, the polymer chains might come closer to each other, leading to changes in the internal structure of the membrane. After curing, the membrane was immersed into an ethanol bath containing 3 wt% of GTA and 1 wt% of HCl (Figure 2.17). The membranes were left into the crosslinking bath overnight to ensure an effective crosslinking reaction. After, the membranes were washed several times with water and ethanol to remove any traces of GTA or ethyl benzoate. The membranes were stocked into a plastic box containing water.
The direct crosslinking consists in adding the crosslinker solution, containing GTA and HCl directly into the as-prepared emulsion (Figure 2.18). The crosslinking reaction takes place already at room temperature. The crosslinker was accordingly kept at 1°C in an ice bath as well as the h-BNNS/PVA emulsion. The crosslinking reaction initiates when the crosslinker is added to the emulsion, so we have few minutes to cast the membrane before the reaction starts due to low temperature of the solutions.

![Figure 2.16 Membrane crosslinking by immersion into a crosslinker bath](image)

![Figure 2.17 Set-ups for the first step of the direct PVA-GTA crosslinking in solution for the membrane elaboration](image)
2.4.5  h-BNNS/PVA membrane characterization

There is a vast number of characterization methods that are employed for the investigation of porous materials or porous material-related composites. Each of them on their own cannot provide sufficient contribution to the determination of the structure, morphology, surface features, porosity, reactivity, conductivity, resistance, etc. Combining different techniques supplies valuable information for a comprehensive characterization study. In this section, we will describe in general terms the different characterization techniques used and how they were used to characterize our materials.

2.4.5.1  Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is a type of electron microscopy that produces images of a sample by scanning the surface with a focused beam of electrons and can provide information about the sample's surface topography and composition. SEM uses a focused beam of high-energy electrons, which scans the surface, and the secondary (inelastic emitted electrons) and backscattered electrons are detected in order to image the surface characteristics. It is desirable that the specimen be rendered electrically conducting; otherwise, a sharp picture will not be obtained. Conductivity is usually achieved by evaporating a film of metal, such as gold or other metals, 50–100 Å thick onto the specimen in vacuum (such a thickness does not materially affect the resolution of the surface details).
The morphology of the intern structure and surface of the obtained membranes was observed using a Hitachi S4800 SEM system. It was equipped with a secondary and backscattered electron detector with an acceleration voltage from 0.1 kV to 30 kV. To carry out the analysis, samples were first coated with platinum using an ion sputter coater.

2.4.5.2 Crosslinking effectiveness

The crosslinking degree was measured using FTIR system (see section 2.2.4.4). For this propose the ratio of maximum intensity corresponding to peaks at 3330 cm\(^{-1}\) and 1720 cm\(^{-1}\) was calculated to give a relative indication on the cross-linking degree.

Crosslinking effectiveness: \[
\frac{\text{Intensity}_{\text{-OH}}}{\text{Intensity}_{\text{C=O}}}
\]

Equation 2.8
2.4.5.3 Water contact angle measurements

The contact angle is defined as the angle formed by the intersection of the liquid-solid interface and the liquid-vapor interface. The interface where solid, liquid, and vapor co-exist is referred to as the “three-phase contact line”. Figure 2.20 shows that the contact angle depends on how the liquid behaves when deposited on a surface. When the fluid spreads over a large area on the surface, a contact angle less than 90 ° is observed; while contact angles greater than 90 ° generally means that wetting surface is unfavorable. Therefore, water contact angles (WCA) smaller than 90° usually refer to “hydrophilic” surfaces, while WCA larger than 90° characterize “hydrophobic” surfaces. WCA were measured using a B-CAM-21-BW (CCCIR) monochrome camera and a Led R60 lamp purchased from CONRAD. For each sample, 3.0 μL of ultrapure water was deposited on the membranes using a needle. The images were recorded by the One Touch Grabber software and treated using the ImageJ software.

![Figure 2.19 Schema of contact angles formed by a liquid drop on a smooth solid surface](image)

**Figure 2.19** Schema of contact angles formed by a liquid drop on a smooth solid surface
2.4.5.4 Swelling capacity

The swelling capacity of a polymer can be determined by the amount of liquid that could be absorbed by the material. Thus, the membrane were cut into 1 × 1 cm² pieces and dried under vacuum for 24 h. The initial weight of the membranes was recorded and equilibrated at ambient temperature in 5 mL of deionized water. The swelling capacity was evaluated periodically by measuring the weight of the films using a microbalance (Sartorius CPA225D with an accuracy of 0.00001 g) after gently blotting the surface with a tissue paper.

The swelling ratio (%) was evaluated as:

\[
\text{SWR} = \frac{W_W - W_D}{W_D} \cdot 100
\]

Equation 2.9

where, \( W_D \) is the weight of the dry membrane and \( W_W \) is the weight of the membrane after wetting. Each data point shown is the average value of three replicates.

2.4.5.5 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and a reference is measured as a function of temperature. In our study, we used the DSC technique to investigate the influence of the addition of h-BNNS in the thermal transition of PVA. Thermal transitions comprise the changes in the polymer melting or in the glass transition temperatures.
Chapter 2

The thermal transition behavior of the membranes was determined by a differential scanning calorimeter (model TA instruments DSC Q20) equipped with a RCS90 cooling system, from 20°C to 200°C. A heating rate of 10°C/min was used under nitrogen atmosphere and at flow rate of 50 mL/min. The samples weight was about 3 mg and they were sealed into an aluminum capsule for the analysis.

2.4.5.6 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is one of the members of the family of thermoanalytical techniques used to characterize a wide variety of materials. TGA provides complimentary and supplementary characterization information to the most commonly used thermal technique, DSC. TGA measures the amount and rate (velocity) of sample mass changes as a function of temperature or time in a controlled atmosphere. The measurements are used primarily to determine the thermal and/or oxidative stability of materials as well as their compositional properties. TGA consists of a pan where the material is deposited; this pan is supported by a precision balance. That pan resides in a furnace and is heated or cooled during the experiment. The mass of the sample is monitored during the experiment. A sample purge gas controls the sample environment.

Thermal behavior of the as prepared membranes was examined by Thermogravimetric Analyzer model TA instruments TGA G500 from 20°C to 800°C. A heating rate of 10°C/min was used under air atmosphere and at flow rate of 60 mL/min. Dry samples weighing about 10 mg were used.
2.4.5.7 Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) is a technique where a small deformation is applied to a sample of a known geometry in a cyclic manner. The sample can be subjected by a controlled stress or a controlled strain. For a known stress, the sample will then deform a certain amount. How much it deforms is related to its stiffness. A force motor is used to generate the sinusoidal wave, which is transmitted to the sample via a drive shaft.

The mechanical properties of the obtained membranes were characterized using the DMA system (Metravib 50N) at a tensile testing speed (crosshead speed) of 0.05 mm min\(^{-1}\). The sample was clamped at top and bottom; thereby the specimen is subjected to an underlying tensile stress to prevent it from buckling during loading. The Young’s modulus of the membranes was calculated from the elastic region of the stress–strain curves.

![Schematic of the dynamic mechanical analysis device.](image)

**Figure 2.20** Schematic of the dynamic mechanical analysis device.
2.4.5.8 Porometry

Gas-liquid (g-l) displacement is one of the dynamic techniques for evaluating pore-size distributions larger than 50 nm. All the pores of the tested membrane are, at first, filled with a wetting liquid, which can penetrate into the pores automatically due to the favorable capillary force; then a gas is forced into the pores to progressively expel the liquid. By monitoring the membrane pressure versus the flux of the displacing liquid, the pore-size distribution can be determined through Laplace’s law (Equation 2.9). The surface tension of gas-liquid systems is about 17 ~ 73 mJ/m² depending on the solvent used to fill the pores. The selection of solvent depends also of the approximate membrane pore size. If the size is smaller than 0.3 µm, isopropanol will be used for analysis. Otherwise, for pores larger than 0.3 µm, water is a good solvent. It should be noted that the mass transport in membrane pores can be complicated when gas is used as the displacing fluid, since the mechanism of gas transport through capillary pores depends on the ratio of the pore size to the mean free path of the displacing gas.

\[
\Delta P = \frac{4 \gamma \cos \theta}{D}
\]

Equation 2.10

where ΔP is the differential of applied pressure, γ is the interfacial tension of solvent, θ is the contact angle between the material and the liquid and D is the pore diameter.

The membrane permeability was measured by solvent permeability; the experiments were carried out using a PRM-2000-LL-R porometer (IFTS-France) with a membrane-active surface area of 2.27 cm². Figure 2.22 shows the porometer system used to test the membranes performances. The advantage of the system is that both solvent permeability and gas-liquid displacement porometry test are carried out in the same membrane.
First, the pure water flux ($J_{PW}$) was measured by circulating pure water through the membrane system using an applied pressure range determined by the porometer. Each point was obtained measuring the flow passing through the membrane during 60 s. At the end of the experiment, all the pores are filled with water. At this point, nitrogen gas was applied through the membrane, and the flow rate was measured as a function of the applied pressure. When a linear dependence is obtained between nitrogen flow and pressure, it means that all pores have been opened. Pore dimension patterns are calculated by applying Laplace’s law (Equation 2.9). Each data point shown is the average value of three replicates.

**Figure 2.21** Schema of the porometer system used to perform the membranes performances.

where, HP and LP are high and low pressure detectors, DG is gas detector and DL is liquid detector.
2.4.5.9 Particle rejection test

The membrane’s particle rejection efficiency was evaluated to corroborate the pore size results obtained by gas-liquid displacement. Frontal filtration experiments were carried out using a stirred dead-end cell (Amicon 8050, Millipore Corporation) with a membrane-active surface area of 2.27 cm² (Figure 2.23). The membranes were first compacted by filtering pure water up to 1 bar until a constant flux was observed. The particles were monodispersed polystyrene latex particles with diameters of 0.1, 1.2 and 3 μm (Thermo Fisher Scientific). The feed solution was prepared by adding the latex nanoparticles (NPs) to 15 mL of ultrapure water solution. The feed was added into the cell and forced to permeate through the membranes using an applied pressure of 0.4 bars. The permeate solution and the feed solution were collected after filtration into a vial and later analyzed by dynamic light scattering (DLS) to estimate the amount of latex NPs passed through the membrane.

![Figure 2.22 Schema of stirred dead-end cell used for particle rejection test](image)

**Figure 2.22** Schema of stirred dead-end cell used for particle rejection test
2.4.5.10 Dynamic light Scattering (DLS)

Dynamic light scattering is a technique used to determine the size distribution profile of small particles or polymers in suspension or polymers in solution. This method relies upon the measurement of scattering intensity of nanoparticles in Brownian motion when illuminated by a monochromatic beam of light. This scattering intensity fluctuates on a microsecond timescale, the fluctuations corresponding to the diffusion rate of the particles. It should also be noted that the scattering of light depends on the refractive index of macromolecules. Since intensity fluctuations of macromolecules are being collected and analyzed in a DLS experiment, the first-hand information on hydrodynamic radii ($R_h$) is based on the intensity distribution that provides z-average $R_h$. As light scattering depends on the refractive index of macromolecules and solvent viscosity, the z-averaged $R_h$ requires input of these two properties.\(^{15}\)

The particle rejection efficiency was finally calculated using the following equation:

\[
\% R = (1 - \frac{I_p}{I_R}) \cdot 100
\]

Equation 2.11

where $I_p$ is the intensity measured on the permeate solution and $I_R$ is the intensity measured on the feed solution retained in the cell. Each data point shown is the average value of three replicates; the membrane permeability was followed after each experiment to verify the membrane performance.
2.5 Conclusion

This chapter provides the information about the different chemicals used for the exfoliation of 2D materials and the preparation of Pickering emulsions. The protocol for the exfoliation of h-BN in presence of gelatin and chloride salts is also described in this chapter. The preparation method for Pickering emulsions stabilized with both GO and h-BNNS was presented in this section, as well as the Pickering emulsions used for the membranes preparation. The information about the different physico-chemical techniques used for the characterization of the obtained materials was briefly described.

The next chapter will be dedicated to the exfoliation of bulk hexagonal-boron nitride (h-BN) into hexagonal-boron nitride nanosheets h-BNNS. Therefore, it will include the procedure for the exfoliation of pristine h-BN assisted with gelatin and chloride salts for the gaining of h-BNNS. The characterization of the obtained h-BNNS by the experimental techniques presented in the present chapter will be described.
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Chapter 3

Exfoliation of Hexagonal Boron Nitride (h-BN) in Liquid Phase by Ion Intercalation*

Abstract

In this chapter, a green approach to prepare exfoliated h-BNNS from commercially pristine h-BN involving a two-steps procedure was investigated. The first step involves the dispersion of pristine h-BN within an aqueous solution containing gelatin and chloride salts using sonication method. The second one involves the removal of larger exfoliated h-BNNS through a centrifugation procedure. The exfoliation was caused not only by sonication effect but also by assisted-gelatin and intercalation of K$^+$ and Zn$^{2+}$ ions. Transmission electronic microscopy, X-ray diffraction and Raman spectroscopy techniques show that the obtained h-BNNS generally display a thickness about few (3-9) layers with an exfoliation efficiency as high as 16.3 ± 0.4%.

* This work has been published as: D. Gonzalez Ortiz, C. Pochat-Bohatier, J. Cambedouzou, M. Bechelany, P. Miele; Nanomaterials, 2018, 8, 716
3.1 Introduction

Two-dimensional (2D) nanosheets, have been receiving great attention in recent years, due to their ultrathin structure with infinite planar dimensions and their outstanding properties.\textsuperscript{1-3} The advantage of these materials is that they have great potential in a huge range of applications at scientific and technological levels due to its exfoliated state, as single- or few-layers. The most known and most widely studied 2D layered material is graphene. It is composed by a one-atom thick planar sheet of $sp^2$ hybridized carbon atoms. Recently, other 2D layered materials, such as layered transition metal dichalcogenides (LTMDs) (\textit{e.g.}, MoS$_2$ and WS$_2$), metal oxides and hexagonal boron nitride (h-BN) have gained a renewed interest. Their lamellar structure, analogous to that of graphite, can be exfoliated into single- and few-layer nanosheets. The structure and morphology of exfoliated 2D layered materials strongly influence their properties: they present high surface area and quantum confinement effects\textsuperscript{4,5} and also high chemical stability and insulating properties.\textsuperscript{6}

In this study, we focus our attention on layered h-BN. Its layered structure consists of a lattice similar to graphite in which boron (B) and nitrogen (N) atoms alternate in hexagonal arrangement within the layers whereas they are in an eclipsed configuration when observed perpendicularly. Therefore, boron nitride nanosheets (BNNSs) are basically composed by sheets of $sp^2$ hybridized 2D layers, organized in honeycomb geometry, with an interlayer distance of \textit{ca.} 0.34 nm. Recently, the interest of scientists in the BNNSs as 2D nanomaterial has increased because of their advantages compared to graphene. Besides the unique chemical and thermal stabilities of BNNS\textsuperscript{7,8} they also present great mechanical strengths and electrical insulating properties (bandgap of 5 ~ 6
eV). Therefore, BNNSs have important applications in nanodevices or functional composites.

Due to its beneficial properties, h-BN has been extensively used in many applications. Traditionally, h-BN has been used effectively as a solid lubricant at extreme temperatures,\textsuperscript{10} UV-light emitters,\textsuperscript{9} and as dielectric materials.\textsuperscript{11,12} Additionally, bulk h-BN has been used in cosmetics and as ceramic in industrial machines.\textsuperscript{13} The nanoscale properties of h-BNNS make them more interesting for different applications. First, due to their high mechanical strength, h-BNNS could be useful for polymer reinforcement.\textsuperscript{14} h-BNNS have already been used to improve the elastic modulus and the strength of film polymers.\textsuperscript{15} Furthermore, h-BNNS can be used as a non-conducting substrate for electronic applications.\textsuperscript{16}

The aim of this study is to develop a new exfoliation method to obtain mono- or few-layered BNNS, minimizing the use of organic solvents and yielding large amount of material. Nowadays, two different approaches exist for large-scale production of BNNSs, bottom-up and top-down processes. The bottom-up approach includes chemical vapor deposition (CVD)\textsuperscript{17,18,19} and segregation method.\textsuperscript{20} This methodology provides single-layer BNNSs but requires extreme conditions of temperature and pressure. Therefore, it is widely considered as unsuitable to synthesize BNNSs at larger scale. On the other hand, the top-down approaches are based on exfoliating bulk h-BN crystals via mechanical\textsuperscript{21-23} or sonication methods.\textsuperscript{15,24,25} Such approaches have already been reported for graphene, for which individual sheets of 2D crystals were successfully separated. However, the B-N bond presents a partially ionic character compared to the covalent C-C bonding of graphene, leading to interactions between adjacent concentric shells or neighboring BN layers (so-called “lip-lip” interaction).\textsuperscript{7} The van der Waals
interactions between graphene layers are much weaker than those of h-BN, and hence it is challenging to exfoliate h-BN.

The mechanical exfoliation was one of the first strategies to produce high quality h-BN monolayers but in very low quantities and with high density of defects. Chemical exfoliation of h-BN was later performed as an alternative and low cost route for the production of h-BNNS. Inspired by the exfoliation of graphene oxide, Hummer’s method has been applied to h-BN, obtaining microsized layers (2-3 layers thickness) of h-BNNS, but in low yields ~ 6.5 %. Liquid phase exfoliation is also one of the most investigated methods for exfoliating h-BN. Different attempts to prepare h-BNNS have been reported, treating the bulk in various organic solvents. Zhi et al. dissolved for instance h-BN in DMF applying vigorous ultrasonication followed by exfoliation. Warner et al. used 1,2-dicholoethane to exfoliate the bulk h-BN by ultrasonic bath. Using these methods, small yield, around 5 %, could be achieved. Besides organic solvents, water has been used as solvent for exfoliation of h-BN using ultrasounds. Gelatin-assisted h-BN exfoliation under ultrasonic conditions has been also reported without large success concerning the exfoliation yield. All these approaches failed to produce h-BNNS with high-yield exfoliation and in an environmentally friendly way. Therefore, a new low cost method to produce large scale and high quality h-BNNS needs to be explored.

Herein, we present a facile and green procedure combining sonication and centrifugation methods to produce high-yield h-BNNS from a commercially available powder. Gelatin and chloride salts were used to assist the exfoliation. The ions intercalation between the layered structures of bulk material facilitates the exfoliation.
The obtained h-BNNS generally display a thickness about few (3-9) layers with an exfoliation efficiency as high as 16.3 wt% and has high crystallinity.

3.2 Experimental part

Materials

Hexagonal boron nitride (h-BN) was supplied from Saint Gobain (CAS n° 10043-11-5, 95 % purity, 325 mesh, 3 µm particle size). Zinc chloride (ZnCl$_2$, 99.99 % trace metal basis), potassium chloride (KCl, $\geq$ 99 %) and gelatin type A (gel strength 300) were purchased from Sigma Aldrich. In all the experiments deionized pure water (18 MΩ) was used.

Methods

h-boron nitride (h-BN) nanosheets were fabricated using liquid phase exfoliation with the assistance of an ultrasound device (model SONOPLUS HD 3100, 100W, 20 kHz) with a 3 mm diameter microtip (MS73). 1.0 g of pristine h-BN was added to 100 mL of water. The solution was heated up to 80 °C, then 20 g of gelatin were added. The gelatin will prevent the re-aggregation of nanosheets. The mixture was kept under stirring at the same temperature until the complete dissolution of the gelatin. Different concentrations of ZnCl$_2$ and KCl were added to the mixture. The dispersion was kept in a bath at 50 °C to avoid the gelatin solidification and it was sonicated for 3 hours at 65 % amplitude with pulse off/on 0.5 – 1 s. After the sonication, the yellowish suspension was subjected to two centrifugation steps. The solution was centrifuged at 3000 rpm for to ensures the separation of large h-BNNSs from light ones by remaining at the bottom of the solution. The supernatant was collected and dried at 60 °C
overnight. In a first step, the resultant material was heated up to 600 °C under air to remove the gelatin. In a second step, the obtained powders were heated up to 1000° under Ar atmosphere with a flux of 200 mL/min, to improve the h-BNNS crystallinity. The obtained h-BNNS were washed several times with water and ethanol to remove any remaining impurities.

Characterization techniques

The transmission electron microscopy (TEM) was performed using a JEOL 2200 FS-200 kV equipped with a STEM module (Scanning Transmission Electron Microscopy) a Bright Field (BF) detector and a CCD Gatan USC 4092x4092px² camera. To carry out the analysis, a drop of h-BNNS/isopropanol dispersion was deposited on the surface of the carbon grids. Atomic force microscopy (AFM) analysis was performed using an AFM NANOMAN 5 from Veeco Instrument controlled with the Nanoscope V software. The exfoliated h-BN was previously dissolved in water and then a drop of the solution was deposited on silicon wafer. X-ray diffraction patterns of exfoliated h-BNNS were recorded using a PANalytical Xpert powder XRD system with Cu Kα radiation, a scan speed of 2° min⁻¹, a 2θ range of between 3 and 70°, and a step rate of about 0.02° per second. The Fourier transformed infrared (FTIR) spectra were recorded with a NEXUS instrument equipped with an attenuated total reflection (ATR) accessoary in the frequency range of 600 – 4000 cm⁻¹. Raman spectra have been obtained from a Horiba xplora, λ= 659 nm. The yield of exfoliated h-BNNSs was calculated from the following equation:

\[
\text{Yield (\%)} = \left( \frac{\text{Weight}_{\text{h-BNNS}}}{\text{Weight}_{\text{h-BN}}} \right) \times 100
\]

\textbf{Equation 3.1}
Chapter 3

3.3 Results and discussion

First, we will discuss the different techniques used to characterize the exfoliated h-BNNS obtained by ion intercalation method.

The starting h-BN powder has a typical lateral particle size in the range of 3 µm. The preparation of h-BNNS was carried out from pristine h-BN in a simple combination of gelatin/chloride salts sonication and centrifugation steps. Additional heating steps were performed to remove the gelatin and improve the h-BNNS crystallinity. The yield of obtained h-BNNS was calculated from Equation 3.1. The results are shown in Table 3.1. The best exfoliation efficiency (16.3 %) is obtained when 1.0 wt% of KCl was used to intercalate the ions within layered structure of h-BN (Table 3.1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial h-BN weight (g)</th>
<th>Purified h-BNNS (g)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>h-BNNS gelatin</td>
<td>1.015</td>
<td>0.065</td>
<td>6.4 ± 0.1</td>
</tr>
<tr>
<td>0.5 wt% K/h-BNNS</td>
<td>1.014</td>
<td>0.143</td>
<td>14.1 ± 0.2</td>
</tr>
<tr>
<td>1.0 wt% K/h-BNNS</td>
<td>1.016</td>
<td>0.165</td>
<td>16.3 ± 0.4</td>
</tr>
<tr>
<td>0.5 wt% Zn/h-BNNS</td>
<td>1.005</td>
<td>0.124</td>
<td>12.3 ± 0.2</td>
</tr>
<tr>
<td>1.0 wt% Zn/h-BNNS</td>
<td>1.009</td>
<td>0.108</td>
<td>10.8 ± 0.3</td>
</tr>
</tbody>
</table>

Table 3.1 Yields of h-BNNS obtained through exfoliation with gelatin, and gelatin assisted ion intercalations with 0.5 and 1.0 wt% of KCl and ZnCl₂.
3.3.1 Transmission electron microscopy

Transmission electron microscopy (TEM) studies were carried out in order to determine the morphology of h-BNNS. The as-obtained dispersion showed the presence of irregularly shaped h-BNNS with lateral sizes ranging from few tens of nanometers to as large as over 1 µm (Figure 3.1). The relative thickness of the h-BNNS could be visually examined by the transparency/darkness of the nanosheets against the electron beam, with thinner nanosheets appearing lighter. It is observed that the h-BNNS flakes obtained when the exfoliation is assisted by KCl (Figure 3.1 a, b) display a nanosheets lateral size mostly less than 200 nm, and the thickness is about few (2-3) layers. These results indicate that the sheets reduced their size by “cutting” the large h-BN sheets into smaller ones. Furthermore, the sonication process allows an effective “peeling out” of nanosheets from the bulk h-BN material, forming mono- and few-layered nanosheets with reduced lateral sized in the dispersion, since the initial size of pristine h-BN is about 3 µm.

The nanosheets obtained when higher amount of salts were used to exfoliate the pristine h-BN are thinner than when a lower concentration of salts is used. This fact could be due to the fact that at higher concentration, more ions can be intercalated into the layered structure of h-BN, weakening the Van der Waals interactions between the layers and then leading to a greater exfoliation.
**Figure 3.1** TEM images of h-BNNS exfoliated with a) 0.5 wt% KCl, b) 1.0 wt% KCl, c) 0.5 wt% ZnCl₂ and d) 1.0 wt% ZnCl₂

In the case of h-BNNS obtained when the exfoliation is assisted by ZnCl₂ (Figure 3.1 c, d), the flakes display a lateral size up to 0.5 μm and are composed with a more significant amount of layers. The exfoliation efficiency using ZnCl₂ is weaker compared to the exfoliation involving KCl. These results might be explained regarding the size of the ionic diameters. The ionic diameter of K⁺ is 2.76 Å while the ionic diameter for Zn^{2+} is 1.48 Å. Taking into account that the interlayer distance of pristine h-BN is 3.3 Å, both
ions are able to intercalate between the h-BN layers, but the K\(^+\) ions are larger than the Zn\(^{2+}\) ions. Thus, the incorporation of K\(^+\) ions should have a higher ability to weaken the inter-sheet interactions and to destabilize the packing of BN sheets. This results in a higher exfoliation degree.

**Figure 3.2** Schematic diagram of the synthesis of h-BNNS using chloride salts assisted exfoliation

### 3.3.2 Atomic Force Microscopy

h-BNNS obtained after liquid exfoliation in water assisted by gelatin and by gelatin with ZnCl\(_2\) or KCl using sonication tip, were characterized as well by AFM. A number of about 100 h-BNNS have been considered for each sample. The images (Figures 3.3, 3.4 and 3.5) indicate a reduction on the thickness of pristine h-BN from 3 \(\mu\)m to 1-3 nm in the case of intercalation of K\(^+\) ions, and reduction of thickness to 2-6 nm for the intercalation of Zn\(^{2+}\) ions. Based on these AFM images and taking into account the width of one nanosheet (0.33 nm), we could assume that our h-BNNS are generally composed of 3-9 layers in the case of exfoliation with 1 wt % KCl. Besides, the h-BNNS exfoliated with 1 wt% ZnCl\(_2\) display a thickness about 2-16 nm, which correspond around 6-48 layers.
Figure 3.3 a) Height of h-BNNS and b) AFM image of h-BNNS intercalated with 1 wt% KCl

Figure 3.4 a) Height of h-BNNS and b) AFM image of h-BNNS intercalated with 1 wt% ZnCl₂
Figure 3.5 a) Height of h-BNNS and b) AFM image of h-BNNS exfoliated with gelatin

Otherwise, when the exfoliation is assisted only with gelatin, we observed that the nanosheets size is reduced in comparison to pristine h-BN, from 3 μm to about 10 – 60 nm. If we compare these resulting nanosheets with the ones obtained when the exfoliation is assisted with gelatin/Zn$^{2+}$ or gelatin/ K$^+$ ions, the exfoliation degree is much lower. Thus, we can say that the addition of ions to the solution during sonication helps to improve the exfoliation degree and to obtain nanosheets with smaller dimensions.
Table 3.2 Summary of thickness of pristine h-BN and exfoliated h-BNNS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness</th>
<th>N° of layers</th>
<th>Lateral size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>h-BN</td>
<td>3 µm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>h-BNNS gelatin</td>
<td>10 – 70 nm</td>
<td>30 - 200</td>
<td>-</td>
</tr>
<tr>
<td>1.0 wt% ZnCl₂</td>
<td>2 – 16 nm</td>
<td>6 - 48</td>
<td>0.5</td>
</tr>
<tr>
<td>1.0wt% KCl</td>
<td>1 – 3 nm</td>
<td>3 - 9</td>
<td>&lt; 0.2</td>
</tr>
</tbody>
</table>

3.3.3 X-ray diffraction

X-ray diffraction (XRD) was used to investigate the phase structure of the as-prepared materials. The h-BN (Figure 3.6) displays the diffraction peaks at $2\theta = 26.66^\circ$, $\sim 40 - 45^\circ$ and $55.05^\circ$ which can be correlated to the (002), unresolved reflections (100) and (101), and (004) planes of the hexagonal phase of BN. No impurity from salts was detected, which indicates that the as-prepared h-BNNSs are pure. However, it is interesting to note that the 002 peak of h-BNNSs, exfoliated via intercalation of Zn$^{2+}$ or K$^+$ ions, becomes broader regarding pristine h-BN.

The full width at half maximum (FWHM) of a peak is sensitive to the variation of the microstructure and stress-strain of the materials. For that, the FWHM of the 002 diffraction peak of h-BNNS was calculated from the XRD patterns. The results are shown in Table 3.3. It is observed that the FWHM increases when the h-BN is exfoliated with KCl and ZnCl₂. The h-BNNS intercalated with 1 wt% of K$^+$ and Zn$^{2+}$ ions display a higher value of FWHM, indicating that the crystallite size might decrease during the exfoliation process.
Figure 3.6 XRD patterns a) pristine h-BN, b) h-BNNS gelatin, c) h-BNNS exfoliated by intercalation of 0.5 wt% ZnCl$_2$, d) h-BNNS exfoliated by intercalation of 1.0 wt% ZnCl$_2$, e) h-BNNS exfoliated by intercalation of 0.5 wt% KCl, and f) h-BNNS exfoliated by intercalation of 1.0 wt% KCl

As it is already known in the literature, the peak broadness is related to crystallite size and it varies inversely with the FWHM: as the crystallite gets smaller, the peak gets broader. For this reason, we also calculated the crystallite size of the pristine h-BN, the h-BN exfoliated with gelatin, and a the h-BNNSs intercalated with Zn$^{2+}$ and K$^+$ at different concentrations using Scherrer equation$^{27}$ (Equation 3.2). The results of calculations are shown in Table 3.3.
Table 3.3 Diffraction peak position, $d$ spacing and crystallite size of h-BN, h-BNNS-gelatin and h-BNNS intercalated with different concentrations of KCl and ZnCl$_2$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak position $(^\circ)$</th>
<th>$d$-spacing (nm)</th>
<th>FWHM $\beta$ $(^\circ)$</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>h-BN</td>
<td>26.69</td>
<td>0.334</td>
<td>0.4</td>
<td>20.6</td>
</tr>
<tr>
<td>h-BNNS gelatin</td>
<td>26.61</td>
<td>0.335</td>
<td>0.4</td>
<td>20.1</td>
</tr>
<tr>
<td>0.5 wt% KCl</td>
<td>26.55</td>
<td>0.335</td>
<td>1.6</td>
<td>4.9</td>
</tr>
<tr>
<td>1.0 wt% KCl</td>
<td>26.55</td>
<td>0.335</td>
<td>2.9</td>
<td>2.9</td>
</tr>
<tr>
<td>0.5 wt% ZnCl$_2$</td>
<td>26.61</td>
<td>0.335</td>
<td>0.7</td>
<td>10.7</td>
</tr>
<tr>
<td>1.0 wt% ZnCl$_2$</td>
<td>26.59</td>
<td>0.335</td>
<td>1.9</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Scherrer equation:

$$D = \frac{0.9 \cdot \lambda}{\beta \cos \theta}$$ \hspace{1cm} \text{Equation 3.2}$$

where, $D$ is the crystallite size, $\lambda$ is the wavelength of the X-ray beam ($\lambda = 0.154\text{nm}$ ), $\beta$ is the FWHM and $\theta$ is the diffraction angle.

Bragg’s law:

$$d = \frac{\lambda}{2 \sin \theta}$$ \hspace{1cm} \text{Equation 3.3}$$

where, $d$ is the distance between adjacent sheets or layers, $\lambda$ is the wavelength of the X-ray beam ($\lambda = 0.154\text{nm}$ ) and $\theta$ is the diffraction angle.
The results obtained with Scherrer equation show that increasing the salts (ZnCl$_2$ and KCl) concentration during the intercalation results in smaller h-BNNS crystallites as compared to pristine h-BN. In the case of exfoliation assisted with gelatin only, the reduction of crystallite size is less pronounced. The initial crystallite size in pristine h-BN is calculated to be 20.6 nm. On one hand, the addition of the K$^+$ ions during sonication shifts the peak to lower angles, from $2\theta = 26.69^\circ$ in pristine h-BN to $26.55^\circ$ in h-BNNS. On the other hand, it reduces the crystallite size of the resulting h-BNNS down to 4.9 nm when 0.5 wt% KCl was used and down to 2.9 nm when 1.0 wt% KCl was introduced. In the case of intercalation with Zn$^{2+}$ ions, the peak is also shifted to lower angles, from $2\theta = 26.69^\circ$ in pristine h-BN to $26.61$ and $26.59^\circ$ in h-BNNS intercalated with 0.5 and 1.0 wt% ZnCl$_2$, respectively. The crystallite size was also reduced regarding to pristine h-BN: from 20.6 nm to 10.7 nm and 4.2 nm when 0.5 and 1.0 wt% ZnCl$_2$ were introduced, respectively. In the case of h-BN exfoliation assisted by gelatin, the FWHM is slightly reduced if compared with pristine h-BN, thus crystallite size is also reduced from 20.6 nm to 20.1 nm. This shift of the peak position in the exfoliated h-BNNS is related to the interlayer distance ($d$-spacing). For this reason, the interlayer distance of pristine h-BN, h-BNNS assisted by gelatin and h-BNNS intercalated with 0.5 and 1.0 wt% of KCl and ZnCl$_2$ was calculated using Bragg’s law (Equation 3.3). The results are shown in Table 3.3. It is observed that the intercalation either with K$^+$ or Zn$^{2+}$ ions has an influence on the BN interlayer distance. Pristine h-BN displays a $d$-spacing of 0.334 nm. The intercalation of 0.5 and 1.0 wt% of KCl gives a larger interlayer distance, i.e. 0.335 nm. Note that the increase of the interlayer distance is too small to be due to remaining ions between the layers. It is more probably due to structural defects coming from the sonication process in the BN planes that modifies their equilibrium distance.
On the other hand, the intercalation of Zn\(^{2+}\) ions produces the same effect; the interlayer distance is increased to 0.335 nm when 0.5 and 1.0 wt% of ZnCl\(_2\) was used, respectively. In the case when gelatin alone is added, the interlayer distance also increases up to 0.335 nm but as we mentioned before, the crystallite size is bigger than when the exfoliation is assisted with both gelatin and ions.

### 3.3.4 Raman spectroscopy

Raman spectra of pristine h-BN, h-BNNS gelatin and h-BNNS exfoliated with the intercalation of K\(^+\) and Zn\(^{2+}\) ions are shown in Figure 3.7. h-BN and h-BNNS spectra exhibit a characteristic peak due to the typical B-N stretching mode (E\(_{2g}\)). Table 3.4 shows the Raman shifts of pristine h-BN, h-BNNS gelatin and h-BNNS intercalated with 0.5 and 1.0 wt% KCl and ZnCl\(_2\). Pristine h-BN displays a peak at ~1366 cm\(^{-1}\). It is observed that the peak intensity becomes progressively weaker and broader in both cases: exfoliation with gelatin and with ions intercalation. In addition, the increase of ion concentration makes this effect more pronounced. The exfoliation assisted with gelatin results in a small shift to higher wavenumbers of this peak at about 1367 cm\(^{-1}\). The exfoliation using 0.5 and 1.0 wt% of KCl results in the shift of the E\(_{2g}\) phonon mode approximately 1370 cm\(^{-1}\), corresponding to a blue shift of ~ 4 cm\(^{-1}\). In general, the shift in the peak position can be linked to strain conditions within the layers\(^{10,18,28}\). Thus, results agree with an effective exfoliation of h-BN into thinner flakes, which leads to a higher in-plane strain and weaker interlayer interactions. This effects is more pronounced when increasing the ion concentration.\(^{29}\)
Figure 3.7 Comparative Raman spectra of a) pristine h-BN, b) h-BNNS gelatin, c) h-BNNS exfoliated by intercalation of 0.5 wt% ZnCl$_2$, d) h-BNNS exfoliated by intercalation of 1.0 wt% ZnCl$_2$, e) h-BNNS exfoliated by intercalation of 0.5 wt% KCl, and f) h-BNNS exfoliated by intercalation of 1.0 wt% KCl.

Raman spectra of h-BNNS exfoliated with the intercalation of Zn$^{2+}$ ions is also shown in Figure 3.7. Similar to the exfoliation of h-BN with K$^+$, the peak intensity becomes progressively weaker and broader as the ion concentration increases. The E$_{2g}$ phonon mode of 0.5 and 1.0 wt% of ZnCl$_2$ is centered at approximately 1368 cm$^{-1}$, corresponding to ~ 2 cm$^{-1}$ blue shift. In this case, the shift is lower than for the intercalation of K$^+$. This fact is in line with the lower degree of exfoliation that has been evidenced by the other characterization techniques presented above.
Table 3.4  Raman shift of h-BN, h-BN gelatin and h-BNNS intercalated with different concentrations of KCl and ZnCl₂

<table>
<thead>
<tr>
<th>Sample</th>
<th>Raman shift (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>h-BN</td>
<td>1365.7 ± 0.1</td>
</tr>
<tr>
<td>h-BNNS gelatin</td>
<td>1366.8 ± 0.3</td>
</tr>
<tr>
<td>0.5 wt% K/h-BNNS</td>
<td>1369.3 ± 0.4</td>
</tr>
<tr>
<td>1.0 wt% K/h-BNNS</td>
<td>1370.2 ± 0.2</td>
</tr>
<tr>
<td>0.5 wt% Zn/h-BNNS</td>
<td>1368.1 ± 0.2</td>
</tr>
<tr>
<td>1.0wt% Zn/h-BNNS</td>
<td>1368.1 ± 0.3</td>
</tr>
</tbody>
</table>

3.3.5  Fourier –transform infrared spectroscopy

Figures 3.8 and 3.9 show the FTIR spectra of pristine h-BN and h-BNNS intercalated with K⁺ and Zn²⁺ ions. Two strong FTIR bands at ~ 1380 cm⁻¹ and ~ 812 cm⁻¹ are present in pristine h-BN, which are attributed to the B-N stretching (in-plane ring vibration, E₁u mode) and the B-N-B bending (out-of-plane vibration, A₂u mode), respectively. Table 3.5 shows the FTIR bands attribution and peak positions presented on the spectra. Intercalated h-BN with 0.5 and 1.0 wt% KCl and ZnCl₂ present the same band than the pristine h-BN.
Exfoliation of h-BN in liquid phase by ion intercalation method

Figure 3.8 FTIR spectra of pristine h-BN of and h-BNNS intercalated with Zn$^{2+}$ at different concentrations (0.5 and 1.0 wt% KCl)

In addition, the FTIR spectrum of h-BNNS intercalated with 0.5 and 1.0 wt % KCl and ZnCl$_2$ show another absorption peak at $\sim$ 3200 cm$^{-1}$, which could be ascribed to hydroxyl group (-OH) vibration. This peak might appear due to the large number of defects such as vacancy defects, dislocations and exposed edges introduced on the h-BNNS surfaces during sonication. Also a new bending mode appears at $\sim$ 1200 cm$^{-1}$ which is correlated to (-OH) vibration.
Table 3.5 FTIR bands attribution and peak positions of h-BN and h-BNNS intercalated with different concentrations of KCl and ZnCl₂

<table>
<thead>
<tr>
<th>Sample</th>
<th>Attribution</th>
<th>Peak position (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>h-BN</td>
<td>B-N stretching</td>
<td>1270.9</td>
</tr>
<tr>
<td></td>
<td>B-N-B bending</td>
<td>759.7</td>
</tr>
<tr>
<td>0.5 wt% K/h-BNNS</td>
<td>O-H stretching</td>
<td>3372.9</td>
</tr>
<tr>
<td></td>
<td>B-N stretching</td>
<td>1359.6</td>
</tr>
<tr>
<td></td>
<td>B-N-B bending</td>
<td>779.7</td>
</tr>
<tr>
<td>1.0 wt% K/h-BNNS</td>
<td>O-H stretching</td>
<td>3340.2</td>
</tr>
<tr>
<td></td>
<td>B-N stretching</td>
<td>1365.4</td>
</tr>
<tr>
<td></td>
<td>B-N-B bending</td>
<td>779.1</td>
</tr>
<tr>
<td>0.5 wt% Zn/h-BNNS</td>
<td>O-H stretching</td>
<td>3355.6</td>
</tr>
<tr>
<td></td>
<td>B-N stretching</td>
<td>1336.5</td>
</tr>
<tr>
<td></td>
<td>B-N-B bending</td>
<td>767.5</td>
</tr>
<tr>
<td>1.0wt% Zn/h-BNNS</td>
<td>O-H stretching</td>
<td>3367.2</td>
</tr>
<tr>
<td></td>
<td>B-N stretching</td>
<td>1288.2</td>
</tr>
<tr>
<td></td>
<td>B-N-B bending</td>
<td>742.5</td>
</tr>
</tbody>
</table>
The exfoliation of these materials can be explained by the effect of acoustic cavitation of high-frequency ultrasound in the formation, growth and collapse of microbubbles in solution. This effect induces shock waves on the surface of the bulk material causing exfoliation. In addition, the introduced ions (K$^+$ and Zn$^{2+}$) could insert themselves into the h-BN layers, inducing an increase in the interlayer spacing. Furthermore, the non-polar chains of the gelatin can adsorb on the surface of flakes through hydrophobic–hydrophobic interactions, which results in the formation of a stable dispersion.
Figure 3.10 Schema of detailed mechanism of the h-BN exfoliation trough ion intercalation method.

1. Pristine h-BN displays an interlayer distance about 0.334 nm

2. The ions are small enough to be intercalated between the layers. When the sonication is applied, particles acquired a specific motion which helps to weaken the interactions between layers.

3. After the sonication, a large part of B-N bonds are broken. Then the mixture will be composed of mono-/few-layered and non-exfoliated h-BN. Furthermore, the ions are still present in the solution.

4. Centrifugation: helps to separate the mono-layers from non-exfoliated h-BN. After centrifugation the exfoliated h-BN will be in the supernatant part.

5. Heating: first heating at 600 °C allows removing the gelatin. A second heating at 1000 °C helps to remove the rest of ions and improve the h-BNNS crystallinity.

6. After washing the resulting powders with water and ethanol we obtain the h-BNNS.
3.4 Conclusion

In summary, a green approach to prepare exfoliated h-BNNS from commercially pristine h-BN involving a two-steps procedure was investigated in this chapter. The exfoliation was caused not only by sonication effect but was also assisted by gelatin and intercalation of K\(^+\) and Zn\(^{2+}\) ions. The latter resulted in the observation of few-layered h-BNNS of reduced lateral size, as well as few-layered h-BNNS with lateral size below 200 nm, as evidenced from TEM images. The yield for h-BNNS intercalated with 1.0 wt% KCl was about 16.3 ± 0.4 %. The crystallinity of the obtained h-BNS was confirmed using XRD. Raman microscopy further confirmed the presence of the few-layered flakes, by analyzing the peak position shift from the pristine h-BN. FTIR showed a band corresponding to –OH functions in the obtained h-BNNS through the intercalation of the ions. These functions could be attributed to the functionalization of h-BNNS, edges or vacancy defects. Future works are in progress in order to improve the yield of the exfoliated h-BNNS by controlling the different factors that could affect the exfoliation, such as the size of pristine h-BN, the sonication conditions (time, power or pulse) or the centrifugation steps.

The h-BNNS that we will use for the preparation of emulsions will be prepared by other approach, in situ sonication with water, due to the ease process even if the obtained nanosheets present lower quality than those prepared with the method presented in this chapter.
REFERENCES

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Exfoliation of h-BN in liquid phase by ion intercalation method


Chapter 4

Inverse Pickering Emulsions Stabilized by hexagonal Boron Nitride Nanosheets (h-BNNS)*

Abstract

The formation of inverse Pickering emulsions using exfoliated hexagonal boron nitride (h-BN) as an effective particulate stabilizer without using any surfactant is reported for the first time. The stability and the type of h-BN Pickering emulsions formulated with different BN concentrations and by varying oil/water (o/w) ratios are studied and discussed. First the emulsion structure is analyzed microscopically through optical and epifluorescence microscopies, and macroscopically by the study of the rheological behaviors. The average droplet size decreases with h-BN concentration whereas the emulsions achieve good stability at 2 wt% BN concentrations and for a one to one o/w ratio. In all formulations, the emulsions are of water-in-oil (W/O) type mainly due to the hydrophobicity of h-BN.

*This work has been published as: D. Gonzalez Ortiz, C. Pochat-Bohatier, J. Cambedouzou, S. Balme, M. Bechelany, P. Miele; Langmuir, 2017, 33 (46), pp 13394–13400
4.1 Introduction

Pickering emulsions or solid-stabilized emulsions were defined at the beginning of the 20th century in pioneering works of Ramsden\textsuperscript{1} and Pickering.\textsuperscript{2} They are described as colloidal suspensions stabilized by solid nanoparticles instead of organic surfactants, which localize at the interface between two phases. As classical emulsions, they can be simply categorized based on the particle wettability in the case of our study: on the one hand, emulsions formed with hydrophilic particles normally stabilize Oil-in-Water (O/W) emulsions, or “direct” emulsions; on the other hand, those prepared with hydrophobic particles more probably form Water-in-Oil (W/O) emulsions. Sometimes W/O emulsions are also referred as “invert” or “reverse” emulsions. Unusual cases such as water-in-water emulsions, or double-emulsions, can also exist.\textsuperscript{3,4} Pickering emulsions have outstanding properties controlled by both formulation and process parameters, such as the kind of nanoparticles, the control of emulsion type and droplet size. These emulsions are good candidates to replace classical emulsions formulated with surfactants. Pickering emulsions offer specific features in life-science that are not shared with surfactant-based emulsions by avoiding the adverse effects of surfactants such as cytotoxicity.\textsuperscript{5} They can also build a barrier to diffusion of drug molecules and therefore behave as encapsulation systems.\textsuperscript{6} Coated emulsions, for example with hydroxyapatite, can play a role in targeting rules due to cell adhesion.\textsuperscript{7} Furthermore porous materials can be prepared using Pickering emulsion droplets as templates,\textsuperscript{8} in the same manner as hexagonal mesophases of surfactants act as templates for the manufacture of mesoporous inorganic materials such as MCM’s.\textsuperscript{9}
In the last years, many researchers have paid attention to the ability of two-dimensional (2D) materials to promote the formation of special class of Pickering emulsions.\textsuperscript{10} In this kind of emulsions, a large reduction of the free energy (Gibbs Energy $G$) is found due to particles localized at the liquid-liquid interface, leading to the stabilization of the droplets. Graphene oxide (GO) is the most studied 2D material and has been considered to promote the formation of emulsions\textsuperscript{11,12} due to its interesting property to act as a colloidal surfactant having a great interfacial activity at air-water, liquid-liquid, and liquid-solid interfaces.\textsuperscript{12-14,15} He \textit{et al.} investigated the effects of different conditions such as type of oil, the sonication time, the GO concentration, the oil/water ratio, and the pH value on the properties of the Pickering emulsions stabilized by GO.\textsuperscript{12} Creighton \textit{et al.} presented the interfacial thermodynamics of 2D materials such as GO at liquid-liquid interfaces with applications in emulsification.\textsuperscript{10} Pickering emulsions stabilized by GO have been used as soft templates to design new functional hybrid materials.\textsuperscript{16,17,18} It should be pointed out that the graphene-based composites were usually synthesized through an “emulsion polymerization” since the graphene moieties can very well stabilize the monomer. Xie \textit{et al.} reported the preparation of polystyrene (PS) particles \textit{via} Pickering emulsion polymerization using GO as the stabilizer\textsuperscript{18} and Dao and co-workers prepared microspheres of poly(methyl methacrylate) (PMMA)/graphene composite with a core–shell structure by Pickering suspension polymerization.\textsuperscript{19}
Inverse Pickering emulsions stabilized by exfoliated h-BN

In this study, we focused on h-BN as 2D material to prepare Pickering emulsions. Two-dimensional (2D) nanosheets, one-dimensional (1D) nanotubes, and zero-dimensional (0D) fullerenes are examples of materials with reduced dimensionality. These low-dimensional structures exhibit new properties due to quantum confinement and/or surface and interfacial effects when compared to three-dimensional (3D) bulk substances.\(^\text{20}\) Similarly to carbon since the C-C bond is isoelectronic with the B-N bond, BN exists in several polymorphs among which the hexagonal (h-BN) and the cubic (c-BN) are the main\(^\text{21}\). Similarly, tubular structures (BN nanotubes) are also known.\(^\text{22}\) Considering the layered structure of the hexagonal form and its relative ease of preparation as well as its availability, h-BN is the polymorph that will be used in this work. It displays a wide range of unique properties. A hexagonal BN crystal structure with an exposed (002) surface have some advantages compared to graphite, such as very high thermal conductivity, mechanical strength and is electrically insulating (band gap of \(\sim 5-6\) eV). Furthermore, the thermal and chemical stability of h-BN is better than that of graphite.\(^\text{23}\) Such outstanding properties are especially promising for fabrication of BN-based functional materials with specific structure and performance. 2D hexagonal Boron nitride crystals, in the form of nanosheets (BNNS), are applied in the nanomedical field due to their good biocompatibility, and in scanning probe microscopy as ultrathin and stiff tips.\(^\text{24}\) They are also applied for filling polymeric or ceramic composites to strongly improve their thermal and mechanical performances.\(^\text{25,26}\)
W/O Pickering emulsions are more suitable for some applications in comparison to direct emulsions due to their higher stability against collapsing. Frelichowska et al. used W/O emulsions for drug release and topic delivery using hydrophobic silica as stabilizer. Fei et al. synthesized modified graphene oxide/polyaniline nanocomposites from W/O emulsion through an interfacial polymerization mechanism. A patent application related to the preparation of O/W and W/O emulsions for cosmetic and dermatological applications has been reported using functionalized BN as stabilizer. In this procedure, surface BN was modified with siloxane polymer and inorganic pigments. While there is a big aim to develop a new method to prepare materials with specific shapes reducing the number of synthesis steps, there are also now important challenges concerning the direct preparation of W/O emulsions without functionalization of the nanoparticles.

One of the most important properties of emulsions for practical uses is their stability over time and when stress is applied which can be characterized from rheological measurements. The particles may form a transient network that reduces the mobility of the droplets, which leads to a better stability. The flow behavior and the deformation of the emulsions stabilized by nanoparticles depend on different factors such as droplet size and morphology, dispersed phase volume fraction (ϕ), particles concentration and nature of interactions between the particles and the droplets in the continuous phase. Among these parameters, the particle concentration will influence the apparent viscosity by forming dispersed phase droplets of various size and droplets number with oil-water interface covered by solid particles.
4.2 Experimental part

4.2.1 Materials

Hexagonal boron nitride (h-BN) was supplied from Saint Gobain (95% purity, 325 mesh, 3µm particle size), fluorescein sodium salt (Bio-Reagent) and ethyl benzoate (purification 99%, Mw = 150 g mol⁻¹ and density = 1.045) were supplied from Sigma Aldrich. In all the experiments deionized pure water (18 MΩ) was used.

4.2.2 Methods

Pickering emulsions were prepared in two steps using a power ultrasound device (model SONOPLUS HD 3100, Germany) with a 3 mm diameter microtip (MS73). In the first step h-BN powder was suspended in water and sonicated for 1 hour at 65% amplitude with pulse off/on 0.5 – 1 s. This step ensures the exfoliation of boron nitride. Due to the weak Van der Waals interaction between BN layers, the sonication procedure is able to break these interactions leading to mono- or few-layered material. The second step leads to the emulsion formation with the addition of the ethyl benzoate followed by the same sonication procedure than in the first step.

In this study the stability of the emulsions was investigated, for that different factors such as the BN concentration, ratio oil/ water (R_o/w) and the sonication procedure were varied.
4.2.3 Characterization techniques

Atomic force microscopy (AFM) analysis was performed using AFM NANOMAN 5 from Veeco Instrument controlled with Nanoscope V software. The exfoliated h-BN was previously dissolved in water and then a drop of the solution was deposited on a silicon wafer.

Small angle X-ray scattering (SAXS) of the emulsions was performed in a laboratory setup involving a molybdenum source, which delivers a 1 mm large squared beam of energy 17.4 keV. Monochromatization was applied using a “Fox3D” multi-shell mirror, and collimation of the beam was achieved using two sets of scatterless slits. The diffraction patterns were recorded using a mar345 two-dimensional imaging plate with typical duration of 1 h. The measurements were performed in transmission geometry, and the emulsions were held in 2 mm large glass capillaries.

Water contact angle (WCA) measurements were performed on a pellet of exfoliated h-BN. The particles were ground and converted into a pellet with the help of a press, applying a 2 N force during 10 min.

The kinetic stability of the emulsion was evaluated. For that, the emulsions were stored and observed for 14 days at room temperature. Emulsion Stability Index (ESI %) is calculated as the ratio between the volume fraction of emulsion after 14-days equilibration (as depicted by the product of the height $H$ with the vial section) and the volume fraction of emulsion after 3-h equilibration ($H_0$), as described by Equation 4.1 (boundary between the creamed and serum layers was monitored by naked eyes):

$$\text{ESI} = \frac{H}{H_0} \times 100$$

Equation 4.1
The emulsions microstructure and type were characterized by optical microscopy (Olympus BX41, Japan) at 5x magnification equipped with a digital camera (U-TV1X-2, Olympus, Japan) and by laser microdissection microscopy (LEICA, LMD 6500) with 10x objective. The pictures were processed using Image J software to determine the droplet diameter. Mean diameter was calculated with 50 determinations.

In order to evaluate the influence of the sonication effect on the emulsions droplet size, two parameters of the ultrasonic probe, amplitude and power delivered, were investigated. The amplitude effect was evaluated in emulsions formulated with 2 wt% BN and an o/w ratio of 1, the amplitude was varied from 20 to 80 %. The effect of the power delivered to the system was also evaluated using the same ultrasonic device. Firstly, the experiment was carried out in samples with the same BN load at different powers (20 to 75 W) and secondly in samples which different BN loads but constant power (40W).

The surface coverage ($C_s$) was determined from the amount of particles added in the emulsion and the water volume effectively trapped within the droplets. The surface that particles may cover can be estimated by:

$$S_p = N_p \cdot A = \frac{m_p}{l \cdot \rho_p}$$

Equation 4.2

where $N_p$ is the number of particles, $A$ is the area that particles can cover, $m_p$ is the particles mass, $l$ is the particle length and $\rho_p$ is the particles density taken as 2200 kg m$^{-3}$. 
The total interface area $S_d$ of emulsion directly linked to the average droplet size is expressed as

$$S_d = \frac{6 \cdot V_d}{D} \quad \text{Equation 4.3}$$

where $V_d$ is the dispersed phase volume (here water) and $D$ the droplet diameter.

The surface coverage $C_S$, defined as $C_S = S_p/S_d$, can thus be estimated after measuring the drop size $D$:

$$C_s = \frac{S_p}{S_d} = \frac{m_p \cdot D}{l \cdot \rho_p \cdot 6 V_d} \quad \text{Equation 4.4}$$

The surface coverage was crudely estimated using the expression above under the following assumptions:

i) Particles are irreversibly adsorbed

ii) Particles are monodisperse and droplets are formed by water

iii) Random Sequential Absorption model was used assuming coverage of 2D disks with a limiting coverage saturation of $\theta = 0.547$
4.3 Results and discussion

In this section we will address in a first time the discussion concerning the obtaining of h-BNNS, their morphology and their hydrophobic behavior. In a second place we will discuss about the different characterization techniques applied to the as-prepared h-BNNS emulsion. The discussion will be focused on the type of obtained emulsion, the different factors affecting the emulsions stability and the droplets size, such as the O/W ratio, the particle concentration and the sonication conditions. At last the rheological behaviors of the most stable emulsions will be deeply discussed.

4.3.1 Atomic force microscopy (AFM)

The h-BN nanoparticles obtained after the liquid exfoliation in water using sonication tip, were characterized by AFM. The images (Figure 4.1) indicate a reduction on the thickness of h-BN from 3 µm to 2-6 nm showing a lateral size in the range of 10 to 90 nm, evidencing the h-BN exfoliation. Based on AFM images and taking into account the width of one nanosheet (0.334 nm), we could assume our BNNS are generally composed of 6-16 layers.
Figure 4.1 a) AFM image of initial BN powder, b) AFM image of exfoliated h-BN, c) Lateral size of h-BN layers and d) Height of h-BN layer

4.3.2 Transmission electron microscopy (TEM)

The TEM images of the exfoliated h-BN fabricated via ultrasonic assisted liquid phase exfoliation are shown in Figure 4.2. Figure 4.2b (inset from Figure 4.2a) reveals the thickness of a few-layered BNNS to be approximately 10 nm, which corresponds to roughly tens BN atomic layers. This values agrees with a semi-quantitative assessment of BNNS thickness through TEM analyses, which suggests an average thickness range of 6–10 nm for exfoliated BNNS. The lateral size is well preserved to be of a few hundred nanometers.
Figure 4.2 a) TEM image from exfoliated h-BN  b) Inset of the image

4.3.3 Water contact angle measurements

Figure 4.3 shows WCA analysis of the exfoliated h-BN. The results show that h-BNNS have a hydrophobic behavior, displaying a contact angle of about 134°. According to the Bancroft law,31 which states that particles with contact angle larger than 90° tend to stabilize water-in-oil emulsions, these particles might form a water-in-oil type emulsion.
4.3.4 Small-angle X-ray scattering

Figure 4.4 shows the SAXS profile of the samples. Particle-containing emulsions are dominated by the scattering of BN and provide additional structural insights. The emulsion profile shows two peaks fitting with the signatures from water and oil, at 14.5 nm\(^{-1}\) and 20.2 nm\(^{-1}\) respectively. Ascending to small angles, the profile displays a \(q^{3.2}\) power-law decay in intensity, in line with the existence of h-BNNS larger than 30 nm and presenting rough interfaces.

The presence of a small but sharp peak around 18.9 nm\(^{-1}\) is observed; this value corresponds to the typical inter-layer distance in boron nitride (0.33 nm) and thus confirms the presence of h-BN in the emulsion.
4.3.5 Confocal laser scanning microscopy (CLSM)

The type of obtained emulsion was identified by confocal laser scanning microscopy. This technique has the advantage that the light travels through the objective lens to illuminate the sample, and then the light emitted from the sample travels back through the same objective to the detector. To obtain the images by fluorescence, one of the phases was labelled with a dye during the emulsification process; we chose fluorescein sodium salt, which is soluble in water but not in ethyl benzoate. In this way, when the sample is irradiated by the light source, the phase that has been labelled will be excited and will emit the light back, while the other will not be excited.

Figure 4.4 SAXS patterns of pure water, pure ethyl benzoate and emulsion formulated with 2 wt% of BN.
Figure 4.5 CLSM images of Pickering emulsion at different BN concentrations and an oil/water ratio of 1. Top images were taken by differential interface contrast (DIC) technique. Bottom images were taken by fluorescence imaging.

On one hand, the top images in Figure 4.5 show the microphotographs taken by differential interface contrast (DIC) technique. A difference of contrast is observed between the continuous and dispersed phase. The disperse phase displays higher contrast than the continuous phase. Also, a black thick layer can be distinguished at the interface between continuous and discontinuous phases, which strongly suggests the presence of a shell of h-BN nanosheets around the droplets. In the other hand, the bottom images in the Figure 4.5 shows the microphotographs taken by fluorescence imaging. These images reveal that the dye-labelled phase is inside the droplets, meaning that the discontinuous phase is formed by water. These results confirm our suspicion that it is an inverse emulsion, i.e. water-in-oil type.
### 4.3.6 Optical microscopy

The emulsion microstructure and droplet size were analyzed by optical microscopy. Figure 4.6 a-d shows microscopy images taken for the emulsions prepared with different h-BN particle concentrations, with ethyl benzoate/water volume ratio constant at 1. The quantification of these results is shown in Figure 4.6 e. The average droplets diameter range from 6 µm at the highest BN concentration (2 wt%) to 43 µm at the lowest BN concentration (0.5 wt%) when the O/W ratio is 1. Thus, Pickering emulsions with different droplet sizes could be obtained by tuning the concentration of BN at constant amplitude settings (65 %). As expected, the average droplet size of solid-stabilized emulsions decreases with increasing particle concentration, as more particles are available to stabilize small droplets.\(^{32}\) Decreasing the solid particle concentration led not only to a larger emulsion droplet size but also to a greater heterogeneity in the droplet sizes and shapes, which signifies less efficient emulsion conditions. In our case, unlike other systems stabilized with spherical particles, the plot between the inverse of droplet size and the BN concentration (Figure 4.6 e) displays a non-linear dependence. This means that the emulsion is not limited by a coalescence phenomenon.

Basically, the stability of a single particle at the interface is governed by the stabilization energy per particle. On the contrary to very small nanospheres (radius below 1-10 nm), it has been shown that the adsorption of graphene-based sheets never reaches a reversible regime due to graphene atomical thickness.\(^{33,34}\) In our system, the surface coverage\(^{35}\) was evaluated assuming that particle anchoring at the oil-water interface was always complete and irreversible. The resulting emulsions exhibit a droplets diameter that is controlled by the mass of particles and their packing at the interface.
Figure 4.6 Optical microscopy images of h-BN emulsions at different concentrations: a) 2 wt% BN, b) 1.5 wt% BN, c) 1.0 wt% BN and d) 0.5 wt% BN with a o/w ratio of 1 (The scale bars in the images correspond to 30 μm length). e) Inverse of the average emulsion drop.
4.3.7 Surface coverage

Assuming that all particles are adsorbed at the oil-water interface, simple geometrical considerations show that the surface coverage is larger than the unit (Table 4.1), which evidences that the droplet are covered by multilayered particles or aggregates.\textsuperscript{36} The multilayer coverage was also reported in the case of GO, where it was estimated to stack up to 10 monolayers under certain conditions.\textsuperscript{37} From thermodynamics calculation, it was suggested that the 2D material multilayers at the interface effectively cover the droplet surface and inhibit collisions-induced coalescence or ripening.\textsuperscript{10} These emulsions stabilized with exfoliated h-BN are comparable in terms of stability and droplets size behaviors with other emulsions stabilized with 2D materials such as GO.

Table 4.1 Estimation of total number of BN particles per droplet

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>Droplet size (µm)</th>
<th>Surface coverage</th>
<th>N° particles/droplet</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>6</td>
<td>1.81</td>
<td>6·10\textsuperscript{5}</td>
</tr>
<tr>
<td>0.15</td>
<td>12</td>
<td>2.95</td>
<td>3·10\textsuperscript{6}</td>
</tr>
<tr>
<td>0.1</td>
<td>27</td>
<td>4.09</td>
<td>1.3·10\textsuperscript{7}</td>
</tr>
<tr>
<td>0.05</td>
<td>46</td>
<td>3.25</td>
<td>3·10\textsuperscript{7}</td>
</tr>
</tbody>
</table>

Preparing emulsions with h-BN has a major interest due to the BN higher biocompatibility and its other unique properties compared to other sheet-like materials, e.g. GO. Furthermore, numerous \textit{in vitro} and \textit{in vivo} assays have confirmed the toxicity of C-based materials. Alternatively, BN possesses a better biocompatibility and a lower cytotoxicity.\textsuperscript{38,39,40}
4.3.8 Emulsion stability

It is known that the droplets size is extremely sensitive to the amount of energy delivered to the biphasic system. This one has a direct relationship with the amplitude and intensity of the ultrasonic device. In order to decouple the influence of the energy delivered to the system with the amount of BN in the droplet size, emulsions formulated with 2 wt% BN and an o/w ratio of 1 were first prepared using different amplitudes (20 to 80 %). Results show (Table 4.2) that the emulsion droplets size does not change when different amplitudes are applied to the system. Then, the influence of the power delivered to the system by the same ultrasonic device on the droplets size was also evaluated (Table 4.3). It does not have a big influence on the droplets size in the range of 20 to 75 W. For higher power, the mean droplet size is slightly smaller, but it is not really significant. So it can be concluded that the provided ultrasonic energy is not the limiting factor in our emulsifying process in order to produce smaller droplets with 2 wt% BN. Samples with different BN loads and same O/W ratios were then sonicated under constant power (40W) (Table 4.4). The obtained results confirm that the BN load is the main parameter affecting the droplets diameter with this ultrasonic probe used as emulsifying device.
Table 4.2 Droplet size for emulsions formulated at 2 wt% BN and Ro/w 1 at different amplitude settings

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amplitude (%)</th>
<th>Droplet Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BN 2wt % _R_o/w 1</td>
<td>20</td>
<td>6.2 ± 1.0</td>
</tr>
<tr>
<td>BN 2wt % _R_o/w 1</td>
<td>40</td>
<td>6.1 ± 0.7</td>
</tr>
<tr>
<td>BN 2wt % _R_o/w 1</td>
<td>60</td>
<td>6.4 ± 0.5</td>
</tr>
<tr>
<td>BN 2wt % _R_o/w 1</td>
<td>80</td>
<td>6.5 ± 0.3</td>
</tr>
</tbody>
</table>

Table 4.3 Droplet size for emulsions formulated at 2 wt% BN and Ro/w 1 at different powers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Power (W)</th>
<th>Droplet Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BN 2wt % _R_o/w 1</td>
<td>20</td>
<td>6.5 ± 0.2</td>
</tr>
<tr>
<td>BN 2wt % _R_o/w 1</td>
<td>40</td>
<td>6.7 ± 0.3</td>
</tr>
<tr>
<td>BN 2wt % _R_o/w 1</td>
<td>60</td>
<td>6.1 ± 0.4</td>
</tr>
<tr>
<td>BN 2wt % _R_o/w 1</td>
<td>75</td>
<td>6.1 ± 0.4</td>
</tr>
</tbody>
</table>
Table 4.4  Droplet size for emulsions formulated at different BN loads and R\text{\textsubscript{o/w}} 1 at constant power

<table>
<thead>
<tr>
<th>Sample</th>
<th>Power (W)</th>
<th>Droplet Size (\textmu m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BN 2wt %_R\textsubscript{o/w} 1</td>
<td>40</td>
<td>6.7 ± 0.4</td>
</tr>
<tr>
<td>BN 1,5wt %_R\textsubscript{o/w} 1</td>
<td>40</td>
<td>13 ± 1</td>
</tr>
<tr>
<td>BN 1wt %_R\textsubscript{o/w} 1</td>
<td>40</td>
<td>27 ± 1</td>
</tr>
<tr>
<td>BN 0.5wt %_R\textsubscript{o/w} 1</td>
<td>40</td>
<td>43 ± 3</td>
</tr>
</tbody>
</table>

The BN based-emulsions have been stored at ambient temperature for 14 days for studying their stability. We observed that emulsions formulated with O/W ratios ≥ 0.6 displayed two phases, one is the emulsified phase composed of 62 to 85% of volume fraction and the other is the oil phase resulting from the separation and sedimentation of the continuous phase due to its higher density (mass density at 20°C is 1045 kg m\textsuperscript{-1}). Above the random close packing (corresponding to a dispersed water volume fraction $\phi\textsubscript{w} > 0.66$), the droplets cannot move freely and they are trapped by the neighbors, leading to emulsion destabilization a few hours after preparation (Table 5.5). It was also observed that the emulsions with higher BN concentration have higher emulsion stability index (ESI), determined from the volume ratio of the emulsified phase after 14 days and emulsion after 3 hours. The emulsion with 2 wt% BN and a O/W ratio of 1 (BN 2wt\%\_R1) is more stable along the time than the other emulsions, and shows an ESI around 94 %. In our system, we observed that when the emulsion completely breaks down above the random close packing, there is a separation between two bulk phases: one very clear corresponds to the water phase and the other being whitish. Thereby we suggest that almost all particles are dispersed in the oil phase due to BN hydrophobicity.
Table 4.5 Stability of $h$-boron nitride stabilized emulsions

<table>
<thead>
<tr>
<th>Sample</th>
<th>[BN] (%)</th>
<th>Ratio o/w</th>
<th>$\phi_w$</th>
<th>Emulsified phase (%)</th>
<th>Emulsion Stability Index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0h</td>
<td>3h</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>1</td>
<td>0.53</td>
<td>95</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>0.8</td>
<td>0.63</td>
<td>95</td>
<td>86</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>0.6</td>
<td>0.81</td>
<td>86</td>
<td>81</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>0.4</td>
<td>-</td>
<td>86</td>
<td>81</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>1.5</td>
<td>1</td>
<td>0.53</td>
<td>95</td>
<td>90</td>
</tr>
<tr>
<td>7</td>
<td>1.5</td>
<td>0.8</td>
<td>0.58</td>
<td>95</td>
<td>86</td>
</tr>
<tr>
<td>8</td>
<td>1.5</td>
<td>0.6</td>
<td>0.86</td>
<td>86</td>
<td>84</td>
</tr>
<tr>
<td>9</td>
<td>1.5</td>
<td>0.4</td>
<td>-</td>
<td>86</td>
<td>84</td>
</tr>
<tr>
<td>10</td>
<td>1.5</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>1.0</td>
<td>1</td>
<td>0.53</td>
<td>95</td>
<td>90</td>
</tr>
<tr>
<td>12</td>
<td>1.0</td>
<td>0.8</td>
<td>0.58</td>
<td>95</td>
<td>86</td>
</tr>
<tr>
<td>13</td>
<td>1.0</td>
<td>0.6</td>
<td>0.86</td>
<td>86</td>
<td>71</td>
</tr>
<tr>
<td>14</td>
<td>1.0</td>
<td>0.4</td>
<td>-</td>
<td>86</td>
<td>71</td>
</tr>
<tr>
<td>15</td>
<td>1.0</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>16</td>
<td>0.5</td>
<td>1</td>
<td>0.53</td>
<td>95</td>
<td>90</td>
</tr>
<tr>
<td>17</td>
<td>0.5</td>
<td>0.8</td>
<td>0.58</td>
<td>95</td>
<td>90</td>
</tr>
<tr>
<td>18</td>
<td>0.5</td>
<td>0.6</td>
<td>0.88</td>
<td>71</td>
<td>62</td>
</tr>
<tr>
<td>19</td>
<td>0.5</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>0.5</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Other phenomena were also observed by Binks et al. when emulsion stability is limited by coalescence phenomenon. Destabilization occurs through the coalescence of spherical particles-stabilized emulsion droplets, causing the rapid growth of hydrophilic tubes.\textsuperscript{41}

In our case, the emulsions are stabilized by multilayers of 2D material which inhibit the coalescence. Thus, we could propose two hypotheses to explain that emulsions are not stable above the close packing. The first one based on that sheet-sheet interaction may promote multilayer film formation. In this case, the first layer packs imperfectly at the interface, leaving bare patches of liquid-liquid (L-L) interfaces that can interact with subsequent layers in a diffuse interfacial zone. For atomically thin plates, the second layer lies very close (within 1 nm) to the L-L interfaces, and on this length scale, thermal molecular fluctuations allow the contact between the layer and both dispersed and continuous phases. In this way, the layers could contain interstitial spaces and then subsequent layers are too far from the interface to interact energetically with both liquid phases. There are two possible deposition pathways. First, the so-called “sequential close packing” route is characterized by an ordered layer-by-layer deposition. Second, a “random ballistic deposition” which has an irrespective prior coverage can take place. In the case of GO, it has been shown that at equal number of material layers, the stabilization energy is lower for the random deposition than close packing. This may explain the instability of emulsion.\textsuperscript{10}
Figure 4.7 Epifluorescence images of Pickering emulsion with BN 2wt%_R1 showing droplet deformation due to particle jamming.

In the second hypothesis, we consider a stabilization mechanism called ‘droplets bridging’. The emulsions prepared by ultrasonic probe display long-term stability when the dispersed phase volume fraction is well below the random close packing ($\varphi = 0.65$). Partially hydrophobic particles with contact angles somewhat greater than 90° tend to stabilize water-in-oil emulsion where particles slightly protrude from droplets surface to maintain the equilibrium contact angle; this also facilitates efficient packing and steric barrier against coalescence. Particles concentration also plays an important role in the surface coverage. In fact, when coverage is very high, significant droplets deformation could be observed due to jamming of the particles at the droplet interfaces (Figure 4.7). Although the droplets were in close proximity, their interfaces were not joined because of the high particle coverage. This effect has been observed by Zhang et al.\cite{42} using layered double hydroxides particles for the preparation of Pickering emulsions. Moreover, droplets bridging has been observed by Frost et al.\cite{43} when ionic liquids are used for Pickering emulsions preparation.
4.3.9 Rheological studies

By rheological measurements, it is also possible to study the emulsion stability. For that purpose, the effect of varying the water volume fraction ($\phi_w$) was investigated by concentrating the emulsions at constant particle concentration using a rheometer working in rotational mode. Figure 4.8 shows the relative viscosity (ratio between the apparent viscosity of the emulsion and the oil phase viscosity) as a function of the water volume fraction. Our system behaves as the literature predicts, increasing the viscosity when rising the $\phi_w$. It is observed that increasing $\phi_w$ increases the relative viscosity from 12.9, corresponding to low volume fraction (< 0.05), to 101.6 for high volume fraction (0.66) when the shear rate is 50 s$^{-1}$. The same behavior was found when the shear rate was 100 s$^{-1}$, the relative viscosity increasing from 9.9 ($\phi_w = 0.05$) to 62.3 ($\phi_w = 0.66$). This fact may be due to the increase of water content and to the possibility that droplets tend to pack closer, adding a significant contribution to the emulsion viscosity. We observed also that W/O emulsions stabilized with exfoliated h-BN formulated with $\phi_w$ above 0.66 and 2 wt% BN concentration are not stable anymore after preparation or after a few hours and break down due to the fact that maximum random close packing has been reached for our system.\textsuperscript{42,44} The present results thus show that the maximum packing fraction for W/O emulsion made with ethyl benzoate and BN is close to 0.64, as described in the literature for monodisperse spherical droplets.
Figure 4.8 Relative viscosity curves in function of water volume fraction ($\phi_w$) for emulsions formulated at 2 wt% BN concentration at shear rate 50 s$^{-1}$ and 100 s$^{-1}$ (Lines are eye-guides). For values of $\phi_w$ above 0.66 the emulsions broke down.

The aim of the study is to use this emulsion as a potential soft template for the preparation of new porous materials. In this case, the inner phase will generate the porosity volume and the continuous phase will form the material matrix. If the continuous phase volume is too limited, it will give weak mechanical properties to the solid material. However, it should be noted that the maximum total porous volume reached with the present emulsion at this point, to make for instance a membrane, would be ca. 64%.
The preparation of porous nanocomposite materials from medium internal phase emulsions has already been reported in the literature. Pickering emulsions containing only 60% of disperse phase could lead to open porous polymer foams with low densities and high degrees of pore interconnectivity. ⁴⁵

**Figure 4.9** Viscosity curves of emulsion with 2 wt% h-BN concentration and different o/w ratios (R=0.7 to 1)

The rheological behavior of pure ethyl benzoate, pure water, and of the obtained emulsions was analyzed by measuring the viscosity as function of the shear rate at 20 °C. The measurement was carried out within the 10 min following emulsification where the emulsions are stable; the duration of experiment was around 4 min and no phase
separation was observed after the analysis. Figure 4.9 shows the viscosity curves obtained for the BN emulsions formulated at 2 wt% of BN and different O/W ratios.

In this study, standard cone-and-plate geometry with 50 mm diameter and a 1° cone angle was used. The maximal acceptable droplets diameter d for this type of geometry is defined by the following equation:

\[ d \leq \frac{a}{10} \]  

**Equation 4.5**

where a is the gap set at the center of the cone. It has a value of 101 µm so the diameter of droplets must be below 10 µm, and our droplets meet this condition with a 6 µm diameter. At any given shear rate, the emulsions have a higher viscosity than pure phases (Figure 4.9), especially at low shear rates due to the even dispersion of h-BN in the water and oil mixture, acting as a stabilizer. The emulsions display a typical shear-thinning flow behavior, characterized by decreasing the viscosity as the applied shear rate increases, approaching to a constant value at high shear rates.

At low shear rates, the measured emulsion viscosity is higher, indicating that at rest the droplet close-packing is responsible of viscosity. When a higher shear rate is applied, the droplets start to be organized into layers or strings, and the rheogram displays a decrease in viscosity. The measurements were performed three times using the same emulsion to ensure the repeatability of the test. The results show (Table 4.6) that the test could be repeated without changes in viscosity data. Values are given as average ± 2x standard deviation for 95 % confident interval, determined on 3 samples. “a” represents the comparison within values (p≤0.05).
Table 4.6  Viscosity values of emulsion with 2 wt% BN for 0.7, 0.8 and 1 o/w ratio.

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>EtBz</th>
<th>BN 2wt%</th>
<th>BN 2wt%</th>
<th>BN 2wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Viscosity at</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>50s⁻¹ (mPa·s)</strong></td>
<td>1.06 ± 0.02</td>
<td>1.24 ± 0.06</td>
<td>132 ± 12²</td>
<td>76 ± 7ᵇ</td>
<td>27 ± 7ᶜ</td>
</tr>
<tr>
<td><strong>Viscosity at</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>100s⁻¹ (mPa·s)</strong></td>
<td>1.00 ± 0.02</td>
<td>1.24 ± 0.06</td>
<td>78 ± 1ᴬ</td>
<td>52 ± 1ᴮ</td>
<td>22 ± 6ᶜ</td>
</tr>
</tbody>
</table>

Figure 4.10 shows the curve of shear stress as a function of the shear rate of an emulsion containing 2 wt% of h-BN and different O/W ratios (R=0.7 to 1). The flow curves exhibit a yield stress dependent on the O/W ratio. The reduction of the O/W ratio from 1 to 0.7 also corresponds to an increase of the inner phase volume (+43% v/v of water) and thus to a concentration of the emulsion with a higher amount of dispersed phase. As a consequence, an increase of the viscosity and of the yield stress is observed. Figure 4.11 shows the viscosity curves of the emulsion containing 2 wt% BN as freshly prepared and after 14 days with an O/W ratio of 1. No change in the apparent viscosity is observed after 14 days.
Figure 4.10 Flow curves of emulsion with 2 wt% h-BN concentration and different O/W ratios (R=0.7 to 1)

Figure 4.11 Viscosity curves of freshly prepared BN 2 wt% _R1 emulsion, and after 14 days.
4.4 Conclusion

In summary, non-modified 2D BN material has been used for the first time as stabilizing agent for the preparation of inverse Pickering emulsions. The epifluorescence images revealed that the emulsions are of water-in-oil type. Microscopy images showed that the average droplet size decreases with increasing the BN concentration. The emulsions possess good stability for 2 wt% BN concentrations and oil/water ratio equal to 1. The kinetic stability showed that the emulsions prepared with 2 wt% BN are the most stable, and rheology tests confirmed this result, showing that no change on the stability occurred after 14 days. In addition, rheological measurements performed on the emulsions with 2 wt% BN exhibited higher viscosity for water volume fraction close to 0.64. This value corresponds to the maximum packing volume fraction of water in ethyl benzoate, for drops of spherical shape stabilized by h-BN nanosheets. These emulsions may be good candidates to design new interesting materials with valuable properties, such as porous membranes. In addition, emulsions formulated with h-BN are particularly interesting due to their high biocompatibility compared with other 2D materials such as GO, and their potential application in biofields, taking into account the fact that inverse emulsions possess higher stability than classical emulsions.

These Pickering emulsions obtained with h-BN have been compared with other Pickering emulsions prepared with other 2D material, i.e. GO. The results of this study are presented in the Annex I.
4.5 Perspectives

This work has uncovered several lines of enquiry that may prove useful in understanding different aspects of the h-BN stabilized emulsions. Specifically, further study is recommended on the different factors affecting emulsion stability. It would be of great interest to study the different responses of the emulsions to small and drastic pH and ionic strength changes. Temperature may also play a role on emulsion stability, thus a short study on the responses of the stability of h-BNNS emulsions to temperature changes would be worth.

Further surface modifications on h-BNNS would be another interest field of investigations. The surface modification can change the hydrophilic behavior of the nanosheets and lead for example to different emulsion types. In addition this type of modification could open a new line of study based on the preparation of new materials from functionalized h-BNNS stabilized emulsions.
References

Inverse Pickering emulsions stabilized by exfoliated h-BN


Chapter 5

Development of h-BNNS/PVA Porous Membranes via Pickering Emulsion Templating*

Abstract

Polymer-based membranes play an important role in water filtration, in particular in the removal of particles, microorganisms and organic pollutants. Developing a reliable fabrication method for membranes presenting both high flux and good selectivity remains challenging. Polyvinyl alcohol (PVA) is a well-known polymer with promising perspectives due to its specific properties, such as nontoxicity, biocompatibility and biodegradability. Herein, a new strategy to produce porous membranes based on PVA has been developed using emulsion templating involving hexagonal boron nitride nanosheets (h-BNNS) as stabilizer. The membranes displaying a pore size around 1µm show a water permeance over 2000 L m⁻² h⁻¹ bar⁻¹ and a rejection efficiency of ~100% for latex nanoparticles of diameter 1.2 µm. Moreover, the membranes did not significantly reduce their performance after filtration.

*This work has been published as: D. Gonzalez Ortiz, C. Pochat-Bohatier, S. Gassara, J. Cambedouzou, M. Bechelany, P. Miele, Green Chemistry, 2018, 20, 4319-4329
5.1 Introduction

Water pollution is one of the most serious issues in the contemporary world. Today, the availability of clean water is becoming a challenging task. According to the World Health Organization (WHO), 1.2 billion people lack access to clean fresh water leading to a big cause of diseases and health issues.\(^1\) Researchers emphasize to address these problems with the development of more effective and lower cost methods for water purification, while minimizing the use of hazardous chemicals and subserve the environment.

Membranes are an important key for water treatment in different areas such as drinking water purification, brackish and seawater desalination, and reuse or wastewater treatment. Currently, polymeric membranes are the most widely used for water treatment due to their easy-forming properties, good flexibility, high perm-selectivity and low cost compared to inorganic membranes. However, there are still several challenges such as the trade-off between permeability and selectivity and the resistance to fouling. The development of new procedures to obtain porous membranes with high permeability, good rejection ratio and antifouling properties are needed for water purification.

Porous polymeric membranes have a wide range of applications spanning from water filtration\(^2\), pharmaceutical purification\(^3\), and battery separators\(^4\) to scaffolds for tissue engineering.\(^5\) Depending on the pore size, the membranes can be classified into microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) or reverse osmosis (RO). A wide range of polymers can be used, such as cellulose derivatives,\(^6\) polyvinylidene difluoride (PVDF),\(^7\) polysulfone (PS),\(^8\) polyacrylonitrile (PAN)\(^9\) and polyvinyl alcohol (PVA). These polymer-based membranes can be tailored to the
specific needs of the process, and they can be used in many separation processes in industry. Among them, polyvinyl alcohol (PVA) polymer, possesses highly hydrophilic character, excellent film-forming properties and outstanding physical and chemical stability, and is a good candidate for the preparation of hydrophilic membranes.\textsuperscript{10}

In the last decades, different techniques have been developed for forming PVA porous membranes. The oldest and most common technique described in literature is the so called ‘phase inversion’. It consists of forming a concentrated solution of the polymer in a solvent and subsequent immersion into a liquid bath in which the solvent is miscible but the polymer is not.\textsuperscript{11} An analogous procedure is the thermally induced phase separation (TIPS), but it plays with the temperature to form the membrane rather than a non-solvent to coagulate the polymer.\textsuperscript{12} Recently, PVA nanofibrous membranes have been developed using electrospun methods, in this case the membrane matrix is fibrous instead of layered.\textsuperscript{13}

In the recent years, the development of porous materials using templating methods draw the scientist attention for their real and potential applications in different areas such as supports for catalysts,\textsuperscript{14,15} drug delivery,\textsuperscript{16} tissue engineering,\textsuperscript{17,18} membranes for separation processes,\textsuperscript{19,20} and as templates for the production of inorganic materials.\textsuperscript{21} Although several methods have been reported on the fabrication of porous polymers,\textsuperscript{22-24} emulsion templates attract great attention owing to the facile tailoring of pore size and size distribution of the polymer materials. In a typical emulsion templating scenario, a biphasic system is generated, and then the continuous phase is polymerized. The colloidal entities serve to create the porosity of the final polymeric material. Depending on the nature of the colloidal systems employed, the pore size can be tuned from a few nanometers to hundreds of micrometers.
Emulsion templating methods represent an attractive route to produce highly porous and permeable polymeric materials with a well-defined porosity. The process has been known since the 1960’s when Bartl et al. described the polymerization of styrene in an “inverse emulsion” (W/O) with as much as 83% internal aqueous phase, resulting in a cellular structure in which cells contained the dispersed water phase. Few years after, Lissant et al. described the term “high internal phase ratio emulsions” or “HIPE emulsions” when they prepared systems with over 90% monodisperse internal phase droplets and produce a ‘solid-polymer-water emulsion’. The inconvenient of conventional HIPE’s is they are commonly stabilized by surfactants and amphiphilic polymers, which are toxic and not environmentally friendly. A large amount of surfactants is required to produce stable HIPE’s (5-50 wt% relative to continuous phase), and they generally show undesirable mechanical strength.

In this work, we focus our attention on the development of porous PVA membranes using Pickering emulsions as soft templates. This method offers a sustainable advantage by avoiding the use of surfactants and sintering steps since no solid organic material is introduced to produce the desired material. Moreover, Pickering emulsions possess many unique features that classical emulsions stabilized by surfactants have not, such as superior stability and low toxicity. The higher stability of solid particles stabilized emulsions is due to their irreversible adsorption at the liquid-liquid interface, thus reducing the energy of the system. The particles form a rigid shell around the droplets and prevent emulsion breaking-up or coalescence. After removal of the droplet phase, a spherical void is left behind in the matrix. Many different types of colloidal materials,
including silica$^{29,30}$, titania$^{31,32}$, alumina$^{33}$, iron oxide nanoparticles$^{34}$ or two-dimensional materials, such as graphene oxide$^{35,36}$ or hexagonal boron nitride$^{37}$ have been used for the fabrication of materials from Pickering emulsions.

Among these materials, boron nitride nanosheets (BNNS) have recently attracted great interest due to their high surface area and their outstanding properties such as high-temperature stability, enhanced oxidation resistance, high hardness, high corrosion resistance and large thermal conductivity.$^{38}$ Furthermore, the incorporation of inorganic nanoparticles into the polymeric matrix improves the hydrophilicity, antifouling, and water permeability.$^{39}$ However, their direct incorporation into the membrane casting solution may also lead to particle agglomeration due to poor compatibility between the inorganic nanoparticles and the polymeric matrix.$^{40}$ The addition of BNNS to a polymeric matrix using Pickering emulsion method has the advantage to avoid their nanosheets aggregation. The nanosheets are irreversibly adsorbed at the water-oil interface, and they will provide to the nanocomposite a defined porosity and enhanced mechanical properties.

Herein, we present a novel and sustainable approach to prepare h-BNNS/PVA porous membranes by an emulsion templating strategy. By this procedure, membranes with different pore size distributions were obtained by tuning the curing time. The membrane morphology and their chemical and mechanical properties were investigated. The membrane pore size was determined by porometry and their performance in water permeability and particle rejection were also investigated.
5.2 Experimental part

5.2.1 Materials

Hexagonal boron nitride (h-BN) was purchased from Saint Gobain (95 % purity, 325 mesh, 3µm particle size), poly (vinyl alcohol) (PVA) (Mw = 27000 g/mol\(^{-1}\), degree of hydrolysis 98), ethyl benzoate (purification ≥ 99 %, Mw = 150 g mol\(^{-1}\) and density = 1.045 g mL\(^{-1}\)), glutaraldehyde (GTA) (Grade I, 25 % in H\(_2\)O) and hydrochloric acid (ACS reagent, ≥ 37%) were purchased from Sigma Aldrich. Polystyrene latex nanoparticles, known also as latex beads, with different sizes (0.1, 1.2 and 3µm) were purchased form Thermo Fisher Scientific. All chemicals were used without further purification. In all the experiments deionized pure water (18 MΩ) was used.

5.2.2 BN/PVA emulsion preparation

Pickering emulsions stabilized with exfoliated h-BNNS/PVA were prepared following a simple two-steps sonication protocol. First, h-BN (2 wt%) powder was suspended in water and sonicated for 1 hour at 65 % amplitude with pulse off/on 0.5 – 1 s using ultrasounds device (model SONOPLUS HD 3100, 100W, 20 kHz) with a microtip of diameter 3 mm (MS73). This step ensures the exfoliation of boron nitride, due to the weak Van der Waals interactions between BN layers that the sonication procedure is able to break, leading to mono- or few-layered material.\(^{37}\) Then, PVA (15 wt %) was dissolved in the exfoliated h-BN aqueous suspension under magnetic stirring at 80 °C for 4h. Ethyl benzoate was added to the as-prepared h-BNNS-PVA suspension with different oil/water ratios. The emulsion was prepared by sonication with the same equipment for 15 min at 65 % amplitude and pulse off/on 0.5 – 1 s.
5.2.3 Membrane Preparation

The membranes were prepared by casting the solution onto a glass support with different initial thicknesses and speeds. Two different sets of membranes were prepared depending on the crosslinking step. The first membrane set were prepared by adding directly into the emulsified solution the crosslinker before casting. The crosslinker consisted in a GTA/HCl solution with a ratio 3:1. Before the addition of the crosslinker solution to the prepared emulsion, both were kept in an ice bath for few minutes to delay the initiation of the crosslinking reaction, which takes place at room temperature. After mixing both solutions, they were hand-shaken for 10 s to ensure the solution homogeneity and quickly casted onto the glass support. The membranes were obtained after curing at room temperature and two-washing steps: first, they were immersed into a water bath to remove the excess of GTA and then they were washed with ethanol to ensure the ethyl benzoate extraction.

The second set of membranes was prepared by immersing them into a cross-linking bath. In that case, the membranes were dried after for few hours. Then, the membranes were cross-linked by direct immersion in a crosslinker bath containing 3 wt% GTA (25 % H₂O) solution and 1 wt% HCl (37 %), ethanol (96 %) was used as a solvent. This step has two functions; first it allows the PVA crosslinking and second it enables ethyl benzoate extraction. Additional washing of membranes was conducted in water and ethanol baths. Finally, the membranes were kept in a water bath to conserve them. The membranes were labeled as BNP-x h (x = 1, 3 or 24 h) depending on the time they were cured before crosslinked them. We have chosen the second strategy to prepare the membranes due to the first leads to some reproducibility problems, maybe due to a low homogeneity when hand-shacking.
Table 5.1 Conditions for the preparation of h-BNNS/PVA membranes

<table>
<thead>
<tr>
<th>Parameters</th>
<th>60</th>
<th>180</th>
<th>1440</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curing time (min)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crosslinker</td>
<td>GTA</td>
<td>GTA</td>
<td>GTA</td>
</tr>
<tr>
<td>Catalyst</td>
<td>HCl</td>
<td>HCl</td>
<td>HCl</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Thickness (µm)</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>Casting speed (s⁻¹)</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
</tbody>
</table>

5.2.4 Study of crosslinking kinetics/Gelation studies

Rheological measurements were performed with a Physica MCR 301 rheometer (Anton Paar). In a first study, the viscosity of the h-BNNS/PVA prepared emulsion was analyzed in function of the shear stress. For the experiment, cone-plate geometry with 0.101 mm gap was used. Gelation studies were also conducted with plate-plate geometry at 10 rad s⁻¹ and 0.01 mm gap.

5.2.5 Membrane Characterization

5.2.5.1 Structural and chemical characterization

The morphology of the membrane, both cross-section and surface, has been observed using a Hitachi S4800 scanning electron microscopy system. For the analysis, the samples were first coated with platinum using an ion sputter coater. The FTIR spectra were recorded with a NEXUS instrument equipped with an attenuated total reflection
(ATR) accessory in the frequency range of 600 − 4000 cm$^{-1}$. The ATR-FTIR spectra were recorded at 4 cm$^{-1}$ resolution, and the signals were averaged from 32 scans. The XRD patterns of cross-linked h-BNNS/PVA membranes were recorded using a PANalytical Xpert powder XRD system with Cu Kα radiation, a scan speed of 2° min$^{-1}$, a 2θ range of between 10 and 70°, and a step rate of 0.02° per second. The thermal behavior of the as prepared membranes was examined by Thermogravimetric Analyzer model TA instruments TGA G500 from 20°C to 800°C. A heating rate of 10°C/min was used under air atmosphere and a flow rate of 60 mL/min. Dry sample weighing about 10 mg was used. The thermal transition behavior of the membranes was determined by Differential Scanning Calorimeter model DSC2920 equipped with a RCS90 cooling system, from 20°C to 200°C. A heating rate of 10°C/min was used under nitrogen atmosphere and at flow rate of 50 mL/min. The samples weight was about 3 mg and they were sealed into an aluminum capsule for the analysis. Water contact angles were measured using a B-CAM-21-BW (CCCIR) monochrome camera and a Led R60 lamp purchased from CONRAD. For each sample, 3.0 μL of ultrapure water was deposited on the membranes using a needle. The images were recorded by the One Touch Grabber software and treated using the ImageJ software. The mechanical properties of the cross-linked h-BNNS/PVA membranes were characterized using the dynamic mechanical analysis system (Metravib 50N) at a tensile testing speed (crosshead speed) of 0.4 mm min$^{-1}$. Young’s modulus of the membranes was calculated from the elastic region of the stress−strain curves.
5.2.5.2 Swelling kinetics

The films were cut into $2 \times 2 \text{ cm}^2$ pieces and dried at vacuum for 24 h. The initial weight of the membranes was recorded and equilibrated at ambient temperature in 5 mL of deionized water. The swelling kinetics was evaluated periodically by measuring the weight of the films using a microbalance (Sartorius CPA225D with an accuracy of 0.00001 g) after gently blotting the surface with a tissue paper. The swelling ratio was evaluated as:

$$\text{SWR} = \frac{W_W - W_D}{W_D}$$

Equation 5.1

where, $W_D$ is the weight of the dry membranes and $W_W$ is the weight of the membrane after wetting.

Each data point shown is the average value of three replicates.

5.2.5.3 Pore Size Determination

The membrane pore size and their distribution were obtained by liquid–gas displacement porometry. The measurements were carried out using a PRM-2000-LL-R porometer (IFTS-France). In this method, the pores of the sample were first filled with water during a wetting step. Then, nitrogen gas was applied through the membrane, and the flow rate was measured as a function of the applied pressure. When a straight line is obtained between nitrogen flow and pressure, all pores have been opened. Pore dimension patterns are calculated by applying Laplace’s law. Each data point shown is the average value of three replicates.
\[ \Delta P = \frac{4 \gamma \cos \theta}{D} \]  \hspace{1cm} \text{Equation 5.2}

where \( \Delta P \) is the differential of applied pressure, \( \gamma \) is the interfacial tension of water, \( \theta \) is the contact angle between the material and the liquid and \( D \) is the pore diameter.

### 5.2.5.4 Permeability Measurements

The membrane permeability was obtained by solvent permeability measurements; the experiments were carried out using a PRM-2000-LL-R porometer (IFTS-France) with a membrane-active surface area of 2.27 cm\(^2\). The membranes were already wet into a pure water bath during 24h. The pure water flux (\( J_{PW} \)) was measured for each membrane by circulating pure water through the membrane system using an applied pressure range of 0–1 bar, each point was obtained measuring the flow passing through the membrane during 60s.

The \( J_{PW} \) (l h\(^{-1}\) m\(^{-2}\)) was calculated using the following formula:

\[ J_{PW} = \frac{Q}{A} \]  \hspace{1cm} \text{Equation 5.3}

Where \( Q \) (mg/s) is the amount of water that passed through the membrane and \( A \) (m\(^2\)) is the area of the membrane. The permeability was determined from the slope of the linear variation of \( J_{PW} \) versus the applied pressure.
5.2.5.5 Particle rejection tests

To corroborate the results of the pore sizes given by porometry, the membranes pores sizes were estimated by polystyrene latex particle rejection experiments. Frontal filtration experiments were carried out using a stirred dead-end cell (Amicon 8050, Millipore Corporation) with a membrane-active surface area of 2.27 cm$^2$. The membranes were first compacted by filtering pure water up to 1 bar until a constant flux was observed. Then, the polystyrene particles were monodispersed polystyrene latex particles with diameters of 0.1, 1.2 and 3 µm. The feed solution was prepared by adding the latex nanoparticles to 15 mL of ultrapure water solution. The feed was added into the cell and forced to permeate through the membranes using an applied pressure of 0.4 bars. The permeate solution and the feed solution were collected after filtration into a vial and later analyzed by dynamic light scattering (DLS) to estimate the amount of latex NPs passed through the membrane. Particle rejection was calculated using the following equation:

\[
\% R = \left(1 - \frac{I_P}{I_R} \right) \cdot 100
\]

Equation 5.4

where $I_P$ is the intensity of counts of the permeate solution and $I_R$ is the intensity of counts of feed solution retained in the cell.

Each data point shown is the average value of three replicates; the membrane permeability was followed after each experiment to verify the membrane performance.
5.3 Results and discussion

An emulsion containing h-BN and PVA was prepared in a first step via ultrasonic power; the exfoliated h-BN is playing the role of emulsifier stabilizing the emulsion. Then the h-BNNS/PVA porous membranes were obtained by casting the emulsion onto a glass support and further crosslinking with GTA. This method allows the generation of porosity using Pickering emulsion as template.

In this section, we will first discuss the preparation of h-BNNS/PVA emulsions and the conditions we have chosen for the development of the membranes. In a second time, the membranes morphology and the physical and chemical characterization will be discussed. Then we will talk about the membrane performances, i.e. water permeability and particle rejection tests and the chapter will end with a conclusion and perspectives of this work.

5.3.1 Preparation and characterization of h-BNNS/PVA emulsions

The h-BNNS/PVA emulsion was prepared at different O/W ratios to check their stability. The emulsions prepared with high O/W ratios did not display long-term stability. We can notice a fraction of oil which creams at the top of emulsion due to its lower density compared to polymer phase. As higher is the oil volume consisting in Ethyl Benzoate, bigger is the creaming fraction. The emulsions prepared with O/W ratios of 0.25 or lower are stable with the time and did not display any kind of creaming. Table 5.2 compiles the observations on the emulsions when they are formulated with different O/W ratios.
Table 5.2 Observations for h-BNNS/PVA emulsions formulated with different O/W ratios and 2 wt% h-BNNS.

<table>
<thead>
<tr>
<th>Solution volume (mL)</th>
<th>Oil volume (mL)</th>
<th>( R_{o/w} )</th>
<th>( R'_{o/w} )</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>10</td>
<td>1</td>
<td>1.27</td>
<td>Fraction of oil creams to the top of emulsion</td>
</tr>
<tr>
<td>12</td>
<td>8</td>
<td>0.67</td>
<td>0.85</td>
<td>Fraction of oil creams to the top of emulsion</td>
</tr>
<tr>
<td>14</td>
<td>6</td>
<td>0.43</td>
<td>0.54</td>
<td>Fraction of oil creams to the top of emulsion</td>
</tr>
<tr>
<td>16</td>
<td>4</td>
<td>0.25</td>
<td>0.32</td>
<td>No oil creaming to the top of emulsion</td>
</tr>
<tr>
<td>18</td>
<td>2</td>
<td>0.11</td>
<td>0.14</td>
<td>No oil creaming to the top of emulsion</td>
</tr>
</tbody>
</table>

The \( R_{o/w} \) is defined by the ratio between the oil fraction and water fraction in the emulsion, and \( R'_{o/w} \) is the real ratio between the oil and water fraction taking into account that the solution is composed by three components (PVA/BN/H\(_2\)O). It can be noted that the creaming of the oil phase indicates that the density of 15 wt-% PVA solution is higher than ethyl benzoate density.
The h-BNNS/PVA emulsion with an O/W ratio of 0.25 was analyzed by optical microscopy (Figure 5.1). The droplets display a size around 2 μm. The droplet size is therefore reduced by PVA addition compared to the droplet size distribution versus % h-BN observed with single W/O emulsion in Chapter 5, ranging from 6.7 to 43 μm.

![Image](image.png)

**Figure 5.1** h-BNNS/PVA emulsion formulated with 15 wt% PVA, 2 wt% BN and Ro/w 0.25 at different magnifications: a) x10 magnification, scale bar corresponds to 20 μm; b) x100 magnification, scale bar corresponds to 2 μm.

### 5.3.2 Study of crosslinking kinetics/Gelation studies

The crosslinking between the PVA and the GTA was followed using a method that consists to determine the gelation behavior or gel point measuring the solution viscosity with a rheometer once the reticulation has started. The crosslinking initiates when the acid catalyst (HCl) and GTA is introduced to the PVA solution. The gelation is identified by an increase of the viscosity. To limit the evaporation, silicon oil was placed around the geometry.
Figure 5.2 Example of monitored crosslinking at 20°C for a PVA 15 wt%, BN 2 wt%, GTA 3 wt%, and HCl 1 wt% mixture.

The Figure 5.2 shows an example of crosslinking monitoring at 20 °C, displaying the viscosity of a solution formulated with 15 wt% PVA, 2 wt% BN, 3 wt% GTA and 1 wt% HCl. A first step is observed without any significant changes in the viscosity. Usually in this first step, some aldehyde groups from the GTA react with the PVA. In the second step, a sharp exponential increase is observed. It is related to the other aldehyde groups in GTA allowing the creation of bridges between the different PVA molecules until the polymeric chains are formed. Once the polymer chains are cross-linked, the gel breaks down due to the shear applied by the rheometer, thus the viscosity evolves in a disordered or non-controlled way.
Temperature is a factor that plays an important role in the crosslinking reaction. For this reason, we studied the gelation behavior of PVA when the crosslinker is added to the solution at different temperatures. Figure 5.3 shows the viscosity evolution in function of time at different temperatures for a given composition. The results concerning the gel point and the viscosity are showed in Table 5.3. It was observed that the gel point strongly depends on the experiment temperature: at low temperature (15°C) the crosslinking reaction takes longer time to initiate than at higher temperature (30°C). This point thus influences the procedure developed for the membrane preparation and explains why the cross-linking solution and the emulsion are both kept in a glass bath for few minutes before mixture.
Figure 5.3 Monitored crosslinking of 15 wt% PVA, 2 wt% BN, 3 wt% GTA and 1 wt% HCl mixtures for different temperatures. The curves were cut after having reached the gel point.

Table 5.3 Gelation time and viscosity of 15 wt% PVA, 2 wt% BN, 3 wt% GTA and 1 wt% HCl mixtures at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Gel point (s)</th>
<th>Viscosity (Pa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1266</td>
<td>112</td>
</tr>
<tr>
<td>20</td>
<td>1062</td>
<td>137</td>
</tr>
<tr>
<td>25</td>
<td>882</td>
<td>172</td>
</tr>
<tr>
<td>30</td>
<td>96</td>
<td>453</td>
</tr>
</tbody>
</table>
5.3.3 SEM observations

The morphology of the PVA and h-BNNS/PVA membranes was analyzed by SEM. Figure 5.4 shows the cross-sections and surface images of the as-prepared membranes with 2 wt% BN and 15 wt% PVA at different curing times and also the membrane prepared from a 15 wt% PVA emulsion free of BN. Different morphologies can be observed in their cross-sections as well as on their surfaces. The membranes prepared from free BN emulsions are dense; they do not present any sign of porosity either on their internal structure or surface (Figure 5.4 a-b). On the other hand, the membranes prepared from h-BNNS/PVA emulsions (Figure 5.4 c-h) present porosity. Depending on the exact curing time, the membrane morphology is different. When the membranes were cured for short term, they present a porous internal structure and surface. The membrane cured for 1 h (Figure 5.4 g) is thicker than the one cured for 3h (Figure 5.4 e) and the pore sizes are different (Figure 5.5): the pores of BNP-3h are smaller than the ones of BNP-1h. This fact is very probably due to slow solvent evaporation (of both water and ethyl benzoate) during the curing time, making PVA chains come closer to each other and leading to a decrease of the pore size. The surfaces of the membranes BNP-1h and BNP-3h both present a similar morphology, but the pores on BNP-3h surface (Figure 5.4 f) are smaller than the pores on BNP-1h surface (Figure 5.4 h). Otherwise, when the membrane was cured for 24 h, it does not present porosity at this magnification on the membrane surface (Figure 5.4 c-d). Curing the membrane for a long time may induce, as previously mentioned, both water and ethyl benzoate removal from the gel structure and could be responsible for PVA chains getting closer, finally leading to a collapse of the pores.
Figure 5.4 SEM images of h-BNNS/PVA porous membranes depending on the curing time before crosslinking a) cross-section of the material originating from PVA emulsion, b) surface of the material originating from PVA emulsion, c) cross-section of BNP-24h, d) surface of BNP-24h, e) cross-section of BNP-3h, f) surface of BNP-3h, g) cross-section of BNP-1h and h) surface of BNP-1h
Figure 5.5 SEM images of h-BNNS/PVA porous membranes depending on the curing time before crosslinking at different magnifications a,b) cross-section of BNP-24h c,d) cross-section of BNP-3h e,f) cross-section of BNP-1h
5.3.4 FTIR analysis

The membranes were analyzed by ATR-FTIR to determine the crosslinking effectivity. FTIR spectra of the PVA and h-BNNS/PVA membranes with different curing times are shown in Figure 5.6. The FTIR curve of the pure PVA membrane displays several characteristic bands, such as OH stretching vibration ($\nu_{\text{OH}} = 3500 – 3000 \text{ cm}^{-1}$) and OH out of plane deformation ($\nu_{\text{OH}} = 920 \text{ cm}^{-1}$), the stretching band of the $\text{CH}_2$ groups of the PVA backbone ($\nu_{\text{C-H}} = 2940 \text{ cm}^{-1}$), the C=O and C-O stretching bands of acetate groups ($\nu_{\text{C=O}} = 1720 \text{ cm}^{-1}$ and $\nu_{\text{COC}} = 1250 \text{ cm}^{-1}$), and the deformation vibration of the $\text{CH}_3$ groups in PVA structure ($\nu_{\text{C-H}} = 1420 - 1330 \text{ cm}^{-1}$). Furthermore, the curves of the h-BNNS/PVA membranes display two main absorption peaks, additional to PVA peaks, of hexagonal BN ascribed to the out-of-plane bending ($\nu_{\text{B-N}} = 850 \text{ cm}^{-1}$) of sp$^2$-bonded B–N–B and the in-plane stretching of sp$^2$-bonded B–N ($\nu_{\text{B-N}} = 1380 \text{ cm}^{-1}$). During the crosslinking of PVA with GTA, the amount of hydroxyl functions decreases to create acetal functions, while the carbonyl functions are supposed to be constant as this peak is resulting from the vinyl acetate functions, which do not react with GTA. GTA add carbonyl functions but they are considered negligible since PVA is in excess over GTA and also since it evaporates during the reticulation process. M’Barki et al.$^{12}$ calculated the ratio of maximum intensity corresponding to peaks at 3330 cm$^{-1}$ and 1720 cm$^{-1}$ to give a relative indication on the cross-linking degree. A lower ratio implies a more important cross-linking degree according to the reduction of –OH related to alcohol functions. Indeed, here the ratios between the peak intensities of the hydroxyl functions at 3400 cm$^{-1}$ and that of the C=O of the ester function at ~1720 cm$^{-1}$ are compared to determine the apparent crosslinking effectivity in the surface.
When the curing time increases from 1h to 24h, SEM images revealed that membranes have a porosity loss. Indeed, this fact is related to the crosslinking effectiveness of the membranes. The ratio between the intensities of hydroxyl and carbonyl functions decreases from 3.23 to 0.63 as the membranes curing time increases from 1 to 24h. This reflects a higher effectivity crosslinking in the membrane that does not present porosity.

**Figure 5.6** FTIR spectra of PVA and h-BNNS/PVA membranes at different curing times: a) PVA, b) BNP-1h, c) BNP-3h and d) BNP-24h
5.3.5 XRD analysis

The XRD patterns of the obtained membranes prepared from pure PVA and h-BNNS/PVA emulsions are shown in Figure 5.7. The XRD patterns reveal a peak around 19.5 ° suggesting the presence of a crystalline microstructure characteristic of PVA. The intensity of the peak decreases by adding h-BNNS to the samples and the peak also becomes broader. Moreover, there is a remarkable decrease of this peak intensity as the curing time of the membranes increases. This fact can be explained by the crosslinking effectiveness of each membrane, since higher is the crosslinking degree, higher is the loss of crystallinity in the PVA microstructure. The XRD patterns of h-BNNS/PVA membranes showed a peak around 2θ ~ 26.7 ° characteristic of the (002) plane in h-BN. The FWHM values of (002) peaks evidences the presence of exfoliated h-BN. Based on Scherrer equation ($\tau = \frac{K\lambda}{\beta\cos\theta}$, where $\tau$ is the thickness of the exfoliated h-BN, $K$ is a constant (typical value 0.9), $\lambda$ is the wavelength of X-ray and $\beta$ is the FWHM), the h-BN crystallites display a ~ 10 nm thickness. This result was confirmed by TEM characterization technique using isolated exfoliated h-BN (see Chapter 5 section 5.3.2).
5.3.6 Thermoanalytical analysis

The thermal degradation behavior of PVA and h-BNNS/PVA membranes was examined by thermogravimetric analysis (TGA) as shown in Figure 5.8. The PVA (grey curve) shows a quick weight loss of about 8% attributed to evaporation of not-bonded water present on the surface of the solids. More significant weight loss (15%) in the temperature range of 150 – 250 °C is due to the PVA de-acetylation. The third region around 250 – 500 °C appeared to be due to degradation of the backbone of PVA composite polymer membrane with a total weight loss of about 55%.

Figure 5.7 XRD patterns of a) PVA, b) BNP-1h, c) BNP-3h and d) BNP-24h membranes
The last degradation step of about 22% is due to the degradation of vinyl acetate groups. The h-BNNS/PVA curves at different curing times (1, 3 and 24h) display the same behavior, so the porosity does not affect the thermal behavior of the polymer membrane. The h-BNNS/PVA curves show the same transition regions than the pure PVA, albeit in different proportions. Not-bonded water represents 3% weight loss. Degradation of the PVA backbone chain represents 50% of the weight loss and degradation of vinyl acetate groups is about 30% of the weight loss. It is observed in the h-BNNS/PVA curves a residual weight that the pure PVA is not displaying. This residual weight of 17 wt% is due to the h-BNNS that are not degraded at 800°C.

Figure 5.8 Thermogravimetric analyses of the PVA and h-BNNS/PVA membranes
The DSC measurements were carried out under inert atmosphere at scan rate of 10 °C min\(^{-1}\) by a heating-cooling-heating cycle and the second heating curves were evaluated (Figure 5.9). The samples and the reference were heated from the same source and the differential of temperature was measured. During the measurements, the samples were first heated from -20 to 200 °C, and they were cooled down to 0 °C. The second heating was performed between 0 and 200°C at a scan rate of 10°C min\(^{-1}\). The glass transition temperature \((T_g)\) of the PVA and h-BNNS/PVA membranes was analyzed. The PVA curve presents an endothermic peak at 124 °C corresponding to the \(T_g\) temperature. The h-BNNS/PVA membranes display a shifting of the peak to higher temperatures, around 130 °C, for the h-BNNS/PVA membranes. One of the factors affecting the \(T_g\) is the ease with which polymer chains can move. The more easily they move, a lower \(T_g\) is display; a higher \(T_g\) means more thermal energy is needed to induce the polymer chains motion.\(^4\) Thus the extent on the curing has a slight influence on the \(T_g\) temperature. The membranes cured for 1h present a \(T_g\) temperature of 131°, increasing the curing time at 3 h the \(T_g\) temperature increase at 132° and if the curing time is extended to 24 h the \(T_g\) peak is shifted at 134°. The \(T_g\) temperatures were calculated by applying the tangents to the curves above and below the glass transition step. The point where the tangents intersect with each other is the \(T_g\) temperature. These results indicate that the extent of the curing time affects the \(T_g\) value of the membranes. As we observed in FTIR the BNP-24h membranes display higher crosslinking degree, this entails polymer chains are unable to move easily and thus an increase on the \(T_g\) value. The addition of h-BNNS also modifies the elastic behavior of the composite by hindering the polymer matrix chains motion.
Figure 5.9 DSC 2nd cycle curves of PVA membrane and h-BNNS/PVA membranes at different curing times

5.3.7 WCA measurements

The hydrophilicity of PVA and h-BNNS/PVA membranes was evaluated through WCA technique. The images (Figure 5.10) revealed the different hydrophilic behaviors of the membranes. The membrane BNP-1h displays a contact angle of $48 \pm 2^\circ$. The WCA tends to increase with the different curing times, the BNP-3h and BNP-24 displays a contact angle of $57 \pm 2^\circ$ and $63 \pm 3^\circ$, respectively. The membrane prepared with pure PVA displays higher contact angle ($70 \pm 2$). The pictures were taken within the first 5 s after the water drop was deposited on the membranes.
Then it was found that the water droplet spread out and immediately penetrates into the membrane, resulting in a change in the WCA to approximately 0°, except for the BNP-24h membrane, which takes longer time to absorb the droplet. These results could be explained by the fact that the BNP-1h and BNP-3h membranes possess porosity in their surface, allowing the water to be absorbed faster than the BNP-24h or PVA membranes which present a non-porous surface. The crosslinking effectivity also plays a role in the membrane hydrophobicity. When the membranes are crosslinked with GTA, the hydroxyl functions of the polymer structure react with aldehyde groups of the crosslinking agents and cause the membrane having a less hydrophilic behavior.\textsuperscript{42} Hence, it is also important to point out that chemical crosslinking modifies PVA original network structure, and this significantly reduces the pore size distribution. The hydrophilicity of the membranes makes them favorable for applications in water purification because it could prevent protein adsorption at the interface and thus fouling along filtration.

\textbf{Figure 5.10} WCA images of a) BNP-1h, b) BNP-3h and c) BNP-24h membranes
5.3.8 Swelling behavior

The swelling capacity of h-BNNS/PVA membranes in water was measured and the results are shown in Figure 5.11. PVA is a water soluble polymer, hence crosslinking the membranes with GTA is essential for long-term application of membranes. Besides, the three h-BNNS/PVA and PVA membranes were crosslinked using the same method. The curing time before crosslinking has influence in their porosity, and therefore may affect their swelling behavior. At first sight, all the membranes present similar swelling patterns. The swelling rate is fast at the beginning and then gradually slows down until reaching a constant value after 3h. However, the BNP-1h membrane presents a higher swelling ratio than pure PVA, BNP-3h or BNP-24h membranes. This fact could be attributed, as mentioned previously, to surface porosity and also to the crosslinking effectivity. Increasing the porosity of the membrane leads to a faster water absorption and a higher water absorption capacity. Besides, higher crosslinking with GTA reduces the hydrophilic behavior, thus the membranes with higher crosslinking degree display lower swelling capacity. BNP-24h membranes display a higher swelling ratio than pure PVA, meaning that it can hold more water. This result gives evidence of residual porous structure despite the pore collapsing observed by SEM after 24h curing time. The pores act as small capillaries, absorbing a larger amount of water compared to the dense structure of pure PVA membrane.
Figure 5.11 Swelling ratio of pure PVA and h-BNNS/PVA membranes at different curing times.

5.3.9 Mechanical properties

The applied stress and elongation ratio curves of these samples are shown in Figure 5.12. The corresponding values of Young modulus, tensile strength and elongation to break ratio values are illustrated in Table 5.4. The BNP-24 h membranes possess the highest Young modulus (1180 ± 31MPa), the highest tensile strength (14.6 ± 0.1MPa) and the lowest elongation at break (7.8 ± 0.2 %). The BNP-1h and BNP-3h membranes exhibit much lower Young modulus, 229 ± 28 and 194 ± 23 MPa, respectively; lower tensile strength, 7.3 ± 1.4 and 5.2 ± 0.8 MPa, respectively; and higher elongation ratio at break, 10.3 ± 0.1 and 11.3± 0.4 %, respectively.
If we compare the results with pure PVA or PVA in presence of h-BNNS prepared without presence of oil, we observed that these membranes are more flexible. They possess a Young’s modulus and tensile strength of $19 \pm 2$ and $6.9 \pm 1.4$, respectively. Thus, the elongation at break is higher than the BNP (1, 3 and 24 h) membranes, with values of $22.6 \pm 0.4$ and $36.2 \pm 0.6$ for PVA and h-BNNS/PVA membranes. The above results might be explained first by the increase in porosity (in BNP-1h and BNP-3h) which significantly weakens tensile strengths and Young’s modulus of the membranes. Secondly, the duration of curing time is significantly more important for the BNP-24h and influences its properties. The Tg, as depicted by DSC measurements, is higher and thus water swelling ratio is lower. The porosity at the membrane surface is hardly visible by SEM. Mechanical results show that a longer curing time (24h) conducts also to higher stiffness. These data associated to FTIR analyses converge on higher cross-linking degree of PVA chains for a 24h curing time. Compared to other materials, our h-BNNS/PVA membranes using the emulsion templating method display better mechanical properties than other PVA-based membranes obtained from TIPS or electrospun methods. The h-BNNS/PVA (BNP-24h) membranes present higher young modulus ($1180 \pm 31$ MPa) and tensile strength ($14.6 \pm 0.1$ MPa) compared to the porous membranes fabricated using TIPS-LCST procedure, $301 \pm 1$ MPa and $1.2 \pm 0.2$ MPa for Young modulus and tensile strength, respectively. In the same way, the mechanical properties were compared with those of fibrous membranes prepared with low molecular weight PVA and by electrospun method. The results clearly shows that h-BNNS/PVA membranes display higher Young modulus and tensile strength than fibrous membranes ($110$ MPa and $4.3$MPa, respectively). However the fibrous membranes display higher elongation at break ($57\%$) compared to h-BNNS/PVA membranes ($\sim 10\%$).
Figure 5.12 Stress-strain curves of PVA and h-BNNS/PVA membranes: a) PVA, b) h-BNNS-PVA c) BNP-1h, d) BNP-3h and e) BNP-24h

Table 5.4 Values of Young modulus, tensile strength and elongation to break ratio

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA</td>
<td>19 ± 2</td>
<td>42 ± 4</td>
<td>22.6 ± 0.4</td>
</tr>
<tr>
<td>h-BNNS/PVA</td>
<td>6.9 ± 1.4</td>
<td>21 ± 3</td>
<td>36.2 ± 0.6</td>
</tr>
<tr>
<td>BNP-1h</td>
<td>229 ± 28</td>
<td>7.3 ± 1.4</td>
<td>10.3 ± 0.1</td>
</tr>
<tr>
<td>BNP-3h</td>
<td>194 ± 23</td>
<td>5.2 ± 0.8</td>
<td>11.3 ± 0.4</td>
</tr>
<tr>
<td>BNP-24h</td>
<td>1180 ± 31</td>
<td>14.6 ± 0.1</td>
<td>7.8 ± 0.2</td>
</tr>
</tbody>
</table>
5.3.10 Membranes performance

To characterize the performances of the membrane, gas–liquid displacement porometry, water flux and particle rejection tests were also performed. The gas–liquid displacement porometry allows determining the surface pore size distribution and the mean pore size of the membranes. Figures 5.13 and 5.14 show the results of the pore size distribution of BNP-1h and BNP-3h membranes obtained by using this technique. These results agree with SEM observations according to which the mean pore size of BNP-3h is smaller than that of BNP-1h. The BNP-3h membrane displays a mean pore size around $0.19 \pm 0.03 \mu m$ while the BNP-1h displays higher pore size around $1.1 \pm 0.3 \mu m$. It was impossible to conduct this characterization in BNP-24h because the water was not able to pass through the membrane. The pore size was thus lower than the detection limit of the instrument. These results confirm that the time the membranes were left to cure has strong influence on their morphology and pore size distribution. At a given pore size distribution, the membranes could be used for microfiltration applications.
Figure 5.13 Relative pore size distribution of BNP-1h obtained from gas–liquid displacement porometry
Figure 5.14 Relative pore size distribution of BNP-3h obtained from gas–liquid displacement porometry
The performance of the BNP-1h and BNP-3h to filter water was characterized by determining the flux versus the applied pressure by using solvent porometry. The flux is determined by the specific resistance of the membrane material under a given differential pressure across the membrane so that the flux increases with the operating area of the membrane and with the applied pressure. The water permeance results are shown in Table 5.5. The BNP-1h membrane displays a high water flux around 2065 L h$^{-1}$m$^{-2}$bar$^{-1}$ in comparison to BNP-3h which displays a water flux of 87 L h$^{-1}$m$^{-2}$bar$^{-1}$. These results evidence that the membrane pore sizes distribution plays an important role in their performance to filter water. If the results are compared with those in the literature for PVA membranes produced by TIPS-LCST$^{12}$, it is observed that the as-prepared h-BNNS/PVA membranes display higher water permeance. The membranes prepared by TIPS-LCST technique with PVA exhibit either too low (less than 1 L h$^{-1}$m$^{-2}$bar$^{-1}$) or too high (more than 10,000 L h$^{-1}$m$^{-2}$bar$^{-1}$) permeance values, demonstrating the difficulty to prepare PVA membranes with controlled porosity. Besides, the fibrous membranes prepared by electrospun methods$^{13}$ possess similar water permeability values compared with BNP-3h membranes but the water flux for BNP-1h is much higher due to the increase in porosity.$^{43}$ Concerning the preparation of PVA-fibrous membranes, it is possible to control the fibers diameter but not the final membrane porosity. In this study, we developed for the first time a new concept on pore tuning for PVA-based membranes by easily controlling the parameters, such as curing time, during membrane preparation using Pickering emulsion templating.
Table 5.5 Water flux permeance of BNP-1h and BNP-3h membranes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water flux (Lh⁻¹m⁻²bar⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BNP-1h</td>
<td>2065 ± 74</td>
</tr>
<tr>
<td>BNP-3h</td>
<td>87 ± 6</td>
</tr>
</tbody>
</table>

To evaluate the ability of hBNNS/PVA membranes to work as microfiltration filters, a particle rejection test using 0.1, 1.2 and 3 µm polystyrene latex particles was performed. First, the membrane permeability was tested using the dead-end cell by flushing MilliQ water at 1 bar for 30 min. Then the cell was filled with the latex NPs solution and they were forced to pass through the membrane by applying a 0.4 bar of pressure. Table 5.6 shows the rejection ratio of the BNP-1h and BNP-3h for the different latex NPs tested. The results show that the BNP-1h membrane with a pore size distribution of 1.1 µm could reject 3.8 ± 0.1, 85.7 ± 0.2 and 99.2 ± 0.1 % of latex NPs particles sizing 0.1, 1.2 and 3 µm, respectively. These observations can be correlated with the pore size data, which indicate that the mean pores size of the membrane is 1.1 µm with a size deviation of 0.3 µm. The rejection rate for the 3 µm particles is not 100 %, which could be explained by the plot of size distribution (Figure 13) which displays a little shoulder between 1.5 and 3.5 µm. The results for the BNP-3h membranes with a pore size distribution of 0.19 µm show that it could reject 76.4 ± 0.2 and 99.7 ± 0.2 % of latex NPs particles sizing 0.1 and 1.2 µm, respectively. These observations are well correlated with the pore sizes distribution of the membrane. It should be noted that for the 100 nm latex NPs could easily get into the porous membrane as many of the pores on the surface were greater than 0.19 µm.
However, when the particles penetrate deeper, the effective pore size in the flow direction becomes smaller due to the winding road shape of the channels making the flushing of particles more difficult. The permeance was tested after the particle rejection test and the membranes did not significantly reduce their performance. The rejection efficiency of latex nanoparticles 1.2 µm in BNP-3h membrane is higher (99.7 ± 0.2%) than in other PVA-based membranes. For example, the PVA-based fibrous membranes with an average pore size of 15.61 µm, leads to a rejection efficiency of 96 % for 0.5 µm particles; this rejection efficiency was already smaller compared to other electrospun melt membranes.  

The membrane pore size might also be tuned apart from the curing time by playing with polymer and stabilizer concentrations as well as the oil/water ratios of the emulsion or the casting parameters. Playing with all the parameters, it could be possible to obtain a membrane with defined porosity and permeability to filter a large set of targeted compounds. This strategy could be applied to produce other polymer or ceramic-based membranes.

**Table 5.6** Rejection ratios of BNP-1h and BNP-3h for different sizes of latex NPs

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Rejection Latex NPs 100 nm</th>
<th>% Rejection Latex NPs 1.2 µm</th>
<th>% Rejection Latex NPs 3 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>BNP-1h</td>
<td>3.8 ± 0.1</td>
<td>85.7 ± 0.2</td>
<td>99.2 ± 0.1</td>
</tr>
<tr>
<td>BNP-3h</td>
<td>76.4 ± 0.2</td>
<td>99.7 ± 0.2</td>
<td>-</td>
</tr>
</tbody>
</table>
5.4 Conclusion

A novel strategy to produce porous membranes based on PVA polymer has been developed using emulsion templating. In a first step, Pickering emulsions based on h-BNNS/PVA mixtures were prepared, and in a second step a porous membrane was produced after casting and crosslinking with GTA. The membrane curing time has been found to play a role in its final morphology. The membranes which were left to cure for shorter duration present higher pore size as well as a more pronounced hydrophilic behavior due to the lower crosslinking effectiveness. As a result of these parameters, the swelling ratio is also higher for the BNP-1h. The h-BNNS/PVA membranes based on emulsion templating present a mean pore size of 1.1 µm and 0.19 µm when they were cured for 1 and 3h, respectively. Due to its higher porosity, the BNP-1h displays water permeability 20 times higher than BNP-3h membrane. The interest of BNP-3h membrane remains in its particle rejection performance; it was able to reject more than 76 % of latex NPs sizing 0.1 µm and 99.7 % of the particles sizing 1.2 µm. A new concept of pore tuning by easily controlling parameters, such as the curing time during membrane preparation using Pickering emulsion templating has been developed in this work for PVA-based membranes. The obtained membranes display higher efficiency in water filtration and particle rejection than other PVA-based porous membranes obtained by electrospun methods. This new strategy opens a new route for the development of porous membranes with controllable pore size from hydrophilic polymers for microfiltration applications.
5.5 Perspectives

This work based on emulsion templating method gives a new insight for the preparation of porous polymer membranes. In this study, we have used PVA with a specific molecular weight ($M_w = 27000 \text{ g mol}^{-1}$) and degree of hydrolysis (98 %). In future work it would be interesting to investigate the influence of different types of PVA (different molecular weights and different degree of hydrolysis) on the preparation of emulsions and membranes. Furthermore, there are different factors that play a role in the stabilization of emulsions, such as the oil type or particle concentration. Therefore, it would be interesting to study the influence of different oils in the preparation of membranes. In this work, ethyl benzoate was used as oil phase for the preparation of h-BNNS/PVA emulsions because it gave good results in the preparation of h-BNNS emulsions (Chapter 4). The nanoparticles concentration also bears a role in emulsion stabilization and droplet size, therefore studying the role of nanoparticles concentration in the membrane morphology would be interesting as well.

There is still work to do in the conditions optimization for the preparation of membranes. A future work could be to deeper study the influence of parameters such as casting temperature, speed and thickness in the membrane morphology and pores size distribution. As we discuss in our studies, the temperature plays a role in the viscosity of polymer, so casting the membranes at different temperatures may lead to structural changes in the membrane. The casting speed and thickness may also have an influence in the membrane structure, so preparing membranes at different speeds and thicknesses could help to tailor the desired conditions.
Further studies using the method we developed here for the preparation of porous membranes based on PVA, could be applied for other hydrophilic polymers beyond PVA, such as polyacrylamide (PAM), or biopolymer such as chitosan.
References


GENERAL CONCLUSION
General Conclusion

This work aimed to develop a green and straightforward approach to developed porous materials reducing synthesis steps and avoiding sintering and the use of surfactants or hazardous solvents. This approach combines the use of Pickering emulsion as soft templates to create porosity and casting method to shape the material into membrane films. The as-prepared materials could be used for water treatment in microfiltration applications. Prior to this study, different studies were carried out: the preparation of hexagonal boron nitride nanosheets (h-BNNS) from pristine h-BN through ion intercalation method; and the role of this h-BNNS stabilizing Pickering emulsions, as well as other 2D materials.

Exfoliated h-BNNS from commercially pristine h-BN involving a two-steps procedure was successfully following a green approach. The exfoliation was caused not only by sonication effects but also by assisted-gelatin and intercalation of K$^+$ and Zn$^{2+}$ ions. The latter resulted in the observation of few-layered h-BNNS of reduced lateral size, as well as bi- and tri-layered h-BNNS with lateral size below 200 nm, as evidenced from TEM images. The crystallinity of the obtained h-BNS was confirmed using XRD. Raman microscopy further confirmed the presence of the bi- and tri-layered flakes, as well as few-layered h-BNNS, by analyzing the peak position shift from the pristine h-BN.
General Conclusion

Non-modified 2D BN material has been used for the first time as stabilizing agent for the preparation of inverse Pickering emulsions. The epifluorescence images revealed that the emulsions are water-in-oil type. Microscopy images showed that the average droplet size decreases with increasing the BN concentration. The kinetic stability showed that the emulsions prepared with 2 wt% BN are the most stable, and rheology tests confirmed this result, showing that no change in the stability occurred after 14 days. Besides, rheological measurements performed on the emulsions with 2 wt% BN exhibited higher viscosity for water volume fraction close to 0.64. This value corresponds to the maximum packing volume fraction of water in ethyl benzoate, for drops of spherical shape stabilized by h-BN nanosheets. These emulsions may be good candidates to design new interesting materials with valuable properties, such as porous membranes.

A novel strategy to produce porous membranes based on PVA polymer has been developed using emulsion templating. In a first step, Pickering emulsions based on h-BNNS/PVA mixtures were prepared, and in a second step, a porous membrane was produced after casting and crosslinking with GTA. The membrane curing time has been found to play a role in its final morphology. The h-BNNS/PVA membranes based on emulsion templating presented a mean pore size of 1.1 µm and 0.19 µm when they were cured for 1 and 3h, respectively. The interest of BNP-3h membrane remains in its particle rejection performance; it was able to reject more than 76 % of latex NPs sizing 0.1 µm and 99.7 % of the particles sizing 1.2 µm.
A new concept of pore tuning by easily controlling parameters, such as the curing time during membrane preparation using Pickering emulsion templating has been developed in this work for PVA-based membranes. This new strategy opens a new route for the development of porous membranes with a controllable pore size from hydrophilic polymers for microfiltration applications.

The results presented in this work are hoped to contribute to the development of green methods for the preparation of porous membranes for water treatment in the near future. The prepared membranes could be used for particles removal in polluted waters. Furthermore, using this approach we demonstrate it is possible to tune the pore size by controlling the curing time; but different parameters such as the polymer, stabilizer or crosslinking agent concentrations, casting thickness and speed could have also influence in controlling the porosity. Future research should be devoted to further improve the control of the material porosity and improve the filtration efficiency. The use of different polymers for the preparation of membranes would be an interesting point of study.
ANNEX I

Pickering Emulsions (PE) Stabilized with Two-Dimensional (2D) Materials: A Comparative Study*

Abstract

In this chapter, we study the preparation of Pickering emulsions using two-dimensional (2D) materials: graphene oxide (GO) and hexagonal boron nitride nanosheets (h-BNNS). The type of obtained emulsions, the droplet size and the rheological behavior were investigated for both GO and h-BNNS based emulsions. The results show that two types of emulsion, direct oil-in-water (O/W) and indirect water-in-oil (W/O) may be produced due to the different hydrophilic properties of the 2D materials. Besides, similar microstructures and droplet size are obtained, as well as analogue rheological behaviors. Thus, depending on the potential application, it is possible to tune the emulsion type, W/O or O/W, by choosing the 2D material possessing the most interesting properties for the sought application.

* This work has been submitted to Colloids and Surfaces A: Physicochemical and Engineering Aspects as: D. Gonzalez Ortiz, C. Pochat-Bohatier, J. Cambedouzou, M. Bechelany, P. Miele
1 Introduction

Recent research has established a new application for 2D materials through the formation of emulsions, where they can serve as ultrathin plate-like interfacial stabilizers in two-liquid systems. Huang et al. conducted pioneering investigations on the interfacial activity of graphene oxide (GO) at different interfaces, proving the behavior of GO as a colloidal surfactant.\(^1\) Few years later, He et al. investigated the different conditions affecting the stability of GO emulsions, such as oil type, sonication, GO concentration and pH values. Thicket et al. studied the stabilization energy associated with GO adsorption for oils with different polarities; they found that GO was better adsorbed in non-polar and aromatic oils.\(^2\) Creighton et al. presented a thermodynamic analysis of the behavior of 2D materials at liquid-liquid interfaces.\(^3\)

The properties of the solid particles, such as the concentration, shape, size and wettability, play a major role in Pickering emulsion behavior. Among these factors, the particle wettability is a key factor in the type of obtained emulsion and its properties. The particle hydrophilicity determines whether the stabilization of oil-in-water (O/W) or water-in-oil emulsion (W/O) will take place. GO nanosheets possess an amphoteric nature,\(^4\) whereby GO assembles at O/W interfaces, and they will tend to stabilize O/W emulsions. Graphene-based emulsions have been used to fabricate GO-based functional materials with specific structure through emulsion polymerization method.\(^5\)\(^-\)\(^7\) Depending on the targeted application, this type of emulsions are not suitable, whereas W/O emulsions are needed. Contrarily to graphene, h-BNNSs possess a hydrophobic behavior,\(^8\) therefore they will tend to stabilize W/O emulsions. This type of emulsions has great interest due to their potential application for the fabrication of materials with specific structures and performance using inverse emulsions as soft templates.
In this chapter, a study based on the different emulsions stabilized by GO and h-BNNS is presented. Depending on the material hydrophilic behavior, two types of emulsions, O/W and W/O, can be prepared using the same biphasic system. The resulting emulsions showed similar droplet size. At higher particle concentration, e.g. 2 wt% of GO and h-BNNS, the emulsion droplets are smaller. The emulsion viscosity is higher at medium values of o/w ratio or dispersed phase volume fraction ($\Phi_{dp}$).

2 Experimental part

2.1 Materials

Hexagonal boron nitride (h-BN) was supplied from Saint Gobain (95 % purity, 325 mesh, 3 µm particle size). Graphite powder (CAS n° 7782-42-5, 99.95 % trace metal basis, < 20 µm), phosphoric acid (H$_3$PO$_4$, CAS n° 7664-38-2, 85%, 99.99 % trace metal basis), sulfuric acid (CAS n° 7664-93-9, 99.99 %, H$_2$SO$_4$), potassium permanganate (K$_2$MnO$_4$, CAS n° 7722-64-7, ACS reagent, ≥ 99.0 %), hydrogen peroxide (H$_2$O$_2$, CAS n° 7722-84-1, ≥ 30%), fluorescein sodium salt (CAS n° 518-47-8, Bio-Reagent), methyl red (CAS n° 493-52-7, ACS reagent) and ethyl benzoate (CAS n° 93-89-0, ≥ 99 %, density = 1.045) were supplied from Sigma Aldrich. In all the experiments deionized pure water (18 MΩ) was used.
2.2 Methods

2.2.1 Synthesis of graphene oxide (GO)

Graphene oxide was synthesized from natural graphite powder, following modified Hummer’s method. Briefly, 3g of graphite were dispersed in concentrated H$_2$SO$_4$:H$_3$PO$_4$ (9:1, 400 mL) solution. Then, 18 g of KMnO$_4$ were added gradually to the mixture and it was stirred for 12 h. Later on, the mixture was cooled down to room temperature and 3 mL of H$_2$O$_2$ were added. A brown precipitate was observed; showing that exfoliation of graphene oxide from graphite was being carried out. After one hour stirring, the GO was separated by centrifugation at 6000 rpm for 10 minutes and the supernatant was decanted away. The resultant precipitates were washed several times with 30% hydrochloric acid and absolute ethanol. Finally, the powder was dried at 50°C for 24 hours to obtain pure graphene oxide.

2.2.2 Emulsion preparation

Pickering emulsions stabilized either with graphene oxide or exfoliated h-BN were prepared following a simple two-step sonication protocol. In a first step, the powder was suspended in water and sonicated for 15 min at 65 % amplitude with pulse off/on 0.5 – 1 s using ultrasounds device. This step ensures the well dispersion of powders in the water. In a second step, ethyl benzoate was added to the suspension with different oil/water ratios (Table A.1) and the mixture was subsequently sonicated with the same equipment for 15 min at 65 % amplitude and pulse off/on 0.5 – 1 s. Depending on the O/W or W/O emulsion, one of the phases was labelled. For O/W emulsions, methyl red dye was added to label the oil phase while for W/O emulsion, fluorescein was used to label the water phase.
Disperse phase volume fraction \((\Phi_{dp}) = 1 / (1+R)\) \hspace{1cm} \textbf{Equation A.1}

where \(R\) is the volume fraction between the oil and the water.

The volume fraction of the disperse phase is influenced by the type of emulsion, in O/W emulsions the disperse phase will be the oil while in W/O water is the disperse phase.

\textbf{Table A.1} GO and h-BNNS emulsions composition

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<tr>
<th>Boron nitride (wt %)</th>
<th>Graphene oxide (wt %)</th>
<th>Ratio o/w</th>
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<td>0.5, 1.0, 1.5, 2.0</td>
<td>1 (R1)</td>
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\subsection*{2.2.3 Characterization techniques}

X-ray diffraction (XRD), Fourier transformed infrared (FTIR) spectra and Raman spectroscopy techniques were used using the same basis than in chapter 4. The kinetic stability, droplet microstructure and emulsion type were determined in the same way than chapter 4.
3 Results and Discussion

In this section, the structure of the obtained materials, GO and h-BNNS, will be discussed in a first step. Then, the obtained emulsions incorporating these two-dimensional materials will be compared regarding the type of emulsion they are able to form, the droplet size distribution in function of the material concentration, the emulsion stability, and their rheological behavior. It has to be pointed out, the results presented in chapter 4 are used here to compare the two types of emulsions.

3.1 X-ray diffraction

The oxidation and exfoliation of graphite into graphene oxide was confirmed using XRD technique. The XRD patterns of graphite and graphene oxide are shown in Figure A.1. The graphite displays a diffraction peak at $2\theta = 26.6^\circ$ corresponding to the (002) plane, which corresponds to a distance between adjacent layers of 3.34 Å. After the introduction of oxygen functionalities via Hummer’s method, the peak shifted to $2\theta = 13.4^\circ$ corresponding to a $d$ spacing of about 6.6 Å (calculated with Bragg’s law, Equation A.2). This increase of interlayer distance is attributed to the intercalation of water molecules between the oxidized graphene layers. The variation of interlayer spacing in GO is the result of variations in the oxidation degree. The width of the most intense peak can also be used to verify the exfoliation degree. The crystallite average size was calculated by the Scherrer equation (Equation A.3). The calculated results show that the crystallite average size of GO is ~3.7 nm

$$d = \frac{\lambda}{2 \sin \theta}$$

Equation A.2

where $d$ is the distance between adjacent sheets or layers, $\lambda$ is the wavelength of the X-ray beam ($\lambda = 0.154$ nm) and $\theta$ is the diffraction angle.
Equation A.3

\[ D = \frac{0.9 \cdot \lambda}{\beta \cos \theta} \]

where \( D \) is the crystallite size, \( \lambda \) is the wavelength of the X-ray beam (\( \lambda = 0.154 \) nm), \( \beta \) is the FWHM and \( \theta \) is the diffraction angle.

The disappearance of the Bragg peak corresponding to the in-plane periodicity of carbon atoms (100 peak) in GO might be due to the extensive presence of defects in the graphene structure, caused by the graphene oxidation.

**Figure A.1** XRD patterns of a) graphite and b) graphene oxide
The XRD patterns of h-BN and h-BNNS are shown in Figure A.2. The patterns in the Figure A.2a show the 002, 101, 100 and 004 diffraction peaks of h-BN, which correspond to $2\theta$ angles of 26.71°, 41.6°, 43.8° and 55.1°, respectively. In h-BNNS, the 002 peak is slightly shifted to $2\theta = 26.60^\circ$. The interlayer distance between layers of h-BN is 3.33 Å, becoming 3.34 Å in h-BNNS. The crystallite average size was calculated by the Scherrer equation (Equation A.3). The calculated results show that the crystallite average sizes of h-BNNS is ~10.5 nm.

![XRD patterns of a) h-boron nitride raw powder and b) h-boron nitride nanosheets](image)

**Figure A.2** XRD patterns of a) h-boron nitride raw powder and b) h-boron nitride nanosheets
3.2 Fourier-transform infrared spectroscopy

FTIR was employed to identify the functional groups on the GO and h-BNNS surface. The FTIR spectra of graphite and GO are presented in Figure A.3. In all spectra, the oxidation is confirmed by the presence of several bands attributed to oxygen functionalization. The wide peak at 3396 cm$^{-1}$ is attributed to the $-\text{C-OH}$ stretching vibration of hydroxyl group. A second peak located at 1740 cm$^{-1}$ is attributed to the $-\text{C=O}$ groups, and the peak at 1617 cm$^{-1}$ to the $-\text{C=C}$ skeletal vibration of non-oxidized graphite. The two absorption peaks at about 1220 cm$^{-1}$ and 1028 cm$^{-1}$ are assigned to the $-\text{C-O}$ stretching vibration.$^{10}$

![Figure A.3 FTIR spectra of graphite and graphene oxide](image-url)
Figure A.4 shows the FTIR spectra of h-BN and h-BNNS. The peak at 812 cm\(^{-1}\) can be attributed to B-N stretching (in-plane ring vibration, \(E_{1u}\) mode) and the broad absorption at 1380 cm\(^{-1}\) can be ascribed to the B-N-B bending (out-of-plane vibration, \(A_{2u}\) mode). In addition, the h-BNNS spectrum shows another absorption peak at 3200 cm\(^{-1}\), which could be ascribed to hydroxyl group (-OH) vibration. This peak might appear due to the large amount of defects such as vacancy defects, dislocations and exposed edges introduced on the h-BNNS surfaces during sonication.

![FTIR spectra of h-boron nitride and h-boron nitride nanosheets](image)

**Figure A.4** FTIR spectra of h-boron nitride and h-boron nitride nanosheets
3.3 Atomic Force Microscopy

GO obtained after oxidation through Hummer’s method and exfoliation was characterized by AFM. A number of about 100 GO nanosheets have been considered for the analysis. Figure A.5 shows the AFM image of GO nanosheets, the results indicate a reduction on the thickness from 20 µm in the case of pristine GO, to 10–30 nm. h-BNNS obtained by exfoliation in water using sonication tip, were characterized as well by AFM. A number of about 100 h-BNNS have been considered for each sample. Figure A6 shows the AFM image of h-BNNS, the results indicate a reduction on the thickness of pristine h-BN from 3 µm to 2-6 nm. Based on these AFM images and taking into account the width of one GO and h-BN nanosheet (0.33 nm), we could assume that our GO is composed about 30-90 layers; and h-BNNS are generally composed of 3-9 layers.

![AFM image of exfoliated GO and height of GO layers](image)

Figure A.5 a) AFM image of exfoliated GO and b) Height of GO layers
The CLSM images of GO and BN with O/W ratio of 1 (R1) are shown in Figure A.7. The top images are from emulsions stabilized with GO, the oil phase was labelled with methyl red dye. This dye has the ability to be dissolved in ethyl benzoate but is not soluble in water. It was observed that the droplets display the colored phase, meaning that the disperse phase is composed with the oil and the continuous phase was found to be water. GO nanosheets therefore turn out to stabilize an oil-in-water (O/W) emulsion. The bottom images are from emulsions stabilized with exfoliated h-BN. In this case, instead of labelling the oil phase, the water phase was labelled with fluorescein dye.

In this case water was found to be the dispersed phase and oil is the continuous phase. Exfoliated h-BN stabilizes water-in-oil (W/O) emulsions. The fact that the 2D materials with such similar morphologies and similar properties behave so differently when stabilizing an emulsion resides in the fact that they display different hydrophilic behaviors.
Figure A.7 CLSM images of a) 0.5 wt % GO_R1 b) 1.0 wt % GO_R1 c) 2.0 wt % GO_R1 d) 0.5 wt % BN_R1 e) 1.0 wt % BN_R1 f) 2.0 wt % BN_R1

3.5 Water contact angle measurements

Figure A.8 WCA of a) graphene oxide b) h-boron nitride nanosheets powders
The characterization of the wettability was performed by measuring the water contact angles of GO or h-BNNS. The powders were compacted into foam pellets to perform the measurements. Figure A.8a shows the WCA of GO and Figure A.8b the WCA of h-BNNS. On one hand, GO displays a hydrophilic behavior with a contact angle around 40.3 ± 0.5 °. The GO particles surface therefore tends to reside more in water than in oil and will rather stabilize O/W emulsions. On the other hand, h-BN shows a hydrophobic behavior with a contact angle of 134.4 ± 0.3 °. In this case, the h-BN particles surface tends to reside more in oil than in water phase, then it will rather stabilize W/O emulsions. This behavior was established by Finkle et al., they stated that in an emulsion containing solid particles, one of the liquids would probably wet the solid more than the other liquid, with the more poorly wetting liquid becoming the dispersed phase. The importance of the wettability of the particles at the oil–water interface, quantified by the contact angle $\theta_{ow}$ that the particle makes with it, was therefore noted. Thus, water-wet particles like silica should stabilize o/w emulsions and oil-wet particles like carbon black should stabilize w/o emulsions.\textsuperscript{11}
3.6 Optical microscopy

Figure A.9 Microscopy images of a) 0.5 wt% GO_R1, b) 1.0 wt% GO_R1 and c) 1.5 wt% GO_R1 d) 2.0 wt% GO_R1

The GO and h-BNNS emulsion microstructures and drop sizes were analyzed by optical microscopy. Figure A.9 shows that the four GO emulsions formulated at different concentrations were successfully used to stabilize O/W Pickering emulsions and they present a relatively homogeneous distribution. The results show that the droplets diameter varies in function of GO concentration from 18 ± 4 μm for the lowest concentration (0.5 wt%) to 6 ± 1 μm for the highest concentration (2 wt%) when the o/w ratio is 1.
Figure A.10 Microscopy images of a) 0.5 wt% BN_R1 b) 1.0 wt% BN_R1 c) 1.5 wt% BN_R1 d) 2.0 wt% BN_R1

Figure A.10 shows the microstructure of h-BNNS stabilized emulsions prepared with different concentrations. The images reveal that the h-BNNS successfully stabilized W/O Pickering emulsions and that the droplets present a good homogeneity at high h-BNNS concentrations. At lower concentration, the heterogeneity is greater. These results point out the same behavior than for GO stabilized emulsions, i.e., the droplets diameter decreases as increasing the concentration of stabilizing agent. For emulsions prepared with 0.5 wt% h-BNNS, the emulsion droplets size was found to be $43 \pm 5 \, \mu m$ while increasing the concentration up to 2 wt% h-BNNS, the droplets size decreases down to $6.2 \pm 0.5 \, \mu m$. 
Both materials are able to stabilize either O/W or W/O emulsions depending on their hydrophilic behavior. It was found that emulsions stabilized with GO are able to form droplets with smaller diameters than those stabilized with h-BNNS (Figure A.11). This behavior can be explained by the fact that ethyl benzoate is an aromatic solvent, which possesses a $sp^2$ network. Indeed, GO is composed also by partially broken $sp^2$-carbon networks and they can interact with the aromatic rings having stronger $\pi-\pi$ interactions. This type of interactions produces emulsions with higher stable volume fraction and with smaller emulsion droplets. In the case of h-BNNS, the interactions between the h-BN p-orbitals and $\pi$-orbitals of the solvent are weaker, and therefore the emulsion droplets become larger.

![Figure A.11](image)

**Figure A.11** Mean droplet size of GO and h-BNNS stabilized emulsions at different concentrations
3.7 Emulsion stability

The GO and h-BNNS based-emulsions were stored at room temperature for 14 days and their stability was followed by eyes. The results of the stability of GO and h-BNNS based emulsions at different concentrations and various O/W ratios are presented in Table A.2 and Table A.3, respectively. Either in the emulsions stabilized by GO or in those stabilized with h-BNNS, the most stable emulsions are those formulated with higher nanosheet concentration (2 wt%). The emulsions stability index (ESI) goes up to 94 % in the case of h-BNNS based emulsions and 96 % for GO based emulsions when the emulsion is formulated with 2 wt% and o/w ratio of 1. The ESI, for both GO and h-BNNS emulsions, decreases with the decrease of concentration as well as with the decrease of $\Phi_{dp}$. It was observed that the emulsion destabilizes in two phases, one is the emulsified fraction and the other phase is resulting from the separation of the continuous phase. Figure A.12 presents a photographic image of emulsions stabilized by h-BNNS and GO taken after 14 days. It can be observed two different behaviors related to emulsion destabilization. In the case of GO emulsions, a phase can be distinguished at the top of the emulsion resulting from the creaming of the water phase (mass density at 20°C is 1000 kg m$^{-1}$) when is separated from the emulsion fraction. Conversely for h-BNNS stabilized emulsions, we observed a phase at the bottom of the emulsion: the oil that tends to sediment due to its higher density (mass density at 20°C is 1045 kg m$^{-1}$).
Figure A.12 Photographic images of the appearance of emulsions stabilized by different concentrations of h-BNNS (top image) and GO (bottom image) with o/w ratio 1 after 14 days emulsification.
### Table A.2 Stability of GO stabilized emulsions

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<th>Sample</th>
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Table A.3 Stability of h-BNNS stabilized emulsions

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Figure A.13 Emulsified fraction of a) O/W emulsions prepared with 2 wt% GO and b) W/O emulsions prepared with 2wt% h-BNNS at different o/w ratios

Figure A.13 shows the evolution of the emulsified fraction with time of GO (bottom graphic) and h-BNNS (top graphic) emulsions formulated at 2 wt% and different O/W ratios. In both type of emulsions, O/W and W/O, the destabilization of emulsions formulated at lower concentration occurs faster than for those formulated with higher concentration. This fact is due to the particle concentration effect, which is an important factor in the formation of Pickering emulsions. The increase of particle concentration induces the migration of the particles from the dispersion media, aqueous dispersion for GO and oil phase for h-BNNS, onto the oil-water interface.
This phenomenon reduces the surface energy of the system by increasing the particle surface area and causing a direct reduction in the free energy, making the system more stable.\textsuperscript{13, 14} Thus, we can conclude that the formation of Pickering emulsion with greater stability could be facilitated by increasing the particle concentration within a certain range, resulting in an increase of the total surface area of particles assembling at liquid-liquid interfaces.

### 3.8 Rheological studies

The effect of water volume fraction on the rheological properties of the GO and h-BNNS stabilized emulsions was studied by diluting the emulsion at constant particle concentration (2wt \%) and thus keeping the droplet size distribution unchanged. Figure A.14 shows the viscosity and flow curves of GO and h-BNNS. The results shown are for measurement made while increasing shear rate, but similar trends are obtained as the shear rate decreases. At low shear rates, the emulsion shear stress remains approximately constant; at higher shear rates, the stress increases as a roughly linear function of the shear rate. This change in flow behavior suggests that the emulsions have a small yield stress at rest, which increases with increasing the volume fraction.
Figure A.14 a) Viscosity and b) flow curves of O/W emulsions with 2 wt% GO and different o/w ratios (R=0.6 to 1); c) Viscosity and d) flow curves of W/O emulsions with 2 wt% h-BNNS and different o/w ratios (R=0.7 to 1)
The existence of yield stress indicates the presence of interactions between droplets. In terms of emulsions viscosity, both GO and h-BNNS emulsion, display a shear thinning flow behavior, characterized by decreasing the viscosity as shear rate increases. This phenomenon could be attributed to droplets organization. At rest, the droplets present a higher close packing; when a shear rate is applied, the droplets start to be organized into layers or strings leading to viscosity decrease. The viscosity of GO and h-BNNS was measured at two different shear rates, 50 and 100 s$^{-1}$. The values are shown in Table A.4 and Table A.5 for GO and h-BNNS stabilized emulsions, respectively. In the case of GO stabilized emulsion, the higher viscosity was found to be $282 \pm 11$ mPa·s and $149 \pm 9$ mPa·s, at 50 and 100 s$^{-1}$ respectively, for an O/W ratio of 0.8 which corresponds to $\Phi_o = 0.44$. For h-BNNS stabilized emulsions formulated with an O/W ratio of 0.7 which corresponds to $\Phi_w = 0.59$, it was found a lower viscosity of $132 \pm 12$ mPa·s and $78 \pm 1$ mPa·s, for 50 and 100 s$^{-1}$ respectively.

The GO emulsions viscosity is higher for all the O/W ratios than the viscosity of h-BNNS based emulsions, even if the dispersed phase volume fraction is higher for h-BNNS ($\Phi_w = 0.59$) compared to those of GO ($\Phi_o = 0.44$). This fact could be explained due to the $\pi-\pi$ interactions between the partially broken $sp^2$ carbon networks of GO and the benzene rings present in the ethyl benzoate, as it was mentioned before. These interactions produce emulsions with higher stable volume fraction and therefore higher viscosity.
Table A.4 Viscosity values of emulsion with 2 wt% GO for 0.6, 0.8 and 1 o/w ratio.

<table>
<thead>
<tr>
<th>GO 2 wt%</th>
<th>GO 2 wt%</th>
<th>GO 2 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>R0.6</td>
<td>R0.8</td>
<td>R1</td>
</tr>
<tr>
<td>Viscosity (mPa·s) at 50s^{-1}</td>
<td>181 ± 7\textsuperscript{a}</td>
<td>282 ± 11\textsuperscript{b}</td>
</tr>
<tr>
<td>Viscosity (mPa·s) at 100s^{-1}</td>
<td>98 ± 7\textsuperscript{A}</td>
<td>149 ± 9\textsuperscript{B}</td>
</tr>
</tbody>
</table>

Table A.5 Viscosity values of emulsion with 2 wt% BN for 0.7, 0.8 and 1 o/w ratio.

<table>
<thead>
<tr>
<th>BN 2 wt%</th>
<th>BN 2 wt%</th>
<th>BN 2 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>R0.7</td>
<td>R0.8</td>
<td>R1</td>
</tr>
<tr>
<td>Viscosity (mPa·s) at 50s^{-1}</td>
<td>132 ± 12\textsuperscript{a}</td>
<td>76 ± 7\textsuperscript{b}</td>
</tr>
<tr>
<td>Viscosity (mPa·s) at 100s^{-1}</td>
<td>78 ± 1\textsuperscript{A}</td>
<td>52 ± 1\textsuperscript{B}</td>
</tr>
</tbody>
</table>
4 Conclusion

In conclusion, two different types of emulsions, either oil-in-water or water-in-oil, can be produced using two-dimensional materials, i.e. GO and h-BNNS, as stabilizers. The emulsions tend to show good stability at high and intermediate oil/water ratios. Microscopy images showed that the emulsions have a relatively homogeneous droplet size distribution, and the average droplet size can be tuned with particles concentration. Emulsion droplets are smaller at higher particle concentration, at 2 wt% GO and h-BNNS the average particle sizes was found to be 4.7 and 6.2 μm, respectively. The rheological behaviors of both O/W and W/O emulsions were investigated. All the emulsions exhibit yield stress indicating interactions between droplets. GO based-emulsions display smaller droplets size and higher viscosity than h-BNNS based-emulsions. These facts are explained by the stronger π-π interactions between partially broken $sp^2$ carbon network on GO and the aromatic ring in the ethyl benzoate, than the π-π interactions between the $sp^2$ network in h-BNNS with benzene rings of ethyl benzoate. This research paves the way for the fabrication of graphene or h-BNNS based functional materials with novel nanostructures and microstructures using Pickering emulsions as soft-templates. Depending on the potential application, it is possible to tune the emulsion type, W/O or O/W, by choosing the 2D material presenting interesting properties for the applications.
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Scientific contributions

❖ Publications

DOI: [10.1021/acs.langmuir.7b03324](https://doi.org/10.1021/acs.langmuir.7b03324)

Danae Gonzalez-Ortiz, Céline Pochat-Bohatier, Sana Gassara, Julien Cambedouzou, Mikhael Bechelany, Philippe Miele; Development of novel h-BNNS/PVA porous membranes via Pickering emulsion templating. *Green Chemistry*, 2018, 20, 4319 - 4329
DOI: [10.1039/c8gc01983e](https://doi.org/10.1039/c8gc01983e)

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Danae Gonzalez-Ortiz, Céline Pochat-Bohatier, Julien Cambedouzou, Mikhael Bechelany, Philippe Miele; Pickering emulsions stabilized by 2D materials: A comparative study (*submitted*)

Danae Gonzalez-Ortiz, Céline Pochat-Bohatier, Julien Cambedouzou, Mikhael Bechelany, Philippe Miele; Current trends in Pickering emulsions: particle morphology and applications (*submitted*)
Scientific contribution

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Oral communications

1. Danae Gonzalez Ortiz, Céline Pochat-Bohatier, Julien Cambedouzou, Mikhael Bechelany, Philippe Miele; *Inverse Pickering emulsion stabilized by hexagonal boron nitride nanosheets*, 5th Mediterranean Young Researchers Days, October 12-13th 2017, Montpellier, France.

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