New Insights into the Formulation and Polymerization of Pickering Emulsions Stabilized by Natural Organic Particles

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Abstract

Pickering emulsions are known to be an efficient and greener alternative to surfactant-stabilized emulsions. Particles, as key component of these systems, are responsible for their higher kinetic stability and in recent years, the use of natural organic stabilizers has emerged as a solution to promote sustainability. By conferring them stimuli-responsiveness and/or by polymerizing the Pickering emulsion itself, the design of smart and advanced systems can be achieved. Radical polymerization has been by far the most studied polymerization route, and a wide range of materials were successfully synthesized: foams, composites, capsules, or imprinted microspheres. Not only the sustainability of these materials is improved, but their

performances and features are also generally enhanced thanks to the presence of the natural organic stabilizers. This perspective is putting into light groundbreaking efforts in the field of the polymerization of Pickering emulsions, suggesting the range of accessible material which can be obtained through this powerful pathway.

1. Introduction

Emulsions are metastable colloids constituted of at least two immiscible liquids. Contrary to microemulsions, emulsions are thermodynamically unstable and surface-active species are required. Usually surfactants, polymers or particles are incorporated in order to generate an electrostatic or a steric barrier against destabilization that confer the emulsion a kinetic stability. In the case of particles, the system is called "Pickering emulsion" in reference to W. Ramsden and S.U. Pickering who discovered the ability of solid particles to stabilize emulsions in 1904 and 1907 respectively[1,2]. These emulsions regained interest in the early 2000's[3,4] likely because the use of surfactants was questioned regarding environment, health and cost issues. Extensive work on Pickering emulsions has been carried out for the past two decades, mainly with synthetic (organic and inorganic) nanoparticles. Indeed, synthetic particles have the advantage of being well defined both in size and in composition, which is essential to perform fundamental work in view of properly understanding the mechanisms involved in emulsion stabilization. However, the use of this type of particles is limited in term of targeted applications. Indeed, synthetic materials may not be considered cost-efficient for industrial scale-up due to the potential multi-step synthesis required to obtain them. Moreover, most of them lack renewability regarding the used reactants, and the resulting particles are rarely

(bio)degradable. Inorganic particles with natural origin have been investigated as an answer to the previous underlined drawbacks, since they are renewable and allow strongly decreasing the production costs. However, in order to be used as Pickering emulsion stabilizers, the particles are usually processed with nanometric dimensions, therefore questioning their end-life. As they are poorly degradable due to their inorganic nature, they threaten to accumulate in soils, water, organisms giving rise to environmental and health issues[5].

Therefore, increasing interest has been put towards environmentally and health respectful systems combining Pickering emulsions and organic particles issued from renewable resources, which, even if nano-sized, will still have the ability to be degraded, and will thus combine sought-after renewability, cost-efficiency, biocompatibility, and innocuity.

1.1. How do Pickering emulsions work?

If some pristine particles are able to stabilize emulsions this is not always the case, and some need to be modified. Indeed, adsorption at a liquid-liquid interface requires affinity of the particle for both phases. This double wettability can be quantified by the contact angle (θ) of the particle. It is commonly known that particles adsorb at fluid interfaces in a way that can be considered as irreversible owing to the high energy barrier that has to be overcome to be removed from the interface:

$$E = \gamma_{o/w}\pi R^2(1 - |\cos\theta|)^2$$

Where $\gamma_{o/w}$ is the interfacial tension between oil and water, R the particle radius, and θ the contact angle formed by the particle with the oil/water interface taken through the aqueous phase.

Application of this equation for 30°<θ<150° reveals that the desorption energy represents several hundred times the thermal energy $k_B T$ where k_B is the Boltzmann constant. This confers Pickering emulsions a real advantage over those stabilized with surfactants. Indeed, molecules being in a constant equilibrium state between adsorbed and desorbed, emulsions stabilized by surfactants usually require more surface-active material. This is not without significance, since the impacts are several: economical, health and environmental.

Taking advantage of this irreversible adsorption, Pickering emulsions droplet size can be narrowly controlled thanks to the limited coalescence phenomenon[6,7]. In a particle-poor regime, emulsions formulated are poorly covered and undergo coalescence. However, since particles are irreversibly adsorbed, the coverage of the droplets increases with increasing coalescence steps. Once a sufficient coverage is reached, coalescence stops, particles generating a steric stabilization. The obtained final emulsion drop size distribution is quite narrow.

1.2 What type of Pickering Emulsions?

Pickering emulsions can be of different type depending on the particles used to stabilize the system but also on the formulation parameters like the nature and volume ratio of the two phases. Usually the dispersed phase is introduced in a lower amount than the continuous phase to produce a diluted dispersed system. However, the most important parameter remains the preferred wettability of the stabilizing particle for either one of the two phases. The final nature of the emulsion can be predicted by Bancroft and Finkle's laws[8,9], stating that a hydrophilic colloid which is

preferentially wetted by the aqueous phase leads to the formulation of a direct emulsion (oil-in-water, noted O/W) and a hydrophobic colloid preferentially wetted by the organic phase leads to an inverse emulsion (water-in-oil, W/O)[10]. Most Pickering emulsions reported in literature are oil-in-water emulsion due to the hydrophilicity of the major part of the discussed organic particles with natural origin. However, thanks to chemical modification of the particles, water-in-oil emulsions were also stabilized.

More complex emulsions can be obtained by combining both direct and inverse emulsions to formulate what is called multiple emulsions. The simplest of them is the double emulsion, W/O/W or O/W/O. It can be obtained in a one-step emulsification process using only one or several types of particles, however usually a two-step emulsification process is required. A first emulsion is produced and serves as dispersed phase for the second emulsification, using two sets of particles for each emulsification step[11]. The imbrication can be reiterated to obtain multiple emulsions (triple, quadruple…). The literature on this topic is still limited, and the major part of the referenced studies restrains the use of particles to only one of the two interfaces, completing with surfactants. Thus, starch particles were selected to stabilize the outer interface of water-in-oil-in-water double emulsions (W/O/W), but the inner interface was stabilized by a hydrophobic polymer polyglycerol polyricinoleate (PGPR)[12]. Nevertheless, more recently double emulsions stabilized solely by natural organic particles were reported. The use of hydrophilic and hydrophobic nanocellulose enabled the formation of O/W/O[13] and W/O/W[14] emulsions. By combination of nanocellulose with rutin particles, Spyropoulos *et al.* successfully stabilized W/O/W emulsions [15].

Stabilization of water-water or oil-oil interfaces by particles was also investigated. These systems demonstrate a very low interfacial tension between the two phases of similar nature. The ability to produce these atypical emulsions resides in the phase separation of the two aqueous or oil phases in a restricted formulation domain. Water-in-water (W/W) emulsion formulation resides in the mix of two aqueous phases containing incompatible polymers, commonly dextran and polyethyleneglycol. These systems demonstrate an interface thicker than the correlation length of the polymers, therefore molecular scale surfactants which are smaller do not encounter any interface to stabilize[16], this is why they are considered inefficient as emulsifiers. Balakrishnan *et al*. showed that protein particles could be efficiently trapped at the interface[17]. Peddireddy *et al*. enhanced macroscopic stabilization using CNCs as stabilizers and as gelling agents in the continuous phase at the same time[18,19]. Similarly, oil-in-oil (O/O) emulsions are obtained by mixing polar and apolar solvents, leading to phase separation, which could be stabilized by the use of modified cellulose nanofibers for instance[20].

All the previous morphologies open the scope for obtaining innovative and complex materials.

Environmental concerns orientated scientific research towards more eco-friendly systems. Firstly, Pickering emulsions have been targeted as a green alternative to the use of surfactants. However as underlined, synthetic particles and natural ones when inorganic suffer from several weaknesses such as lack of renewability, cost-efficiency, biodegradability, and therefore also innocuity. This is why we chose to focus our present discussion onto Pickering emulsions stabilized only by organic

particles with natural origin and polymerized systems obtained thereof. A special focus will be dedicated to complex engineered systems combining these promising Pickering emulsions with polymerization and/or stimuli-responsiveness. However, one should be aware that the systems which will be presented should not be automatically considered as fully sustainable as it may depend on several parameters: chemical/physical modifications and processes operated on the stabilizing pristine materials and additional chemicals used for the formulation (solvents, monomers, catalysts).

2. Organic particles with natural origin as Pickering emulsion stabilizers

Natural organic particles exhibit important qualities such as renewability, biocompatibility, cost-efficiency, valorization of biomass and industry by-products, and biodegradability. The latter should be considered carefully, as the degradation time scale is very wide and can require specific external conditions. This review proposes to focus on the use of organic particles with natural origin, made from biopolymers (polysaccharides, lignin, proteins), microorganisms or molecular assemblies, which scarcely need processing (Figure 1). As only few particles are able to stabilize emulsions in their pristine form, their modification strategy will be discussed, the idea being to enhance their stabilization efficiency, to enable them to stabilize inverse (W/O) or atypical emulsions (double emulsions, W/W, O/O), or to provide stimuli-responsiveness (Figure 2). The main challenge concerning this category of particles is the homogeneity of the material itself. Indeed, as usually for a natural resource, variability can originate from the various sources of extraction or even from the period of extraction from a unique source.
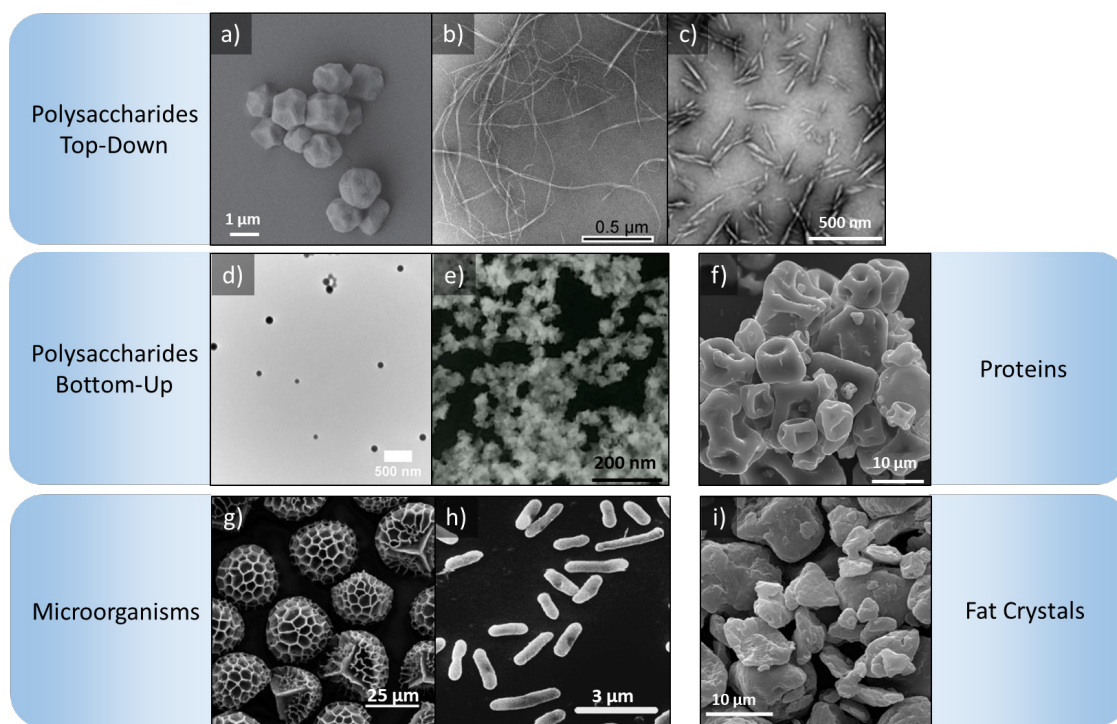
Figure 1: Examples of organic Pickering emulsion stabilizers with natural origin. Various scales and shapes are available, from micrometers to hundreds of nanometers, a) native starch granules (Adapted from[21]), b) wood cellulose nanofibers (Adapted from[13]), c) cotton cellulose nanocrystals (Adapted from[22]), d) dextran nanoparticles (Adapted from[23]), e) chitosan nanoparticles (Adapted from[24]), f) spray-dried soy protein particles, Supro 651 (Adapted from[25]), g) *Lycopodium clavatum* spore particles (Adapted from[26]), h) *Escherichia coli* DH5α bacteria (Adapted from[27]), i) Microklear 418 particles, derived from the natural yellow Carnauba wax (Adapted from[28]).
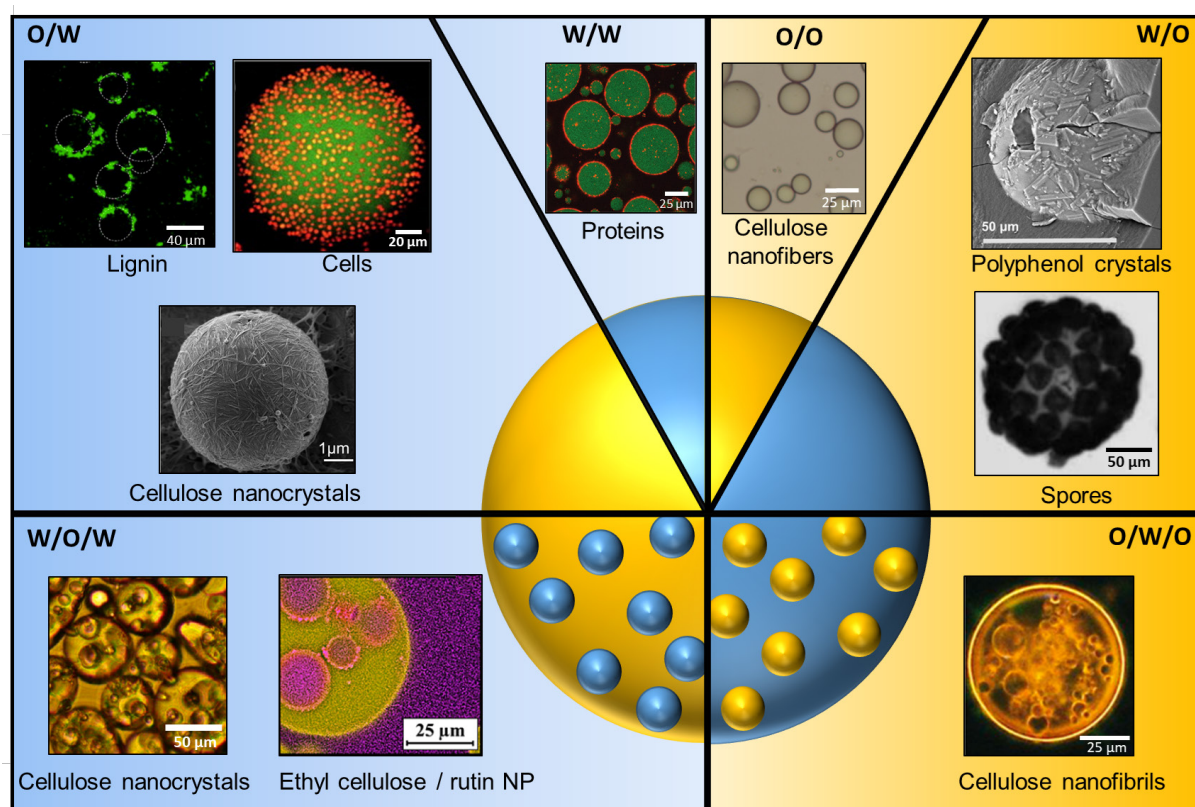
Figure 2: Various Pickering emulsion systems. Simple emulsions: direct (O/W[29–31]), inverse (W/O[32,33]); double emulsions (W/O/W[14,15], O/W/O[13]); peculiar emulsions (W/W[17], O/O[20]) stabilized by organic particles with a natural origin.

2.1. Biopolymers

Biopolymers[34,35] are polymers produced by living organisms. Because of their high biocompatibility they have been widely used for bio-related applications, like biomedical, food, packaging or cosmetic purposes. However, within common applications, these polymers have been employed under their soluble form as thickening agents or polymeric stabilizers and their use as particles enables a widening and complexation of the possible accessible systems. Biopolymers include polysaccharides (cellulose, chitin, starch, dextran), complex polyphenolic lignin, and proteins.

2.1.1. Polysaccharides

Polysaccharide-based particles have gained increasing interest over the past years due to their renewability, low cost, low toxicity, biodegradability, biocompatibility, and modification ease. Polysaccharides are polycarbohydrates in which the carbohydrate units are linked together by glycosidic bonds, produced by living organisms (plants, animals, microorganisms). Some polysaccharides exhibit semi-crystalline structure, alternating ordered crystalline regions with amorphous ones linked together by intra- and inter- hydrogen bonding (cellulose, chitin, starch). This structure enables to isolate micro- and nano- particles from raw natural resources following a top-down strategy. The reverse bottom-up route consisting in assembling linear polysaccharides into particles was also investigated to produce Pickering emulsifiers.

Cellulose is the most abundant biopolymer on earth, and also the most prevalent polysaccharide of the vegetal reign, being present in most vegetal cell walls. After extraction from natural vegetal sources, it can be isolated under different insoluble forms and thereafter used without further modification to stabilize Pickering emulsions. Indeed, by physical destructuration it is possible to isolate microfibrils[36] (CMF), themselves constituted of nanofibrils[37–40] (CNF), and by acid hydrolysis of the amorphous parts of these respective fibers one can obtain microcrystals[41–43] (MCC) and nanocrystals[22,44–46] (CNC), the latter being purely crystalline objects. It has been demonstrated that these objects are highly hydrophilic but present amphiphilic properties thanks to their surface chemistry[31,47]. As their surface present a lot of hydroxyl functions, chemical modification is easy to perform. Covalent modifications like silylation [48], oxidation[49,50] or esterification[51,52] were performed to provide efficient O/W emulsions stabilizers[53,54]. Non-covalent modifications by adsorption of salts[55,56]

or proteins[55,57,58] were also considered. Both modifications contributed in increasing hydrophobicity of the particles and also enabled the stabilization of inverse emulsions[14,59–61].

Another strategy, when working with cellulose as stabilizer, is to generate particles from linear soluble homopolymers (methyl-, ethyl- cellulose), following a bottom-up process. Both hydrophilic and hydrophobic nanoparticles were obtained by nanoprecipitation or complexation and were used as emulsions stabilizers[62–66].

Chitin is a linear polysaccharide present in the shell of crustacean, insects and microorganisms. Because of its semi-crystalline structure, chitin nanofibers[67,68] and nanocrystals can be isolated by acid hydrolysis. Tzoumaki *et al*. showed that it was possible to stabilize direct emulsions using chitin nanocrystals as sole stabilizer[69]. Chitosan can be obtained from deacetylation of chitin, and exhibits amino pending groups conferring an intrinsic pH-sensitivity. It has equivalently been proven to be an efficient Pickering emulsion stabilizer, under the form of core-shell nanoparticles, for instance[64]. Its pupose will be further discussed in the following, among other stimuli-responsive particles.

Starch is the most abundant carbohydrate of the human diet; its composition depends on the grain it is extracted from. Being also a semi-crystalline polymer, starch nanocrystals have been extracted from maize and have demonstrated good ability to stabilize Pickering emulsions[70]. However, in most cases, starch which is isolated under a granule form, is described as a poor Pickering emulsions stabilizer due to its high hydrophilicity. A comparative study conducted by Li *et al*. evidenced that emulsion stability was enhanced when formulated with the smallest starch

granules[71]. Therefore physical modification of native starch was investigated as a mean to reduce the particle size, as well as inducing changes in the chemical structure at the same time[72,73]. Solvent-free media milling was used as a sustainable process to decrease the size of the starch granules[74], simultaneously enabling the formation of a 3D network in the continuous phase of the emulsion[75]. Chemical modifications were also studied to bring double wettability to the particles. Esterification by octenyl succinic anhydride (OSA) has been extensively studied[76–78], but is now limited because of legislative restrictions in the food industry. Other chemical modification pathways were considered to achieve similar changes, performing esterification or complexation with fatty acids[72,73] or citric acid[79]. Abdul Hadi *et al*. showed that emulsion stability was improved with increasing fatty acid chainlength[80]. If O/W emulsions were successfully stabilized, very little literature is dispensed on the stabilization of W/O emulsions[81,82], and their obtaining is mostly due to catastrophic phase inversion of direct emulsion and lack of stability[83]. As a result, double emulsions with starch were only studied with the combined use of surfactant stabilizing the W/O interface[12].

Other linear polysaccharides, as dextran or alginate also showed ability to stabilize direct emulsions under a particulate form following a bottom-up conceptualization[64,84–86]. The peculiarity of these linear polymers is that they can self-assemble into particles with very small average diameters (hundreds of nanometers) with very narrow size distributions. However, contrary to equivalent inorganic particles, their biological nature and biodegradability prevent them from accumulating into water, soils or organisms, hence annihilating their toxicity. Maingret *et al*. showed accurately that the use of pH-sensitive dextran, self-assembled into 200 nm large

particles, was efficient in stabilizing Pickering emulsions[23]. A slight acidic pH change into the continuous phase enabled the destabilization of the emulsions at the scale of a day through the disassembly of the particles, thus delivering the emulsified oil phase without any toxic residues (only dextran, ethanol and acetone).

2.1.2. Lignin

Lignin, a heterogeneous cross-linked polymer present in woody plants cell walls constitutes the second most abundant biopolymer after cellulose. It represents an interesting resource since it is a major by-product of paper industry with important tonnages, but still poorly valorized. Lignin particles can be obtained by jet homogenization[29], or prepicipitation[87] of molecular lignin and show good ability to stabilize Pickering emulsions[88]. Depending on the extraction process, alkaline conditions can be used, resulting in so-called alkali lignin which possesses pH-responsiveness[89]. Following the idea of valorization and recycling of biomass, studies showed that lignin-containing powders were promising. Commercial cocoa powder[90–92] and residual coffee grounds[93] were identified as emulsifiers. Gould *et al*. underlined that the particles containing the highest lignin content were the most efficient as Pickering emulsions stabilizers. Furthermore, hydrothermal treatment of coffee grounds resulted in the migration of lignin content on the particles outer surface enabling the stabilization of inverse W/O emulsions.

2.1.3. Proteins

Because of their biological origin, proteins have been widely used in the emulsion stabilization domain as surface-active macromolecules. However, applying the adapted process in the right pH conditions they can self-assemble into particulate

shape to act as Pickering emulsifiers. Hence, both plant-based (soy[25,94,95], zein[96]) and animal-based (casein[97], whey[98,99], lactoglobulin[100], BSA[101,102]) protein particles were efficiently used to stabilize both O/W and W/O emulsions. Often, proteins are used in synergy with polysaccharides under the form of complexes[103]. However, this type of particles will not be further discussed since their stabilization mechanism is not always clearly stated. Some reviews on this particular subject can be consulted[104,105].

2.2. Miscellaneous particles

Particles obtained from biopolymers can be pointed out as energy-costly, generally requiring several steps from extraction to modification and even processing before being ready to use as stabilizers, limiting their large-scale production. Furthermore, this type of particles can suffer from high polydispersity, and purity of the final material can be questioned (traces of reactants from extraction or modification steps). As a result, several studies focused on the use of mono- or multicellular microorganisms or molecular assemblies of biosourced molecules, which possess the advantage of being easily obtained, with highly controlled dispersity.

2.2.1. Microorganisms

Mono- and multi-cellular organisms were at first investigated to understand emulsification occurring during petroleum fermentation[106–108]. But soon, they emerged as truly monodisperse amphiphilic particles able to adsorb at interfaces[27,30,65,109–111]. Intact spore particles found in up to 500 million year-old sediments showed incredible stability against harsh conditions (temperature,

pressure, pH), and were able to stabilize both direct and inverse emulsions[26,33]. They also occasionally possess complex structures, hard to mimic by synthetic means[112], interesting to obtain naturally anisotropic colloids.

2.2.2. Molecular assemblies of biosourced molecules

Traditional emulsions in food products such as ice cream or margarine naturally demonstrate stabilization by natural particles. Indeed, fat present in the oil continuous phase crystallizes at the droplets interface generating steric hindrance and therefore stability. Fat crystals are particles of interest, as they are easy to prepare and offer facile scale-up possibilities. Inverse emulsion formulation can be performed above the fat melting temperature, and then cooled down to induced *in-situ* crystallization at the droplets interface[113]. Or particles can be formed upstream by maintaining the whole time a temperature below the melting point of the crystals[114,115]. This specific feature was studied by Binks *et al.*[28], who showed that resulting emulsions were intrinsically temperature sensitive. Polyphenols, naturally occurring in fruits, vegetables, leaves, seeds, tea, chocolate or wine only exist under particulate form, due to their poor solubility in both water and oil. Their intrinsic activity against inflammation and oxidation has long raised interest for their use as encapsulated compound. Luo *et al*. showed that they were also able to stabilize O/W emulsions[116]. This stabilization was extended to W/O emulsions by Zembyla *et al.*[32,117] using quercitin and curcumin-derived particles.

2.3. Sensitive particles

Pickering emulsions are highly kinetically stable, but this greatly desirable specificity can become an issue for the release of active compounds or for catalysis purposes. The use of stimuli-responsive particles allows achieving on-demand destabilization of Pickering emulsions, which are appealing systems for the design of innovative applications. Many efforts have been made in this specific field as their appearance in literature started from 0 to reach almost 60 papers/year over the last fifteen years (trend estimated from Scopus). More specifically, particles made of biosourced materials which are recyclable or (bio)degradable are of growing interest and necessity. In the following, the stimuli-responsiveness is exclusively the consequence of the use of stimuli-responsive particles.

The possible stimuli are very diverse: pH, CO_2 concentration, temperature, light, magnetic field, ionic strength, the presence of a specific ion or chemical and even electrochemical stimuli. Although there are less examples than for their inorganic counterparts, organic biosourced materials offer many advantages and can be as efficient in many aspects. Works about such particles responding to one stimulus are summarized in Table 1. They are classified with respect to the brick material used for their design.

Table 1: An overview of the brick bio(based) materials used for the design of stimulus-responsive particles

Brick material	pH/CO_2	Temperature	Light	Magnetic (hybrids)	Chemical presence	Electrochemical
Alginate	118,119		120			
Cellulose/Lignin	89,121–123	124,125		126,127		
Chitin/Chitosan	24,118,119,1			134	135	

	[28–133]		
Cyclodextrin		[120]	[136]
Dextran	[23]		
Fat crystals		[137]	
Peptides/Proteins/Gums	[138–142]	[143]	
Starches	[141,142,144, 145]	[146,147]	
Yeast		[134]	

Among all the brick materials available to design stimuli-responsive particles, some are naturally stimulus-responsive like chitosan which can undergo a reversible sol-gel transition upon pH change[129,130]. However, in most cases a modification step must be performed on the brick material to make the final particle stimulus-responsive.

pH-responsiveness is the most extensively studied stimulus as it is easy to implement. Among these works, two very recent studies can be underlined. Li and coworkers developed starch/zein nanocomposites with a double pH-responsiveness (demulsification occurred at pH 2 or 10) (Figure 3A)[142]. From this, emulsification can be triggered by adjusting the pH to 6. Recently, our group used dextran, a bio-friendly material obtainable from wastes, as a new brick material to design pH-responsive nanoparticles stabilizing Pickering emulsions[23]. Acidic pH induced the total degradation of these nanoparticles, producing only three simple bio-(macro)molecules and the total destabilization of the emulsion.

Moreover, as stimulus-responsiveness is additive, some works focused on the design of multi-responsive particles. In contrast with Table 1, Table 2 summarizes bio-based Pickering emulsion stabilizers which can respond to at least two different decorrelated stimuli.

Table 2 : An overview of the brick bio(based) materials used for the design of multi stimuli-responsive particles

Brick material	pH/CO_2	Temperature	Light	Magnetic (hybrids)	Specific chemical or ion/ionic strength	Ref.
Chitosan	X	X				[148]
Chitosan-coated alginate	X				X	[149]
CNCs	X	X				[150]
CNCs	X	X				[151]
CNCs-Fe_3O_4 composites	X			X		[152]
Cyclodextrin		X	X		X	[153]
Cyclodextrin	X	X				[154]
Protein (zein)	X				X	[96]

Work published by Zeng and co-workers is noteworthy as it consists in the design of triple-responsive core-shell Pickering emulsions stabilizers, obtained from the self-assembly of Poly(4-vinylpyridine)-b-Poly(N-isopropylacrylamide) (P4VP-b-PNIPAM) in solution following by cross-linking of P4VP core (Figure 3B)[153]. To start, natural β-Cyclodextrin (β-CD) was grafted on PNIPAM chains. Then, azobenzene-capped P4VP chains (P4VP-AZO) were introduced. Inclusion interactions between trans-AZO and β-CD moieties led to the self-assembly of nanoparticles which exhibited cross-linked core thanks to the reaction of 4VP units with 1,4-dibromobutane. First, reversible thermo-responsive morphological transition of PNIPAM chains could lead to the destabilization of the Pickering emulsion. Second, light-triggered trans- to cis-transition of AZO groups could lead to the rupture of the inclusion interactions and finally to the disassembly of the stabilizer. Third, the introduction of amantadine

hydrochloride (AMH) could induce the rupture of inclusion interaction between β-CD and trans-AZO as it was a better guest than AZO, also leading to the disassembly of the stabilizer. Therefore, the resulting Pickering emulsion stabilizer properties could be annihilated by temperature, light or competitive guest.
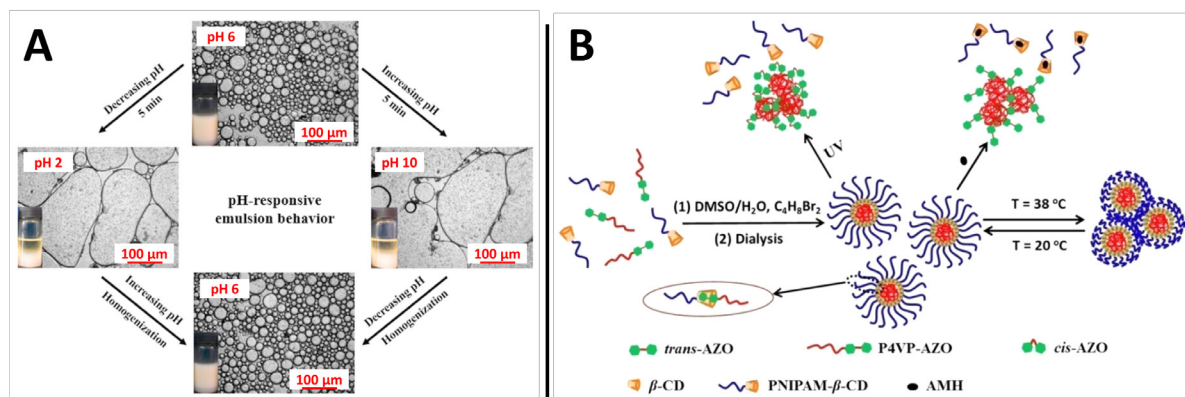
Figure 3: (A) Starch/zein nanocomposites with pH-responsive emulsion behavior, adapted from [142], (B) Design of temperature, light and competitive guest sensitive particles based on cyclo-dextrin, adapted from [153].

Pickering emulsions stabilized by biosourced particles are a great opportunity to associate sustainability and technology. On top of that, adding responsiveness to such nanoparticles is an open path to the design of smart and green materials.

3. Polymerization of Pickering emulsions stabilized with natural organic particles

Historically, Pickering emulsions were discovered at the very beginning of the 20th century and their polymerization started to be studied between the 1930s and the 1950s as stated in the review of Tang *et al.*[155]. However, the lack of characterization

methods at the micro/nano scale was a huge hindrance to their full development. In the last decades, this obstacle was overcome, and polymerization field has tremendously evolved. With the growing need of sustainable and smart micro/nanomaterials, the formulation of Pickering emulsions and consequently their polymerization became again a major topic of interest. Compared to heterogeneous polymerization using traditional surfactants, polymerization of Pickering emulsion allows reducing foam formation, costs and environmental pollution while stability is increased[89,156–158]. Moreover, the presence of surfactants in the final product can be deleterious for performances and their removal is time consuming[159,160] while Pickering emulsion stabilizers can be more efficiently removed/recycled[155] and on the contrary, their presence is sometimes desirable as it can enhance mechanical properties when used in composites for instance[161].

In this aim, many stabilizing materials have been used to formulate and polymerize Pickering emulsions, however, the use of natural-based ones is more in line with sustainability and also more suitable for applications in food, cosmetics or pharmaceutics[162].

Finally, the polymerization of Pickering emulsions stabilized by stimuli-responsive particles may open the door to advanced applications. Indeed, as such emulsions can be destabilized on-demand thanks to a stimulus (or several stimuli), control of the polymerization degree may be achieved as well as easier purification. This kind of system can offer advanced platforms for catalysis as the particles can be recycled[89], or it can be used for the design of functionalized micromaterials[163] which can eventually be degradable[128].

Radical polymerization of one of the two phases represents most of the polymerization examples in Pickering emulsion. Interfacial polycondensation examples can be found but are scarce in the literature, that is why we chose to not discuss them as a distinct section. In the following, the polymerization of Pickering emulsions has been addressed first by considering the polymerization of the dispersed phase and then the polymerization of the continuous phase.

3.1. Polymerization of the dispersed phase – latex synthesis

It is worth reminding that the polymerization of a Pickering emulsion is defined as the polymerization of an emulsion which is stabilized by particles. This includes different processes that can occur such as mini-emulsion polymerization or suspension polymerization, depending on the formulation and polymerization conditions. The reader can refer to several reviews on existing polymerized systems in Pickering emulsion (mainly stabilized by inorganic particles) and polymerization mechanisms involved[164,165].

By polymerizing the inner phase of a Pickering emulsion, it is possible to obtain latexes ranging from nanometers to millimeters. In most cases, the particles remain at the interface of the produced latexes. There is an interest of letting the particles on the surface of the latexes to improve the mechanical properties of their blend for instance[166,167]. Stabilizers may also be removed from the latexes, that are then bare and/or imprinted with a specific print/functionality[163,168]. Then the removed stabilizers may be recycled and used to redo an emulsification step.

Free radical polymerization is by far the most used polymerization technique in Pickering emulsions systems. However, controlled radical polymerization becomes more and more available and opens new pathways to further advanced applications.

In the following, various free and controlled radical polymerization systems implemented in a Pickering emulsion system are presented. More specifically, relationships between system parameters and obtained morphologies/properties are discussed. Finally, some original and practical applications are shown separately. Non-exhaustive list of the works dedicated to the polymerization of the dispersed phase of a Pickering emulsion stabilized by natural-based organic particles can be found in Table 3.

3.1.1. Free radical polymerization

Its ease to implement and the soft required conditions (low sensitivity to oxygen, water compatible) make the free radical polymerization technique very advantageous. However, it results in a poor control over the polymerization degree.

As briefly reminded above, there are some misunderstandings and amalgams about the (free radical) polymerization of Pickering emulsions. More specifically, the latter does not imply the nucleation of oligomers into micelles as in conventional emulsion polymerization because there are no surfactants in the system. Depending on the formulation and polymerization conditions, (micro)suspension or mini-emulsion polymerization can be favored. However, in the presence of available stabilizers or initiators in the continuous phase for instance, some concomitant secondary

nucleation of latexes in the continuous phase can occur. In the literature, some work may use the term "Pickering emulsion polymerization" to describe these phenomena which are rather complex. In order to harmonize the terms used, the term of Pickering heterogeneous polymerization will be preferred.

In the following, impact of formulation and polymerization parameters over the different obtained morphologies are discussed. We decided to organize the works available in the literature in three different sections. Firstly, the influence of the initiator and secondly that of the monomer in an O/W Pickering emulsion system are addressed. Finally, the polymerization of W/O Pickering emulsions is discussed separately as there are very few examples in the literature.

Initiator influence in an O/W Pickering emulsion

First, some original initiator systems may be highlighted because their use implied major changes in the experimental set-up and over the resulting latexes. For instance, photo-initiated polymerization has many advantages over the conventional thermo-polymerization: fast curing speed (from seconds to minutes), easy control and insensitivity to oxygen[128]. One other example is the use of an enzyme-catalyzed polymerization system[169]. In a coniferyl alcohol-in-water Pickering emulsion stabilized by CNCs, the polymerization was initiated by the addition of horseradish peroxidase (HRP) enzyme and H_2O_2 in the continuous phase. This set-up allowed the authors to grow hydrophobic dehydrogenative polymer chains (DHP) *in-situ* onto the CNCs surface.

Now considering conventional redox and mostly thermo-initiators, many studies have shown their influence on the polymerization of Pickering emulsions using organic biosourced stabilizers.

Recently, Cazotti *et al.*[170] highlighted the fact that during the polymerization of a monomer droplet, the hydrophobicity of the phase is being under changes and could interfere in the stabilization properties of the Pickering emulsion stabilizers. Moreover, they observed that Pickering mini-emulsion polymerization (using 2-2'-Azobis(2,4-dimethylvaleronitrile) (Vazo-52) as an oil soluble initiator) allowed them to produce latex particles of polystyrene (PS) in a nearly one-to-one copy regarding the size of the initial monomer droplets. Using a water soluble initiator could also be considered as the probability of nucleation inside the droplets becomes much higher when their size is decreasing (total amount of surface is increasing)[164]. However, Errezma *et al*. explained that scale-up of such Pickering mini-emulsion polymerization systems is difficult as it would require high amounts of energy and sometimes additional surfactants[160].

In their recent study, Glasing *et al.*[171] evaluated the influence of various oil-soluble initiators: Azobisisobutyronitrile (AIBN), Lauroyl peroxide (LPO) and Vazo-52 on the particle morphologies they could obtain. To do so, they formulated Pickering emulsions of styrene stabilized by CNCs. As LPO was the most hydrophobic used initiator, it greatly reduced the initiator diffusion outside the dispersed phase and so the possible initiations in the water medium. Thus, no secondary nuclei were formed, and the size distribution of the particles obtained was the same as the one of the emulsion droplets, which was not the case with the two other initiators. Our group also demonstrated that the initiator choice has a huge impact on the free radical polymerization of the common hydrophobic monomer styrene in a CNCs-stabilized

Pickering emulsion system[51]. Indeed, depending on the activation temperature and gas production from the decomposition of the initiator, various morphologies/sizes could be obtained. Specifically, micro-latexes, but also nano-latexes were systematically produced when using a gas-producing initiator (AIBN, 2,2'-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70)) although they possess different activation temperatures (70°C and 35°C respectively) and even after removal of all free CNCs that could have resulted in a secondary nucleation in the continuous phase). However, when using LPO, no gas was produced during decomposition and only micro-latexes were obtained. Morphological observations of the latexes led to the conclusion that nano-latexes were obtained from the extrusion of the micro-latexes during polymerization. This was because of the expelling of gas bubbles from the microbeads surface resulting from the incomplete coverage of the styrene droplets by the CNCs. Experiments where the coverage was improved thanks to the presence of NaCl led only to microbeads.

The use of an aqueous initiator can change the polymerization process from a (micro)suspension to a "Pickering heterogeneous emulsion polymerization" as showed by Ben Ayed and coworkers[172]. In their work, they used starch nanocrystals functionalized with vinyltriethoxysilane to stabilize Pickering emulsions of butylmethacrylate (BMA) in presence of citric acid. The polymerization was triggered by addition of H_2O_2 in the continuous phase. The authors explain that during the polymerization, the droplets containing the monomer acted like pools to feed newly nucleated oligomers initiated in the continuous phase. The progressive depletion of the monomer droplets made nanoparticles available and able to stabilize the growing nucleates.

This effect was also observed by Haaj *et al.*[166,167]. They additionally found out that the presence of charges onto the growing polymer chains could dramatically impact the final size of the particles. Indeed, using the redox initiator H_2O_2/ascorbic acid system instead of potassium persulfate (KPS) led to a decrease of the polymerized particle diameter by a factor of two.

The choice of the initiator is of great importance, as well as its location. Errezma *et al*. showed that it was possible to initiate the polymerization of BMA from aldehyde-functionalized CNCs produced by periodate oxidation[160]. This alternative concomitant *in-situ* initiation from the surface of the CNCs improved their attachment onto the surface of the latexes.

Monomer influence in an O/W Pickering emulsion

Monomer with a partial solubility in the continuous phase

Free radical polymerization of a wide range of common hydrophobic monomers (styrene, acrylates) have been well studied[161,173]. Although they are called hydrophobic, they still possess a partial solubility in the continuous phase, which has a critical impact on the obtained morphologies. Indeed, Jiménez *et al.*[159] showed that the partial solubility of the monomer in the aqueous continuous phase is the key parameter to tune the size distribution of the latexes (balance between nano/micro latexes). Pickering emulsions of three monomers were formulated and then polymerized. Coexisting micro and nano-sized droplets of styrene were obtained, producing micro and nano-sized latexes after polymerization. Lauryl methacrylate (LMA) emulsion droplets were micro-sized and so the resultant latexes. Finally, isoButylAcrylate (isoBuA) emulsion droplets were micro-sized but when polymerized

micro and nano-sized latexes were obtained. The latter is the consequence of the aqueous partial solubility of the used initiator (AIBN) and of this specific monomer which led to secondary nucleation in the continuous phase.

In the work of Pei et al. [174], the authors studied the influence of pH and starch nanoparticle (SNP) concentration onto the morphologies of the PS latexes obtained through Pickering heterogeneous polymerization. For instance, they showed that bare or raspberry-like particles are produced depending on the SNP content. For low concentration, monomer droplets were partially covered by SNPs and the styrene could rapidly diffuse into the aqueous phase to nucleate a large number of PS particle and to propagate polymerization. There were not enough nanoparticles to stabilize and adsorb onto the growing polymer particles leading to bare PS latexes. With the increase in the content of SNPs, the leakage of monomer droplets was suppressed resulting in less secondary nuclei which grew slowly, giving time so that SNPs adsorb onto the grown PS particles leading to the formation of raspberry-like PS particles.

The influence of the monomer solubility into the continuous phase is a driving force for the size of the obtained latexes (micro/nano) but there is also a synergetic effect with the initiator decomposition and solubility as well.

Friendly Monomer

As the need for greener materials is increasing dramatically, the use of biosourced and/or degradable materials is urgently needed. In this respect, some works using environmentally friendly monomers are worth noticing. For instance, Kanomata *et al.*[169] used the polymerization of coniferyl alcohol from lignin to tune up the

hydrophobicity of the surface of CNCs in a biomimetic fashion. In another work, Liu *et al.*[128] produced degradable particles of trimethylolpropane tris(3-mercaptopropionate) (TMPTA) and trimethylolpropane triacrylate (trithiol) by photopolymerization. They observed that trithiol could act as a particle cross-linker. In addition, they obtained the same distribution for the latex particles as the Pickering emulsion droplets. The polymer latexes were quite degradable (71-82%) under alkaline conditions (1.0 M NaOH) at 37°C after 7 days.

Free radical polymerization of a W/O Pickering emulsion

The scarce literature about the polymerization of W/O Pickering emulsions using natural organic particle emulsifiers may come from two challenges. The first one may be the almost inevitable modification of these originally hydrophilic materials to stabilize W/O Pickering emulsions and the second the restricted library of available hydrophilic monomers. However, their development is a great opportunity to design biocompatible hydrophilic materials.

Zhai *et al.* used butyl glycidyl ether and palmitate groups to modify SNPs so that they could stabilize a W/O Pickering emulsion of acrylamide and acrylic acid (monomers) and N,N'-Methylenebisacrylamide (MBA, cross-linker)[175]. The polymerization of this Pickering emulsion, initiated with ammonium persulfate (APS), produced millimeter-sized hydrogel beads of cross-linked Poly(acrylamide-co-acrylic acid). A huge difference between the size of the original Pickering emulsion droplets (around 50 μm) and of the produced hydrogel beads was observed and could come from adsorption of monomers from other droplets and progressive swelling during polymerization, according to the authors. The swelling of the hydrogel beads was directly related to the presence of acrylic acid units. Increasing or decreasing the pH

of the medium led to the swelling or shrinking of the beads respectively. The pH-responsiveness of this system was demonstrated to be relevant for drug-delivery-like applications. In a former work, the same group also used modified SNPs (with acetic and phthalic anhydrides) to stabilize a W/O Pickering emulsion of NIPAM, MBA and APS[82]. That time the polymerization of the Pickering emulsion allowed them to obtain raspberry-like thermo-responsive microgels of PNIPAM surrounded by SNPs.

Instead of SNPs, Zhang *et al.*[176] used cinnamate modified CNCs as W/O Pickering emulsion stabilizers for the polymerization of NIPAM using almost the same conditions (MBA as cross-linker, APS as initiator). However, in this case the authors used the insolubility of the cross-linked PNIPAM in water to obtain hollow capsules (cross-linked PNIPAM migrated at the W/O interface). The capsules were then thermo-sensitive and could be inflated or deflated when adding or removing ethanol and water respectively.

3.1.2. Living radical polymerization

Living radical polymerization (LRP) allows controlling very precisely the degree of polymerization. Consequently, morphologies of polymerized objects can be better monitored and tuned. Indeed, control of the loci of initiation and growth can be achieved, leading to only a (micro)suspension polymerization mechanism. Thus, the resulting latexes should have the same size distribution as the Pickering emulsion droplets.

To obtain these highly desirable results, it is mostly needed to work in a controlled atmosphere because these techniques are more sensitive to the presence of oxygen. This can be partially solved using alternative formulation and/or adapted LRP systems.

In the following, RAFT polymerization and ATRP implementations in Pickering emulsion systems (stabilized with organic natural-based particles) will be discussed.

RAFT polymerization

Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization involves the use of a Chain Transfer Agent (CTA) which provides the control over polymer chain growth. While many RAFT polymerizations in heterogeneous media investigated the use of inorganic Pickering emulsion stabilizers, few of them focused on the use of natural organic ones[177] and all of them exhibit a different use of the CTA as shown on Figure 4.
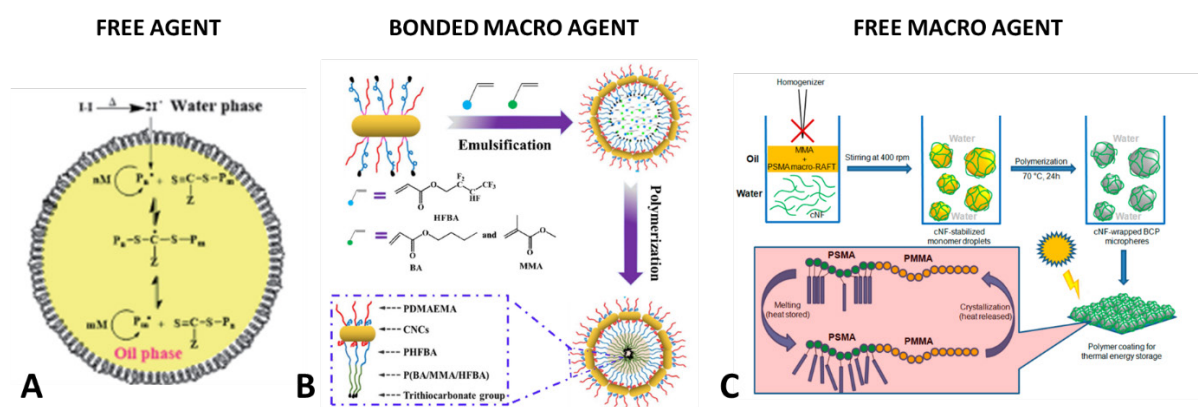
Figure 4: Various strategies using RAFT polymerization with a (A) free CTA, adapted from[178], (B) bonded macro-CTA, adapted from[179] or (C) a free macro-CTA, adapted from[180].

The CTA can be introduced in the dispersed phase like in the work of Bai and coworkers[178] who performed the polymerization of MMA into an O/W Pickering emulsion, initiated by KPS (Figure 4A). They used modified CNCs with random hydrophobic copolymers to stabilize the Pickering emulsion. CNCs particles could be ultimately recovered by centrifugation of the obtained latexes and then recycled.

Another strategy presented by Zhou *et al.*[179] consisted in linking covalently a Poly(2,2,3,4,4,4-hexafluorobutyl acrylate) (PHFBA) trithiocarbonate macro-CTA to CNCs as Pickering emulsion stabilizers[179,181,182] (Figure 4B). In this case, the CNCs remained strongly attached to the surface of the produced latexes as the chains grew from the covalently linked macro-CTA. Consequently, the CNCs remained well dispersed and thus provided additional mechanical strength to the latexes without losing optical transparency. Finally, Chakrabarty and co-workers produced block copolymers nanocomposites surrounded by CNFs[180]. To do so, RAFT polymerization of MMA using a macro-CTA, the Poly(stearyl methacrylate)-CTA (PSMA-CTA), was performed (Figure 4C). The resulting material is a phase change material which possesses abilities to absorb and restore energy. Those interesting materials and their production *via* the polymerization of Pickering emulsions are discussed further in the original applications section.

ATRP

In the same decade as RAFT polymerization, Atom Transfer Radical Polymerization (ATRP) started to be developed. ATRP leads to typical first-order kinetics as it is designed to minimize the termination events and to promote an equal propagation of polymeric chains. However, the presence of radical scavengers (like oxygen) is deleterious and takes away the kinetics from its first order. Thus, the control over the polymerization degree and end-chain functionality may be lowered. To overcome this challenge, the addition of a reducing agent (AGET-ATRP) and/or the degassing of the polymerization medium may be considered (but it can limit the potential scale-up of these systems[183]). ATRP implementation into dispersed systems such as

Pickering emulsions is an innovative way to design materials with well-controlled architectures.

SET-LRP

Moreno and Sipponen developed a Pickering emulsion single electron transfer living radical polymerization (SET-LRP) system which could be used under air condition without deleterious effects[183]. To do so, they designed Pickering emulsion stabilizers made of successively adsorbed chitosan and Glucose Oxidase (GOx) onto lignin nanoparticles. The ability of GOx to produce H_2O_2 from O_2 and of lignin/chitosan to produce H_2O from H_2O_2 worked in a synergic way (Figure 5A). Thus, the system allowed the controlled radical polymerization of styrene, butyl methacrylate and of methyl acrylate in an open vessel without degassing nor using a reducing agent. Kinetics perfectly fitted first order without induction period. Strikingly, the control over the polymerization kinetics was slightly better compared to traditional degassing with N_2 mainly because of residual O_2 contamination in the latter case. The absorption of GOx allowed working at higher temperatures (80°C vs 50°C), without losing enzyme activity, compared to the case where GOx was free in the polymerization medium. This system allowed the authors to obtain a high chain-end fidelity, which is a requirement to design more complex architectures such as block or multi-block copolymers. Consequently, they successfully performed a chain extension with a nearly perfect chain-end functionality. Finally, the obtained latexes had the same size as the Pickering emulsion droplets and could be purified to recover bare latexes of PS, PBMA, PMA or blended to produce composites.

This innovative Pickering emulsion SET-LRP system is a relevant example of the use of natural organic stabilizers to design sustainable and advanced materials with controlled properties.

AGET-ATRP

Werner *et al.*[14] worked on the synthesis of hybrid polymer materials made by AGET-ATRP of O/W Pickering emulsions stabilized by modified CNCs. As a reducing agent, ascorbic acid was introduced in the polymerization medium. This controlled polymerization was performed from the surface of the stabilizers (Pickering Emulsion Interface Initiated – PEII). Depending on the reactivity of the studied monomers (styrene and n-Butyl acrylate), different morphologies could be obtained: capsules and beads respectively (Figure 5B).

PET-ATRP

Photoinduced electron transfer ATRP (PET-ATRP) was performed in a CNCs-stabilized Pickering emulsion by Wang *et al.* (Figure 5C)[184]. Using Eosin Y as a photocatalyst and visible light, polymethyl methacrylate (PMMA) with well-controlled molecular weight could be obtained. Thus, during the polymerization a typical first-order kinetics was observed. This photoinduced technique is advantageous because of its ease of initiation (visible light) and most of all because it does not use transition metal catalysts and consequently is suitable for the precise design of biomaterials. However, limitations of the use of light in dispersed systems (multi refraction, diffusion, penetration depth) were not discussed. Finally, by solubilizing the produced latexes, the stabilizing CNCs could be recovered and reused for the next

emulsification step. Recycling of the stabilizers without compromising the latex morphology is addressed in the following original application section.
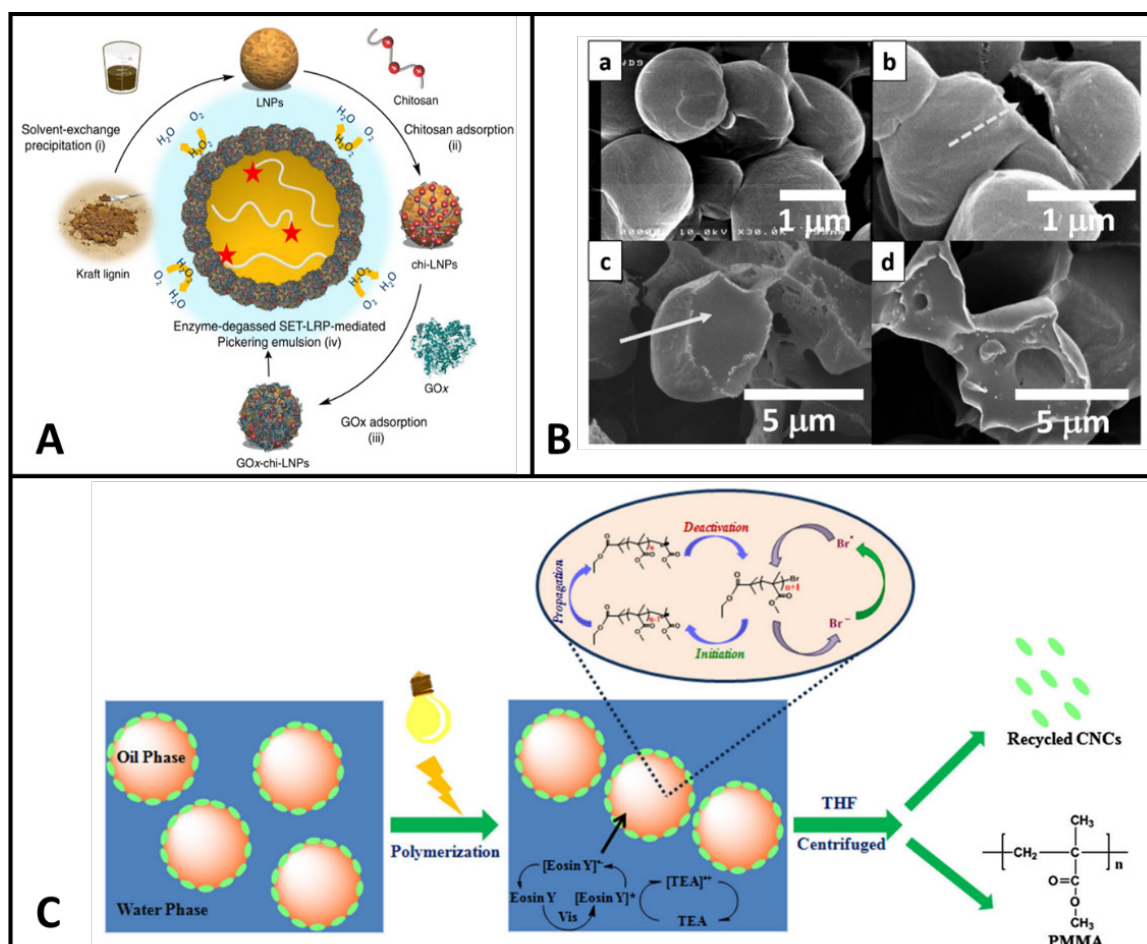
Figure 5: (A) Implementation of SET-LRP in a Pickering emulsion system without degassing, adapted from[183]. (B) PS capsules (top SEM pictures) and PBuA plain beads (bottom SEM pictures) obtained through AGET-ATRP in a CNCs-stabilized Pickering emulsion system, adapted from[14]. (C) PET-ATRP approach to obtain well defined and controlled PMMA chains and recycled CNCs, adapted from[184].

3.1.3. Original applications of polymerized Pickering emulsion systems

The polymerization of Pickering emulsions (using organic natural-based stabilizers) is a powerful tool to design materials for targeted applications in a large range of fields including environment, energy, drug-delivery, catalysis or coatings. Using particles

instead of surfactants allows generally preserving the material properties. Moreover, the use of natural-based organic Pickering emulsions stabilizers is sometimes the only way to achieve the targeted structures. In this section, some original applications from the polymerization of Pickering emulsions using such stabilizers are discussed.

Imprinted materials

The polymerization of Pickering emulsions can be used as a tool to produce imprinted objects. Recognition of ions, proteins, bacteria for life sciences, analytical studies and catalysis are in the scope of the applications. To be efficient, such objects require high selectivity and their design is sometimes only achievable by the polymerization of Pickering emulsions. Of course, some imprinted materials can be obtained from emulsion templates using surfactants. However, the alternative use of Pickering emulsions has many advantages that have already been discussed.

Molecular Imprinted Polymers (MIP) are highly selective tools for the adsorption of ions or molecules which are generally hazardous, for their quantification and/or removal. The general procedure consists in the formation of a link between the targeted ion/molecule and a monomer. After polymerization and removal of the template, the formed cavity is the complement to the template, that is to say a recognition site[185]. The alternative use of natural organic stabilizers such as chitosan and lignin for the formulation of Pickering emulsion templates instead of inorganic particles and furthermore instead of surfactants shows again highly desirable advantages: higher sustainability with lower cost and toxicity[185–187]. Moreover, as shown before, the obtained polymerized microspheres are less prone to be contaminated by surfactants, which may hinder their efficiency. As an original

example of polymerization of Pickering emulsions, Pan *et al*. published the polymerization of the oil intermediate phase of a double Pickering W/O/W emulsion with tunable porosity which allowed them to reuse several times their molecularly imprinted microspheres[188].

Pickering emulsions have also been successfully used to develop bacterial imprinted polymerized beads whereas the conventional procedure could not be achieved for the recognition of large objects (Figure 6A)[168]. Herein, an *E. coli*/acryloyl chitosan complex was used both as a stabilizer and as a template for the selective recognition of bacteria (Figure 6B). Carbohydrates have a high affinity with bacteria, which makes them suitable candidates for the formation of a complex able to stabilize Pickering emulsions. Furthermore, a vinyl group was added onto the carbohydrates to improve the free radical polymerization of the (presumed since it was not specified) MMA monomer and ethylene glycol dimethacrylate (EGDMA) cross-linker in the emulsion droplet. High specificity was achieved despite the large size of the template.
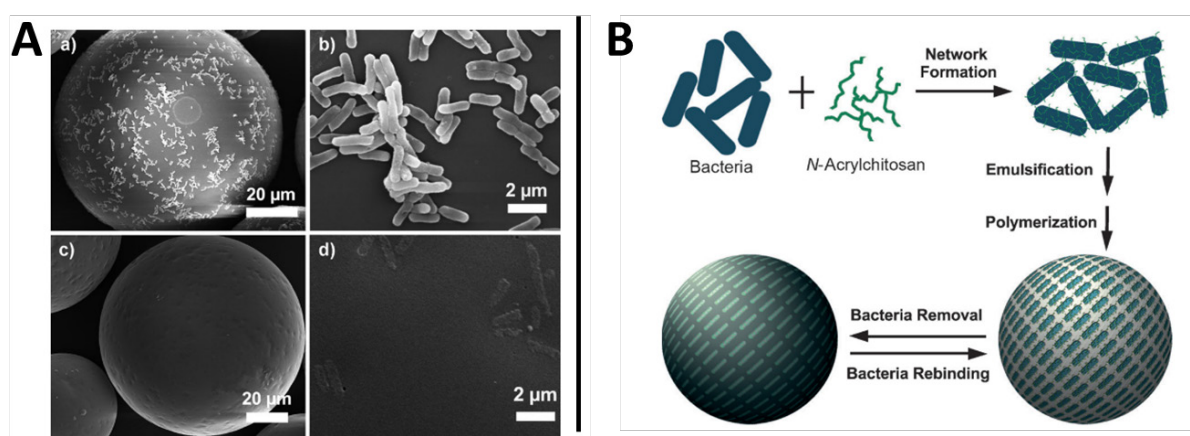

Figure 6: (A) SEM pictures of bacteria attached on the surface of the latexes after polymerization (top pictures) and of the resulting cavities after their removal (down pictures). (B) Principle of bacterial imprinting using Pickering emulsion template. Adapted from[168].

The same strategy was used by Zhao *et al*. for the sensitive and visual detection of *Listeria Monocytogenes* which are foodborne pathogens[189]. The authors used the same stabilizing system complexed with CdTe quantum dots. This system was able to stabilize an O/W Pickering emulsion composed of trimethylolpropane trimethacrylate (TMPTA) and divinyl benzene (DVB) as cross-linkers and BPO as initiator. After polymerization, the bacteria were removed to form the recognition cavities, which were endowed of embedded quantum dots. Because of the fluorescence quenching in presence of the target bacteria, visual fluorescence detection was possible.

Polymerization of Pickering emulsions stabilized by naturally occurring organic materials is then an innovative and sustainable way to produce objects for highly demanding technologies such as the recognition of key targets at the ion[187], molecular[185,186,188] and microorganism[168,189] scales.

Phase change materials

Phase change materials (PCMs) are efficient tools to absorb, store and release thermal energy for construction, biomedicine or textile applications[190]. Their use alone can be limited because of their inherent flammability and tendency to leak. Encapsulation into capsules from polymerized emulsions allows overcoming these issues but is generally done using costly surfactants with poor sustainability[190,191]. In this respect, the polymerization of a Pickering emulsion stabilized with natural and organic stabilizers offers a greener and cheaper alternative.

The work of Chakrabarty and coworkers presented above (see RAFT polymerization section) is a powerful example of those PCMs to store thermal energy[180]. The PSMA block introduced *via* the CTA could store energy when it melted and release it when crystallizing. The storage capacity could be tuned by varying the PSMA/PMMA ratio. This process is ultrasound-free, requiring only magnetic agitation and thus making it easily scalable. Similar results were obtained using this just described system and with a conventional sodium dodecyl sulfate-based one, meaning that the latter can be reasonably replaced to promote sustainability without compromising morphologies. Moreover, the efficiency in terms of crystallization and glass transition temperature were even improved due to the presence of the CNF as Pickering emulsion stabilizers. This illustrates the benefits of Pickering emulsions and more specifically the choice of appropriate natural organic stabilizers.

Another noticeable example is given by the production of antibacterial phase change microcapsules from lignin-stabilized Pickering emulsions by Xiang *et al*. (Figure 7A)[190]. The authors encapsulated n-eicosane constituting the core of a Poly(urethane) (PU) core-shell particle using interfacial polycondensation. Silver ions were reduced on the surface of the stabilizing lignin particles embedded in the PU shell. The silver decorated microcapsules possessed therefore antibacterial properties. In this study, lignin particles were chosen for two purposes: they stabilized the Pickering emulsion and they reduced silver ions on their surface. Also using lignin as Pickering emulsion stabilizer, Wang *et al*. took benefit from the interfacial deposition of polymerized PMMA to micro-encapsulate 1-tetradecanol[191]. Fatty alcohols are a green alternative to traditional phase change materials and their encapsulation allows alleviating the inherent issues of their use such as flammability or leakage. Another green alternative is the use of coconut oil as a phase change

material. Zhang *et al*. encapsulated it in a CNCs-stabilized styrene Pickering emulsion (Figure 7B)[192]. After polymerization, they found out that the heat capacity and stability of these microcapsules surrounded by a CNC shell were excellent. Moreover, using paraffin wax they were able to determine that these performances were increased when the amount of CNCs was larger.
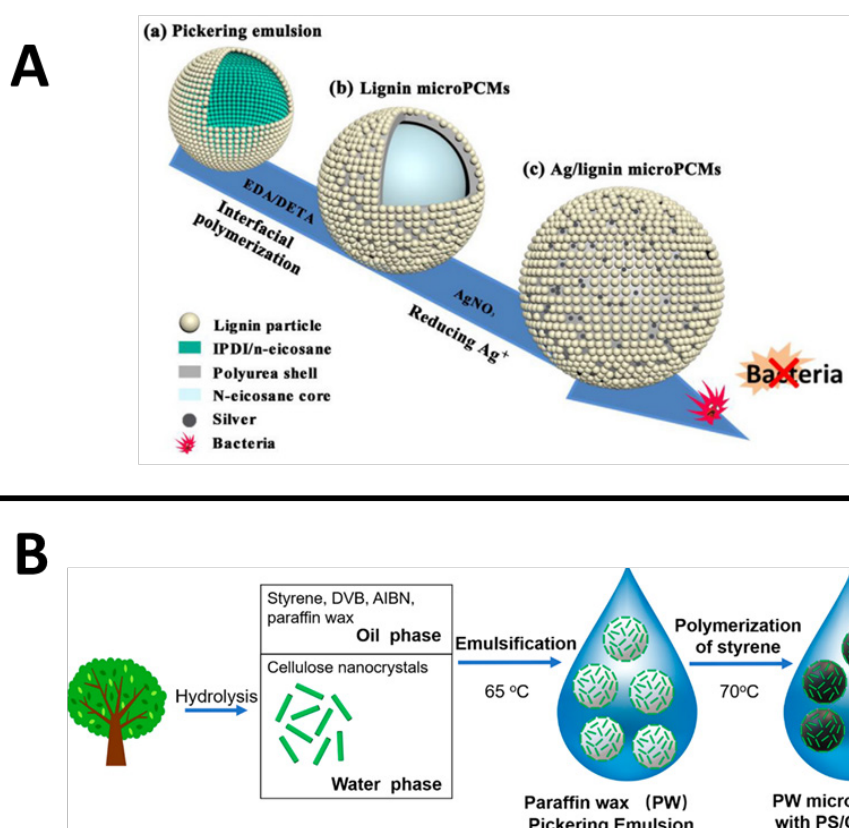
Figure 7: (A) Design of phase change material loaded into PU microcapsules based on lignin-stabilized Pickering emulsion, adapted from [190].(B) Paraffin wax loaded into Pickering emulsion templated PS microcapsules, adapted from [192].

Such developments of phase change material objects perfectly illustrate the advantage of the use of naturally occurring organic material for the stabilization and polymerization of Pickering emulsions compared to conventional ways which are more costly, time consuming and environmentally deleterious. Moreover, the

production of such advanced materials may only be achievable, or just easier, using a Pickering emulsion.

Polymer microbeads and hollow microcapsules

Emulsions are often used as a template to design capsules mostly for the protection, the storage and the controlled release of active compounds. To do so, microbeads or hollow capsules loaded with an active are of interest. Specifically, polymer hollow microcapsules possess unique structures, which find applications in various areas such as micro-reactors, drug carriers, coatings or cosmetics. The use of an emulsion template is already a simplified procedure compared to the hard template conventional technique. However, the removal of resulting surfactants, as in other applications, remain a problem because of its difficulty and cost. Natural-based organic particles to stabilize Pickering emulsion offer a sustainable alternative, which is eventually a requirement especially in food, cosmetics or pharmaceutical domains.

Encapsulation of an insect repellent using Pickering emulsion templated capsules was described by Kadam and coworkers[20]. First, they formulated a modified CNF-stabilized Pickering emulsion containing the active. Then, through interfacial polycondensation, they were able to obtain capsules with a PU shell (Figure 8A). Release experiments and mathematical analysis with models (Ritger-Peppas) put forward the supplementary role of the modified CNFs (mCNFs). Indeed, their presence in the shell of the capsules lowered their permeability, leading to a more prolonged release of the active (release rate constant divided by a factor 3) while the achieved encapsulation efficiency was about 92-98%. However, Liu *et al.* observed no difference concerning the release of ibuprofen (model drug) between

microspheres coated with chitosan particles and bare microspheres, both obtained *via* Pickering emulsion photo-polymerization[128]. Tunability of the release was only achieved by playing around with temperature and pH (impact solubility of the drug).

Hollow microcapsules can be obtained from microbeads. Indeed, Nypelö *et al*.[126] used CNC-CoFe$_2$O$_4$ hybrid stabilizer for the formulation and polymerization of an O/W Pickering emulsion. The so-obtained PS microbeads were shown to be efficient for the removal of pollutants in water. Furthermore, the dissolution of their polymer core was performed with toluene to obtain hollow microcapsules ("sacrificial core" technique). The magnetic response of the Pickering emulsion stabilizers (embedded in the microbeads or shell of the hollow microcapsules) was advantageously used for the easy separation of substances immobilized from substrates. With the same sacrificial core strategy Noguchi *et al*.[193,194] designed PS hollow particles from a chitosan-fibers stabilized Pickering emulsion. Toluene allowed solubilizing the core of the particles. The authors introduced pyrene dye by both covalent and physical methods into the hollow particles as a proof of concept for encapsulation purposes. A different and interesting technique to obtain hollow microcapsules was proposed by Zhang *et al*.[176]. They started by formulating an O/W Pickering emulsion stabilized by modified-CNCs. The oil phase contained toluene, styrene, DVB and AIBN. During polymerization, the non-solvent interactions between newly formed cross-linked PS and toluene induced migration of the first one at the oil/water interface, thus forming the hollow structure (Figure 8B). The same strategy was used to produce pH-responsive hydrophobic hollow microcapsules of P4VP (using toluene) and hydrophilic thermo-responsive hollow microcapsules of PNIPAM using water as non-solvent. The ease of modification of the CNCs was beneficial for the formulation of

the W/O Pickering emulsion. Stimuli-responsiveness of the capsules came from the polymer but may also be introduced thanks to the stabilizing particles as described earlier for Pickering emulsion systems.
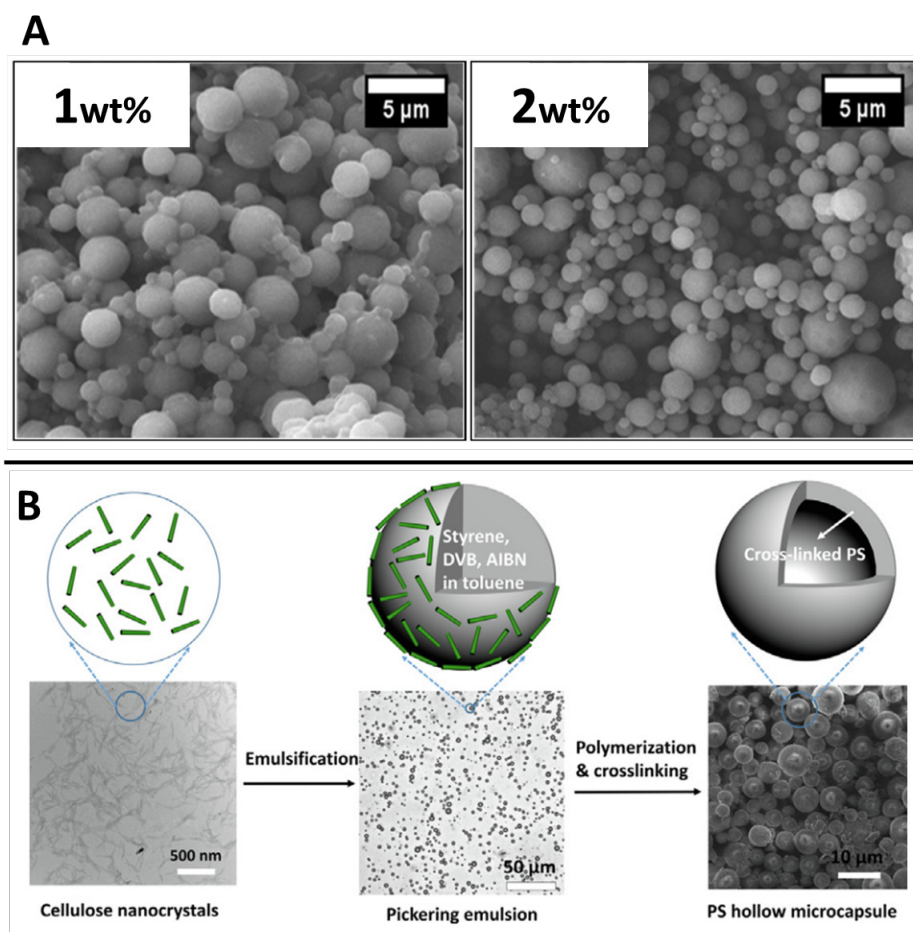
Figure 8: (A) SEM images of PU microcapsules containing an insect repellent from mCNF-stabilized Pickering emulsion templates at 1wt% and 2%wt of mCNFs, adapted from [20]. (B) Hollow microcapsules general formation procedure involving phase separation between the cross-linked polymer and the inner solvent, adapted from [176].

Finally, Li prepared ionic liquid loaded PU microcapsules, showing the wide range of possible applications for (hollow) microcapsules from polymerized Pickering emulsion templates[195].

Composites

Composites are a combination of at least two different entities which aim at enhancing the properties of the final material compared to the initial ones. As an example, the introduction of strengthening agents into neat polymer matrices aims at producing composites with better mechanical resistance when casted into films/coatings while staying transparent. CNCs are of great interest as strengthening agents because of their intrinsic mechanical properties. On top of that, CNCs but also other particles like starch provide a green alternative to conventional loads. However, due to their inherent hydrophilicity, such particles cannot be well dispersed in hydrophobic polymer matrices (using the so-called *ex-situ* method). Consequently, the performances of the resulting composite in terms of mechanical resistance for instance, but also optical transparency, are much lower[160,196]. A way to overcome this issue and improve the material properties is the polymerization of Pickering emulsions stabilized by the agent (natural organic particles conferring targeted properties)[159,172–174,179,182,197,198]. This so-called *in-situ* method is followed by the melting and casting of the produced latexes. Again, Pickering emulsions offer advantages compared to surfactants: no decrease of the mechanical or water resistance properties and lower toxicity[166,167]. Moreover, the particles herein act as stabilizers and loads ensuring their own good dispersion.

Thus, Werner *et al.* showed that mechanical performances can be improved because of the good packing of CNCs on the initial drops surface and consequently of the CNCs good dispersion in the final film[161]. In addition, smaller monomer droplets (due to more CNCs) led to a better final dispersion state of the CNCs and an improvement of the mechanical properties. Other films with improved mechanical and/or thermal properties and preserved transparency have been produced based on the *in-situ*

method[166,167,197]. In their work, Haaj *et al*. produced nanocomposites of starch nanocrystals and PBMA *via* the *in-situ* method. A typical raspberry-like morphology of these latexes was obtained (Figure 9A). The relative storage modulus of the resulting composite was 100 to 250 times larger than the one of the neat polymer matrix. With the *ex-situ* method, this increase was only characterized by a factor 34 to 50[167].

Enhancement of the mechanical properties is not the only possible achievement when aiming at producing composites. Indeed, additional features can be implemented as shown in the work of Moreno *et al*. [183]. SET-LRP was employed in a Pickering emulsion stabilized by adsorbed chitosan and GOx onto lignin nanoparticles. As explained earlier (see SET-LRP part), the association of chitosan and lignin allowed avoiding radical scavengers' deleterious effects. The obtained latexes exhibited a uniform dispersion of the nanoparticles on their surface and could be blended to elaborate composites not only with antioxidant but also with UV-protective properties because of the used natural-based organic stabilizers. Once again, their inherent properties helped to improve the performances of the composite.
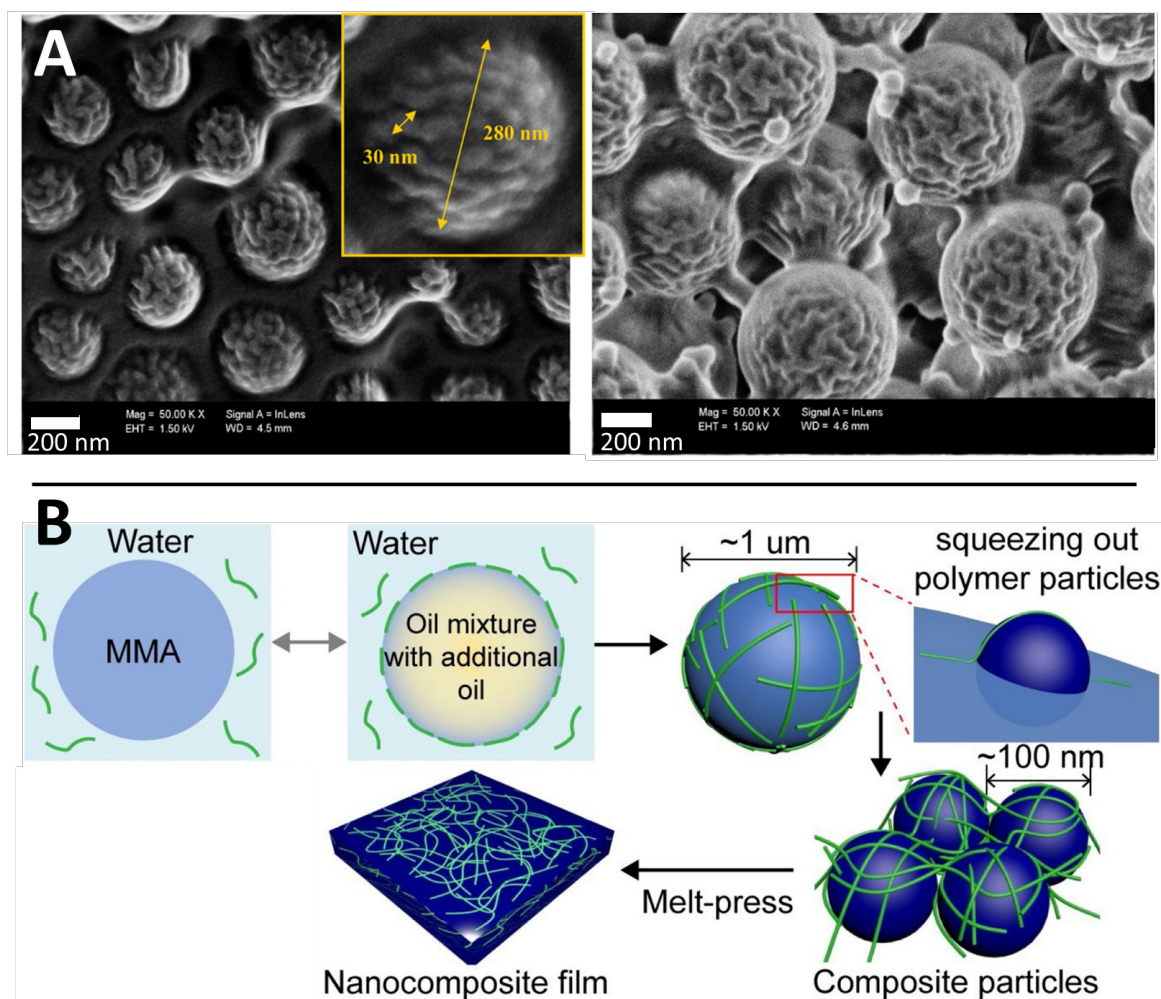
Figure 9: (A) FE-SEM micrographs of the raspberry-like morphology of PBMA/Starch nanocrystals composites prepared via the free radical polymerization of Pickering emulsion, adapted from[167]. (B) Fabrication of PMMA-CNFs nanocomposites using an additional oil in a Pickering emulsion system, adapted from [199].

A smart strategy to obtain nanocomposite films from CNFs-stabilized Pickering emulsions was described by Kim *et al*. (Figure 9B)[199]. As CNFs were not able to stabilize Pickering emulsion of sole MMA due to the too low surface tension, they used an additional oil to increase it. As a result, Pickering emulsions could be obtained and during the polymerization process, polymer particles were squeezed out from the monomer droplet and precipitated in the water medium. Finally, they could be purified, and nanocomposite films were obtained using the melt-press

process. The authors also observed that the higher the CNFs content, the better the optical, mechanical and thermal properties. This additional oil strategy could be applied to produce other nanocomposites from Pickering emulsion templates. Even if being quite new and not widespread, the use of natural organic stabilizers and of such alternative strategies led to an enhancement of the properties of the resulting materials while being sustainable.

The main issue of the *ex-situ* method is the hydrophilicity of the strengthening agents. To overcome it, Kanomata and coworkers described a biomimetic modification route of CNCs to make them hydrophobic[169]. To do so, they took advantage of the enzyme-catalyzed polymerization of coniferyl alcohol into a Pickering emulsion stabilized by CNCs. The so-hydrophobized CNCs could be then separated and used as strengthening agents in different polymer matrices as they could be dispersed. Thus, *ex-situ* method seems to be more versatile compared to the *in-situ* method. However, dispersion states and performances were not compared to *in-situ* analogues.

Stimuli-responsive particles for a sustainable production or functionalization of latexes

As described before, in the Sensitive Particles section, stimuli-responsive Pickering emulsion stabilizers are of high interest for the elaboration of sustainable and smart systems. Among all, two different strategies are presented hereafter: recycling of the Pickering emulsion stabilizers after polymerization and functionalization of the latexes using stimuli-responsiveness.

Recycling of the Pickering emulsion stabilizers

As a noticeable example, Wei *et al.*[89] worked on pH-responsive alkaline lignin nanoparticles to operate recyclable polymerization of Pickering emulsions of styrene using AIBN (Figure 10A). The stabilizing lignin nanoparticles dissolved in basic conditions and re-assembled in acidic conditions. Thus, after the polymerization step, a basic treatment of the dispersed system allowed recovering separately, after centrifugation, bare PS microspheres and solubilized lignin chains. The latter medium could then be acidified to re-obtain nanoparticles able to again stabilize an O/W Pickering emulsion of styrene and AIBN for another polymerization cycle. With the same aim, Liu *et al.*[128] worked on the sustainable fabrication of degradable microspheres *via* the thiol-ene photopolymerization of an O/W Pickering emulsion of trithiol and TMPTA monomers (Figure 10B). The authors employed pH-responsive chitosan nanoparticles to stabilize the Pickering emulsion droplets. After polymerization, microspheres surrounded by chitosan nanoparticles were obtained. Acid hydrolysis of the medium allowed recovering separately bare microspheres of Poly(trithiol-co-TMPTA) and a solution of water-soluble protonated chitosan. The latter could be basified so that chitosan chains re-assembled into nanoparticles, which were re-used for other emulsification and polymerization steps. However, the authors saw that the mean diameter of the chitosan-coated microspheres increased with the cycling numbers. We suggest that this evolution is due to the high dependency of the droplets size towards the amount of stabilizing material (relative to the volume of the dispersed phase) illustrated by the limited coalescence phenomenon of Pickering emulsions[6,7]. Thus, recycling should imply to have a precise method to measure the amount of recovered material. Then, adding a complementary amount of stabilizers to balance the possible loss of material during

the recovering step would ensure robustness of the recycling process. Because of numerous ester linkages in the microspheres introduced by trithiol and TMPTA, the resulting microspheres were degradable in alkaline condition.
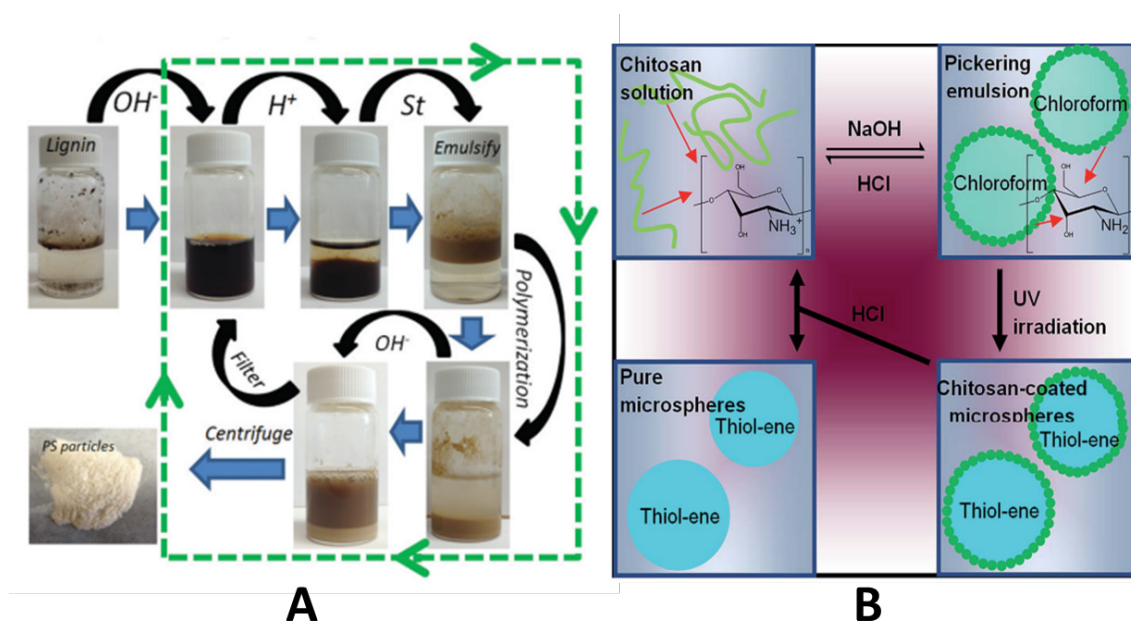
Figure 10: Two strategies involving the recycling of the Pickering emulsion stabilizers using (A) lignin particles, adapted from [89] and (B) chitosan particles, adapted from [128].

Functionalization of latexes

An interesting strategy to obtain amino surface functionalized microspheres is presented by Du *et al.*[163]. They formulated a Pickering emulsion of styrene stabilized by pH-sensitive CNCs. To obtain these, they modified CNCs thanks to a hydrazone reaction (creation of a C=N bond) followed by an amidation reaction. It resulted in the production of 18-C alkyl chain-grafted CNCs linked by a C=N bond which can be cleaved in acidic pH. Thus, after polymerization of styrene in the Pickering emulsion droplets, acidic hydrolysis of the C=N bond led to the separation of CNCs from the microspheres. The latter kept alkyl chains embedded and presented amino moieties

at their surface. The CNCs could be recovered separately and re-used. This strategy of cleavable bond to functionalize particles is interesting as it can be easily transferable to other polymer systems.

It is also worth noting that the use of stimuli-responsive particles can bring additional functionality to all the applications described above. We believe that the combination of advanced smart systems and sustainability is not only possible but also highly desirable and advantageous.

To conclude, Table 3 aims at providing the readers an overview of the studies about the polymerization of the dispersed phase of a Pickering emulsion stabilized by natural organic particles. Brick material(s), monomer(s), polymerization type and aim along with complete reference date are gathered.

Table 3. Studies concerning the polymerization of the dispersed phase of a Pickering emulsion stabilized by natural organic material-based particles

Pickering emulsion stabilizers brick material(s)	Emulsion type	Monomer(s)	Polymerization type	Aim	Team, year	Ref
CNCs	O/W	St, LMA, isoBuA, MMA, BMA	FRP (AIBN / ACPA)	Nanocomposites	Jiménez et al. 2019	159
CNCs	O/W	Coniferyl alcohol	Enzymatic dehydrogenative polymerization	CNC surface modification with DHPs (lignin)	Kanomata et al. 2020	169
CNCs	O/W	St	FRP (AIBN, Vazo-52, LPO)	Microbeads / mechanistic approach	Glasing et al. 2020	171
CNCs	O/W	St / DVB	FRP (AIBN)	PS latexes with amino groups	Du et al. 2017	163

CNCs	O/W	St	FRP (AIBN)	nanolatexes	Che et al. 2020	[200]
CNCs	O/W	St	FRP (AIBN)	Microencapsulation Phase Change Materials	Zhang et al. 2019	[192]
CNCs	O/W	St	FRP	Hollow microcapsules	Zhang et al. 2019	[176]
CNCs	O/W	BMA	FRP (KPS, CNC-SO_3°)	Nanocomposites films	Errezma et al. 2018	[160]
CNCs	O/W	St, tBuA	AGET-ATRP	Capsules, beads	Werner et al. 2019	[14]
CNCs	O/W	St, tBuA, nBuMA, MMA, MA, Vac	FRP	Nano/micrometer beads	Werner et al. 2018	[161]
CNCs	O/W	St	FRP (AIBN, V-70, LPO)	Nano/microlatexes	Werner et al. 2017	[51]
CNCs	O/W	MMA	RAFT (free CTA) (KPS)	Beads + Recycling stabilizing particles	Bai et al. 2018	[178]
CNCs	O/W	HFBA, BA, MMA, HFBA	RAFT (free CTA)	Armored latexes / latex film	Li, H., Zhou, J. et al. 2020	[179]
CNCs	O/W	MMA	PET-ATRP	Polymer chains	Wang et al. 2019	[184]
CNCs	O/W	HFBA, BA, MMA	RAFT (bonded CTA) AIBA / AIBN	Core-shell armored latexes	Zhou et al. 2019	[182]
methyl cellulose coated CNCs	O/W	MMA	FRP (BPO)	Nanocomposites latexes	Kedzior et al. 2017	[173]
CNCs-CoFe₂O₄	O/W	St	FRP (ADVN)	Microbead hollow capsules	Nypelö et al. 2014	[126]
CNFs	O/W	MMA	RAFT (PSMA macro-RAFT) AIBA	Block copolymer microspheres for thermal energy storage	Chakrabarty et al. 2020	[180]
CNFs	O/W	St	FRP (AIBN)	Beads / composites (hot pressing)	Jiang et al. 2019	[197]

CNFs	O/W	MMA	FRP (KPS)	Composites for films	Kim et al. 2020	[199]
CNFs	O/O	U	Interfacial Polycondensation	Microcapsules	Kadam et al. 2019	[20]
CHITOSAN	O/W	EGDMA	FRP (AIBN)	Molecular imprinted microspheres	Jalilian et al. 2020	[187]
CHITOSAN	O/W	MMA, EGDMA	FRP (AIBN)	Magnetic imprinted polymer	Ou et al. 2015	[185]
CHNFs	O/W	St	FRP (KPS)	Composites / hollow spheres	Noguchi et al. 2019	[193]
CHNFs	O/W	St, MMA	FRP (KPS)	Composites / hollow spheres / dye encapsulation	Noguchi et al. 2020	[194]
CHITOSAN	O/W	Trithiol / TMPTA	FRP Photopolym.	Microspheres encapsulation IBU	Liu et al. 2014	[128]
CHITOSAN/BACTERIA	O/W	MMA/EGDMA	FRP (AIBN)	Bacterial imprinting at Pickering emulsion interfaces	Shen et al. 2014	[168]
CHITOSAN/BACTERIA/QDS	O/W	TRIM/DVB DMA	FRP (BPO)	Bacterial imprinting at Pickering emulsion interfaces	Zhao et al. 2019	[189]
LIGNIN/CHITOSAN	O/W	BMA	SET-LRP	Composites for coatings	Moreno et al. 2020	[183]
LIGNIN	W/O/W	MMA, St	FRP (AIBN)	Molecular imprinted microsphere	Pan et al. 2015	[188]
LIGNIN	O/W	St	FRP (AIBN)	PS Latexes	Wei et al. 2012	[89]
LIGNIN	O/W	EGDMA	FRP (AIBME)	Molecular imprinted microsphere	Gan et al. 2014	[186]
LIGNIN	O/W	U	Interfacial polycondensation	Microcapsules Phase Change materials	Li, X. et al. 2020	[190]
LIGNIN	O/W	U	Interfacial polycondensation	Beads, lubricants	Li, H., Chen, S. et al. 2020	[195]

LIGNIN	O/W	MMA	FRP (AIBN)	Phase Change materials (encapsulation)	Wang et al. 2020	[191]
STARCH	O/W	St	FRP (APS)	Bare / raspberry particles	Pei et al. 2016	[174]
STARCH	W/O	AM, AA	FRP (APS)	Hydrogel beads	Zhai et al. 2020	[158]
STARCH	W/O	NIPAM	FRP (APS)	Thermo-responsive nanocomposites	Zhai et al. 2019	[82]
STARCH	O/W	MMA	FRP (KPS)	Nanocomposites films	Haaj et al. 2014	[167]
STARCH	O/W	St, MMA, BMA	FRP (Persulfate) FRP (Vazo-52)	Latexes	Cazotti et al. 2020	[170]
STARCH NANOCRYSTALS	W/O/W	St	FRP (BPO)	Expanded polystyrene beads containing water droplets	Ajelou et al. 2019	[201]
STARCH NANOCRYSTALS	O/W	BMA, BMA, EHA	FRP (citric acid / H_2O_2)	Pressure-sensitive adhesives composites	Ben Ayed et al. 2020	[172]

3.2. Polymerization of the outer phase – porous solids synthesis

Pickering emulsions have also been used as polymerization templates to obtain low density materials (Figure 11). In this specific case, the polymerization system is located in the outer continuous phase. Emulsions can either be direct O/W or inverse W/O depending on the monomer nature, to produce respectively hydrophilic or hydrophobic scaffolds (Table 4). However, the use of natural organic particles stays scarce, and most related studies were conducted recently, with more than 20 papers being published over the last decade, showing the growing interest in focusing on

greener alternatives. Among the particles, papers mainly reference the use of polysaccharides (cellulose[14,202–211], starch[201,212,213], chitosan[134]), lignin[214,215], proteins[216–219] and microorganisms[134,220,221] (Table 4).
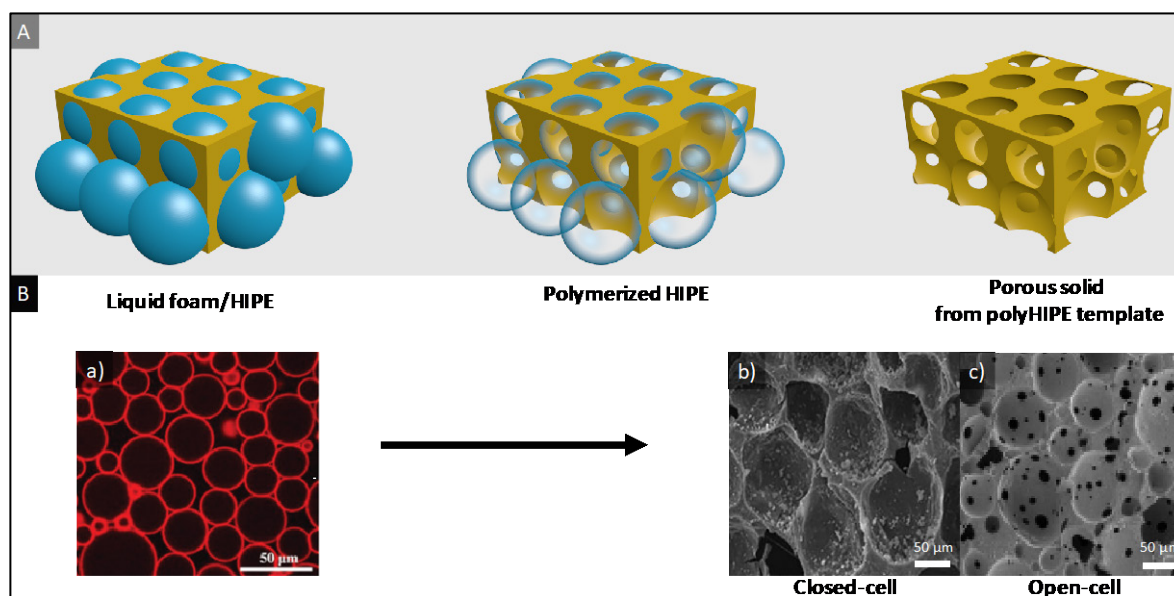
Figure 11: Foam obtained from polymerized Pickering emulsion. (A) general formulation concept scheme; (B) result a) before and b-c) after polymerization, with different porosity morphologies (adapted from Tan et al.[217], Lu et al.[220] and Gong et al.[216]).

One popular route to obtain low-density materials is the recourse to medium and high internal phase emulsions (MIPE and HIPE respectively)[222–224], which are emulsions containing at least 30%vol and 64%vol of dispersed phase respectively. Solidification of the continuous phase to form a porous solid can be achieved with the advantage of keeping the initial emulsion characteristics, provided that the emulsion remains stable during polymerization. At 64%vol of dispersed phase, all droplets are in contact, and above this random close packing fraction, they start to deform. Hence, after solidification of the continuous phase, MIPEs usually lead to so-called closed-

cell morphology (unless the drops are in contact and adhesive), when HIPEs favor the formation of interconnected open-cell solids. The porosity nature is an important feature when it comes to porous materials as it governs the final range of accessible applications, bio-related for open-cell and insulation for closed-cell for instance. Even if most of porous materials obtained from Pickering emulsion templates are termed closed-cell, various achieved systems exhibited an open porosity[222]. Also, additional porosity can be induced by incorporating porogens (usually toluene, chlorobenzene, 2-chloroethylbenzene or 1-chloro-3-phenyl-propane). Similar results can be obtained through the use of particle-stabilized foams, which are similar to HIPE, except that the dispersed phase is constituted of air (A/W)[209,220,224].

Polymerization of these systems (polyMIPE, polyHIPE, polymerized foams), presents the advantage of conferring a solid continuous network to the system, compared to simple freeze-drying generally leading to brittle materials with poor mechanical properties. It should be noted that in the case of polyMIPE and polyHIPE, an additional step consisting in the removal of the dispersed phase is required. Free radical polymerization[205–208] is the most frequently studied polymerization route, followed by polycondensation[209,214,215] and controlled radical polymerization[14]. Indeed, the field of Pickering polyHIPE being recent, studies still focus on the deep understanding of the phenomena involved to control the properties of the resulting porous solids. Apart from stability concerns, the choice of natural organic stabilizers was initially justified by the production of an overall sustainable material along with biosourced monomers[206,208] (Acrylated epoxidized soybean oil), or by the will to ensure high biocompatibility[212]. However, several works succeeded in taking further advantage of the presence of the particles in the resulting material.

3.2.1. Improvement of the mechanical properties

One major objective was the improvement of the mechanical properties of the solid material. Similarly to composites, the presence of particles with high intrinsic mechanical properties (namely cellulose nanoparticles) within the polymer showed to improve the Young modulus of the polyHIPE[207,210,217]. However, Lee *et al.*[225] specified that this synergy was only possible provided a good compatibility between the particle and the matrix, this hypothesis was later confirmed by Dupont *et al.*[205]. As a result, covalent linkage was considered by Werner *et al.* initiating the ATRP from the stabilizing particles surface[14], and by Lu *et al.* by covalently linking stabilizing CNCs to the polymer matrix by Michael addition[208]. Unfortunately, in both previous works, no study of the impact of this compatibilization over the mechanical properties was considered. However, this strategy can be encouraged by Liu *et al.* 's observation. Indeed by inducing additional gelation of the continuous phase by the presence of the stabilizing CNC, it was possible to increase the compression modulus with increasing particle content[204].

3.2.2. Enhancement of specific applicative performances

A large focus is often devoted to mechanical properties, but specific properties can be enhanced thanks to the nanoparticles presence, to increase the final material performance towards its targeted application. Hence, Lu *et al.* succeeded in synthesizing porous solids for metal ion adsorption, and observed that yeast particles used to stabilize the initial emulsion were complexing with the targeted ions, improving the absorption efficiency of their material[134,220]. Adsorption of targeted protein was also enhanced by Sun *et al.* who chose to use the imprinted polymers

strategy[218,219]. The targeted protein served as well as stabilizing particle for polyHIPE obtaining, and as sacrificial material, which was ultimately removed to leave specific imprints and thus binding sites, similarly to the previously described imprinted polymers. The resulting adsorption was enhanced and highly specific. Using a different system, which consists in polymerized inverse emulsion shaped into beads, Nikfarjam *et al*. found that particles present within the walls of their polymerized beads were useful. Indeed, their strategy to produce sustainable expanded polystyrene beads consisted in stabilizing water droplets within polystyrene beads, using whether cellulose or starch-based particles. They were then able to expanse their polystyrene beads into polystyrene foams by heating them above the glass-transition temperature of polystyrene, inducing water evaporation which was responsible for the polymer deformation. During this expansion step they found that the presence of the particles at the water/polystyrene interface prevented the cell wall collapse and reduced water diffusion by barrier effect[201,203,211,213].

Table 4: polyHIPE synthesized from Pickering emulsion template with natural organic stabilizers and their main characteristics, AESO: Acrylated epoxidized soybean oil.

	Particle and modification	Monomer(s)	Type	Aim/application	Porosity, nature	Ref
POLYSACCHARIDE	Stearoylated MCC	St/DVB	W/O	Proof of concept	89% Open/closed	202
	Dialdehyde MCC NP	Melamine/formaldehyde	O/W	Proof of concept	80% Open/closed	209
	Hydrophobized Bacterial cellulose nanofibrils	AESO	W/O	Renewable nanocomposite polymer foams	70% -	206
	Acetylated Bacterial cellulose	AESO/DVB/1,6-hexanediol diacrylate	W/O	Proof of concept Bio-based solid foam	70-90% Closed	207
	Bacterial cellulose	AESO	A/W	Proof of concept	60%	225

					Open	
	CNC-UPy	Gelatin methacrylate/MBA	O/W	Tissue engineering	80% Open	[204]
	CNC-Br	St (ATRP)	W/O	Proof of concept	60% Open	[14]
	CNC-Br	St/DVB	W/O	Theoretical study	79-84% Open	[205]
	CNC *in-situ* modification with APTS	AESO	W/O	Bio-based material	50% Open/Closed	[208]
	CNC + Methyl cellulose	Acrylamide/MBA	A/W	Proof of concept	82% Open	[210]
	Citric acid cross-linked starch NP	Acrylamide/MBA	O/W	Cell culture	63% Open	[212]
	CNF, CNC, Starch NP, Starch nanocrystals	St	W/O	Expanded polystyrene foam	- Closed	[201,203,211,213]
LIGNIN	Lignin	Melamine formaldehyde	O/W	Adsorption of ions	75-90% Open	[214]
	Lignin	Urea-formaldehyde	O/W	Adsorption of phenolic compounds	80% Open/Closed	[215]
PROTEIN	Soy-bean protein isolate	Acrylic acid/MBA, Acrylamide/MBA	O/W	Adsorption of heavy metals	75% Open	[216]
	Gelatin NP	Acrylamide	O/W	Cell culture	80% Open	[217]
	Denatured Casein NP	Dopamine Interfacial polymerization	O/W	Recognition of protein (BHb) Molecular imprinted polymer	50% Open	[218]
	Bovine hemoglobine (BHb) colloid NP	Dopamine	O/W	Recognition of protein (BHb) Molecular imprinted polymer	75% Open	[219]
MICRO-ORGANISM	Yeast NP	Acrylic acid/MBA	O/W	Absorption study	75% Open	[220]
	Yeast-Fe_3O_4 NP with *in-situ* adsorbed chitosan	Acrylamide/MBA	O/W	Adsorption study Rb^+ Sr^+ (radioactive)	50% Closed	[134]
	Pine pollen + sepiolite (mineral)	Acrylamide	A/W	Adsorption of antibiotics	- Open	[221]

Future prospects concerning the formulation of porous solids from emulsion templates with particular organic natural stabilizers are wide open. Indeed, as a recent field of research, only few works have been conducted, with a scope narrowed to understanding studies or "ready-to-use" technologies, in comparison to more complex objects obtained from the polymerization of the dispersed phase. It could also be considered working with sensitive particles, or sensitive polymers to create responsive materials to external stimuli. Little work has dealt with responsive particles, and their intrinsic properties only helped during the formulation step and did not add any feature to the final material[134,212]. Other polymerization routes than free radical polymerization could be investigated, following the work of Werner *et al.* and Lu *et al.* on the improvement of the mechanical properties for instance. Broad horizon is thus open to investigation since the mechanisms start to be more precisely understood, leaving space to innovation and experimentation toward the obtaining of advanced materials.

Conclusion

Although Pickering emulsions have been discovered more than a century ago it remains a field of active research due to their outstanding kinetic stability. One of the major challenges working with these systems remains the end-life of the nanoparticles. In order to address this issue and comply with societal and industrial considerations, the use of natural organic particles should be encouraged. Stimuli-responsiveness can be further added to the particles to induce on-demand destabilization of the related Pickering emulsions. The possibilities to propose innovative materials from Pickering emulsion templates widen even more when adding polymerization steps. Free radical polymerization is by far the most studied polymerization route because of its ease to implement. More recently, controlled radical polymerization (ATRP, RAFT) has gained interest and applicability, making it possible to access better controlled morphologies and consequently even more advanced materials. Furthermore, as it has been shown in this review, introducing natural organic particles does not only provide sustainability to the resulting materials but can also enhance their final performances. Hence, the combination of colloidal and polymer sciences along with sustainable consideration enables the production of new engineered objects with various applications. Among them one can find catalysis supports, encapsulation, composites, chemical detection, energy storage or even tissue engineering. In our opinion, future materials on the model of the examples given in this review, will likely be created and proposed for everyday applications in the future keeping in mind the evolution towards less energy consumption, better biomass valorization, higher biocompatibility and reduction of waste and by-products.

Notes

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New insights into the formulation and polymerization of Pickering emulsions stabilized by natural organic particles

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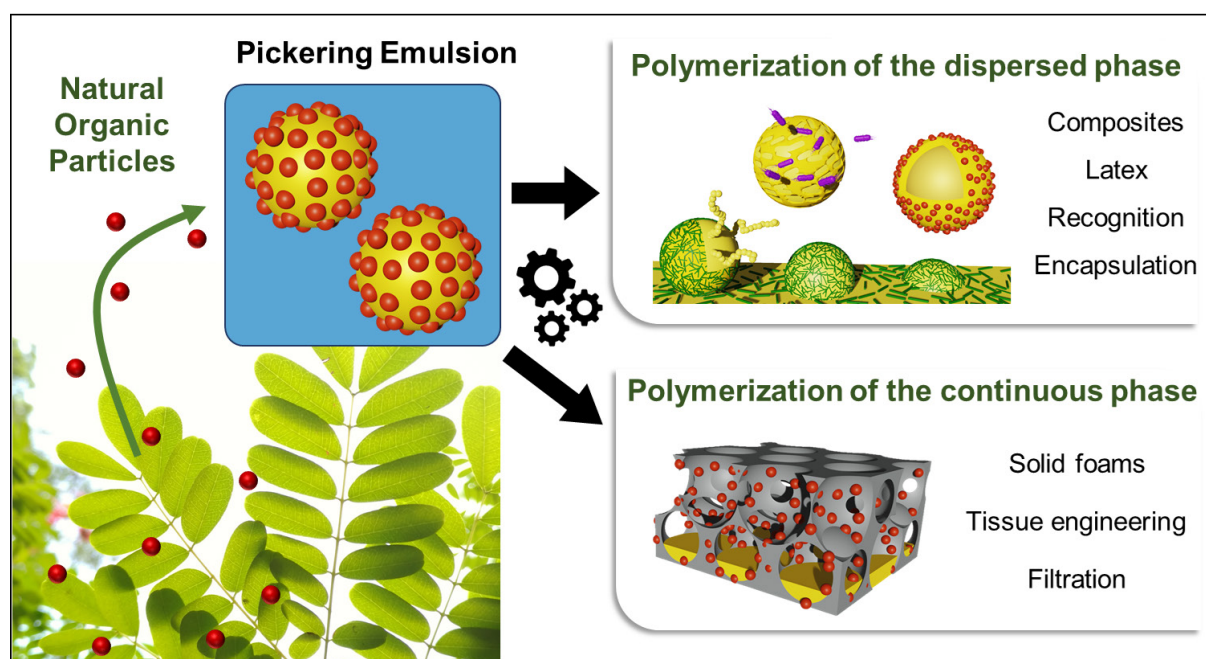
Hanaé Dupont received her engineering degree from Chimie ParisTech – PSL and her MSc in Chemistry and Material Science from the Sorbonne University in 2018. She is currently pursuing her PhD at both the Laboratoire de Chimie des Polymères Organiques (LCPO) and the Centre de Recherche Paul Pascal (CRPP) in Bordeaux under the supervision of Dr. V. Héroguez and Dr. V. Schmitt. Her research focuses on the stabilization and polymerization of Pickering emulsions using cellulose nanocrystals, the formation of materials like solid foams, latexes and double-emulsion templated encapsulation vessels.

Valentin Maingret received his chemical engineering degree from Chimie ParisTech - PSL University and his MSc in chemistry from the Sorbonne University in 2018. He started his PhD research the same year between the Centre de Recherche Paul Pascal and the Laboratoire de Chimie des Polymères Organiques under the supervision of Dr. Véronique Schmitt and Dr. Valérie Héroguez. His work involves the development of bio-friendly and stimuli-responsive Pickering emulsions stabilized by self-assembled modified polysaccharides.

Véronique Schmitt is a senior researcher. After a Ph-D in Strasbourg devoted to wormlike micelles, she moved to Lund in Sweden for a post-doctoral position before getting hired at CNRS in Nancy with a permanent position. Since 1998, she is working at Centre de Recherche Paul Pascal in Bordeaux, France. Her research focuses on the elaboration and characterization of dispersed model systems like suspensions, emulsions and foams in view of addressing the link between structure and properties. She has a special interest on emulsions and foams stabilized by particles referred to as Pickering emulsions and foams.

Dr Valérie Héroguez received her engineering degree from Polytechnic Institute of Bordeaux in 1986 and obtained her PhD in Polymer Chemistry from the University of Bordeaux 1 in 1989. She was recruited by the CNRS in 1989 and joined the Laboratoire de Chimie des Polymères Organiques (LCPO) as Associated Scientist. She became Senior Scientist in 2005. Her main contributions are in the field of macromolecular engineering. Her research area includes the ROMP of cyclo-olefins and macromonomers and the synthesis of advanced functional nanoparticles (by macro-, micro-, miniemulsion, suspension, dispersion) for applications in aeronautic, nanotechnology… Her current research concerns the development of new stimuli-responsive Pickering emulsions for the design of smart materials. She is the authors of more than 100 publications, as listed on the HAL database.