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ABSTRACT

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

Pickering emulsions or solid-stabilized emulsions were defined at the beginning of the 20th century in pioneering works of Ramsden[1] and Pickering.[2] They are described as colloidal suspensions stabilized by solid nanoparticles instead of organic surfactants, which localize at the interface between two phases. As classical emulsions, they can be simply categorized based on the particle wettability: on the one hand, emulsions formed with hydrophilic particle normally stabilize Oil-in-Water (O/W) emulsions, or "direct" emulsions; on the other hand, those prepared with hydrophobic particles more probably form Water-in-Oil (W/O) emulsions. Sometimes W/O emulsions are also referred as "invert" or "reverse" emulsions. Unusual cases such as water-in-water emulsions, or double-emulsions, can also exist.[3-4] Pickering emulsions have outstanding properties controlled by both formulation and process parameters, such as the kind of nanoparticles, the control of emulsion type and droplet size. These emulsions are good candidates to replace classical emulsions formulated with surfactants. Pickering emulsions offer specific features in life-science that are not shared with surfactant-based emulsions by avoiding the adverse effects of surfactants such as cytotoxicity.[5] They can also build a barrier to diffusion of drug molecules and therefore behave as encapsulation systems.[6] Coated emulsions, for example with hydroxyapatite, can play a role in targeting rules due to cell adhesion.[7] Furthermore porous materials can be prepared using Pickering emulsion droplets as templates, in the same manner as hexagonal mesophases of surfactants act as templates for the manufacture of mesoporous inorganic materials such as MCM's.[8]

In the last years, many researchers have paid attention to the ability of two-dimensional (2D) materials to promote the formation of special class of Pickering emulsions.[9] In this kind of emulsions, a large reduction of the free energy (ΔG) is found due to particles localized at the liquid-liquid interface, leading to the stabilization of the droplets. Graphene oxide (GO) is the most studied 2D material and has been considered to promote the formation of emulsions[10-11] due to its interesting property to act as a colloidal surfactant having a great interfacial activity at air-water, liquid-liquid, and liquid-solid interfaces. [11-13,14] He et al. investigated the effects of different conditions such as type of oil, the sonication time, the GO concentration, the oil/water ratio, and the pH value on the properties of the Pickering emulsions stabilized by GO.[11] Creighton et al. presented the interfacial thermodynamics of 2D materials such as GO at liquid-liquid interfaces with applications in emulsification.[9] Pickering emulsions stabilized by GO have been used as soft templates to design new functional hybrid materials. [15,16,17] It should be pointed out that the graphene-based composites were usually synthesized through an "emulsion polymerization" since the graphene moieties can very well stabilize the monomer. Xie et al. reported the preparation of polystyrene (PS) particles via Pickering emulsion polymerization using GO as the stabilizer[17] and Dao and co-workers prepared microspheres of poly(methyl methacrylate) (PMMA)/graphene composite with a core–shell structure by Pickering suspension polymerization.[18]

In this study, we focused our attention on h-BN as 2D material to prepare Pickering emulsions. Two-dimensional (2D) nanosheets, one-dimensional (1D) nanotubes, and zero-dimensional (0D) fullerenes are examples of materials with reduced dimensionality. These low-dimensional structures exhibit new properties due to quantum confinement and/or surface and interfacial effects when compared to three-dimensional (3D) bulk substances.[19] Similarly to carbon, BN can displays layered (hexagonal, h-BN), cubic (c-BN), and tubular structures

(BN nanotubes).[20] An hexagonal BN crystal structure with an exposed (002) surface have some advantages compared to graphite, such as very high thermal conductivity, mechanical strength and is electrically insulating (band gap of˜ 5-6 eV). Furthermore, the thermal and chemical stability of h-BN is better than that of graphite.[21] Such outstanding properties are especially promising for fabrication of BN-based functional materials with specific structure and performance. 2D hexagonal Boron nitride crystals, in the form of nanosheets (BNNS), are applied in the nanomedical field due to their good biocompatibility, and in scanning probe microscopy as ultrathin and stiff tips.[22] They are also applied for filling polymeric or ceramic composites to strongly improve their thermal and mechanical performances.[23-24]

W/O Pickering emulsions are more suitable for some applications in comparison to direct emulsions due to their higher stability against collapsing. Frelichowska *et al*. used W/O emulsions for drug release and topic delivery using hydrophobic silica as stabilizer.[25] Fei *et al*. synthesized modified graphene oxide/polyaniline nanocomposites from W/O emulsion through an interfacial polymerization mechanism.[26] A patent application related to the preparation of O/W and W/O emulsions for cosmetic and dermatological applications has been reported using functionalized BN as stabilizer. In this procedure, surface BN was modified with siloxane polymer and inorganic pigments.[27] While there is a big aim to develop a new method to prepare materials with specific shapes reducing the number of synthesis steps, there are also now important challenges concerning the direct preparation of W/O emulsions without functionalization of the nanoparticles.

One of the most important properties of emulsions for practical uses is their stability with time and when stress is applied which can be characterized from rheological measurements. The particles may form a transient network that reduces the mobility of the droplets, which leads to better stability. The flow behavior and the deformation of the emulsions stabilized by nanoparticles depend on different factors such as droplet size and morphology, dispersed

phase volume fraction (ϕ), particles concentration and nature of interactions between the particles and the droplets in the continuous phase.[11] Among these parameters, the particle concentration will influence the apparent viscosity by forming dispersed phase droplets of various size and droplets number with oil-water interface covered by solid particles.

In this work, the stability of W/O Pickering emulsions stabilized by exfoliated h-BN and without further functionalization was evaluated for different concentrations and for various oil/water volume ratios. Ethyl benzoate was ascribed as the oil phase, because this aromatic organic solvent is almost completely insoluble in water and has been already successfully used for preparing Pickering emulsion with graphene oxide by He *et al.*[11] The characteristics of Pickering emulsions will be discussed using a multiscale approach. First, the BN nanosheets were characterized by AFM and SAXS. Then the emulsion structure was analyzed microscopically through optical and epifluorescence microscopy, and macroscopically by rheological responses. The future perspectives with the proposed emulsion is to use them as templates to design new interesting materials with valuable properties, such as porous membranes or injectable scaffolds for drug delivery.

The h-BN stabilized emulsions were prepared by adding ethyl benzoate, in different o/w ratios, to aqueous suspensions of BN after a two-steps sonication procedure. The first step helps to exfoliate the BN with initial particle size of 3 μm and thickness around 1 μm, the second step leads to the desired emulsion. Atomic force microscopy (AFM) was performed to confirm the BN exfoliation, leading to h-BN nanoparticles with a thickness around 2-6 nm and a lateral size in the range of 10 to 90 nm (Supporting Information, Figure S1). Based on AFM images and taking into account the width of one nanosheet (0.36 nm), we could assume our BNNS are generally composed of 6-16 layers. A SAXS analysis was performed on an emulsion prepared with 2 wt% BN and an o/w ratio equal to 1. The SAXS plot (Supporting information, Figure S2) of the emulsion displays a combination of the peaks characteristic of

5

intermolecular distances of water and ethyl benzoate, and also a sharp peak at $q=18.9$ nm^{-1} corresponding to the BN inter-layer distance, giving the evidence of the presence of these three components.
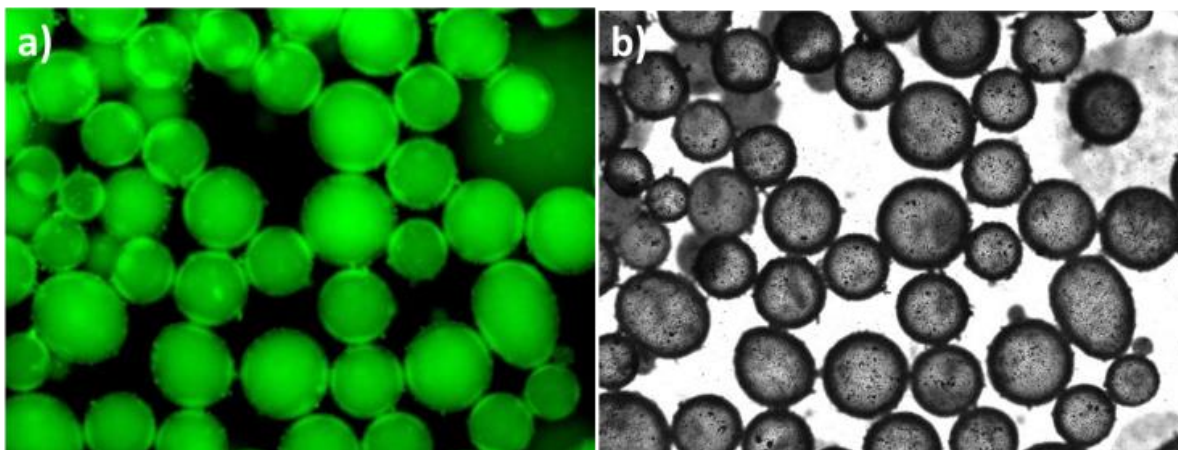

Figure 1. Epifluorescence images of Pickering emulsion BN 2wt%_R1 a) Fluorescence and b) Differential interface contrast (DIC) techniques.

The type of obtained emulsion was identified by epifluorescence microscopy. **Figure 1**a shows labeled water inside the droplets stabilized by h-BN. The continuous phase outside droplets is thus assumed to be ethyl benzoate. These microphotographs clearly evidence that the obtained emulsions are of W/O type. **Figure 1**b shows differential interface image contrast (DIC) images. A contrast difference is observed between the continuous and dispersed phase, namely oil and water. A black layer can be distinguished at the interface between oil and water which strongly suggests the presence of a shell of h-BN nanosheets around the droplets.

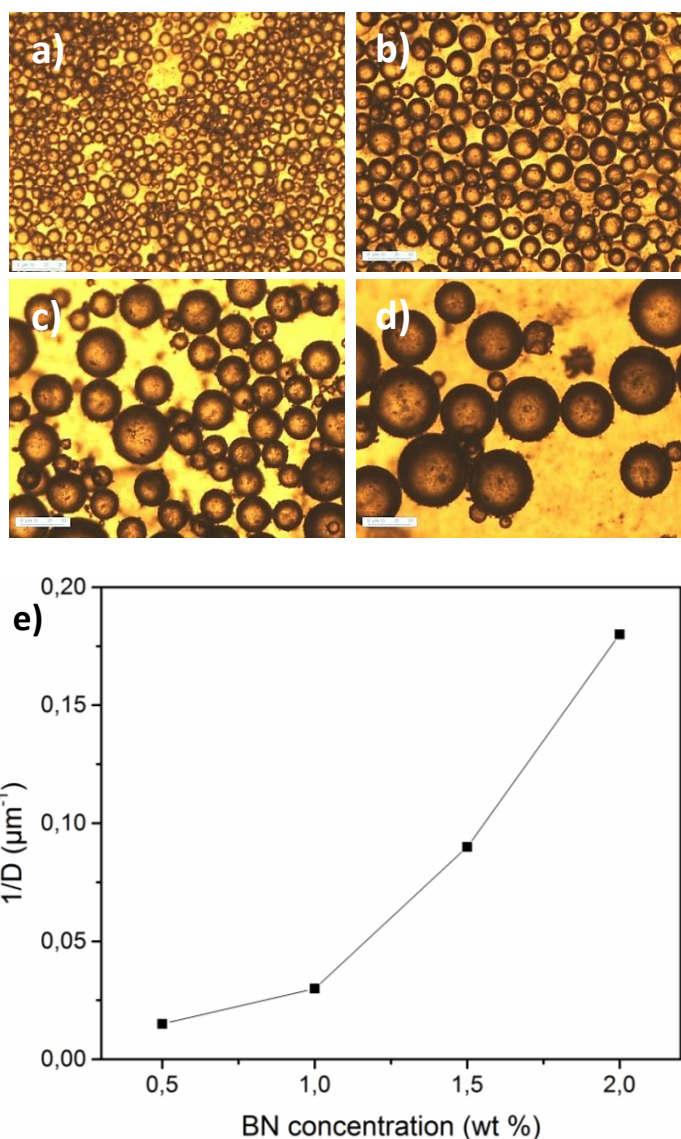**Figure 2.** Optical microscopy images of h-BN emulsions at different concentrations: a) 2 wt% BN, b) 1.5 wt% BN, c) 1.0 wt% BN and d) 0.5 wt% BN with a o/w ratio of 1 (The scale bars in the images correspond to 30 µm length), e) Inverse of the average emulsion droplet size stabilized with h-BN particles at different concentrations (0.5-2 wt%) at a fixed o/w ratio of 1 (measurements based on 50 droplets).

The emulsion microstructure and drop size were analyzed by optical microscopy. **Figure 2**a-d shows microscopy images taken for the emulsions prepared with different h-BN particle concentrations, with ethyl benzoate/water volume ratio constant at 1. The quantification of these results is shown in **Figure 2e**. The average droplet diameters range from 6 µm at the highest BN concentration (2 wt%) to 43 µm at the lowest BN concentration (0.5 wt%) when the o/w ratio is 1. Thus, Pickering emulsions with different droplet sizes could be obtained by tuning the concentration of BN at constant amplitude settings (55 %). As expected, the average drop size of solid-stabilized emulsions decreases with increasing particle concentration, as more particles are available to stabilize small droplets.[28] Decreasing the solid particle concentration led not only to a larger emulsion droplet but also to a greater heterogeneity in the droplets sizes and shapes, which signifies less efficient emulsion conditions. In our case, unlike other systems stabilized with spherical particles, the plot between the inverse of droplet size and the BN concentration (**Figure 2e)** displays a non linear dependence. This means that the emulsion is not limited by a coalescence phenomenon. Basically, the stability of a single particle at the interface is governed by the stabilization energy per particle. On the contrary than very small nanospheres (radius below 1-10 nm), it has been shown that the adsorption of graphene-based sheets never reaches a reversible regime due to graphene atomical thickness.[29-30] In our system, the surface coverage[31] was evaluated assuming that particle anchoring at the oil-water interface was always complete and irreversible. The resulting emulsions exhibit a drop diameter that is controlled by the mass of particles and their packing at the interface. Assuming that all particles are adsorbed at the oil-water interface, simple geometrical considerations show that the surface coverage is larger than 1 (Table S6), which evidences that the droplet are covered by multilayered particles or aggregates.[32] The multilayer coverage was also reported in the case of GO, where it was estimated to stack up to 10 monolayers under certain conditions.[33] From thermodynamics

calculation, it was suggested that the 2D material multilayers at the interface effectively cover the droplet surface and inhibit collisions-induced coalescence or ripening.[9] These emulsions stabilized with exfoliated h-BN are comparable in terms of stability and droplet size behaviors with other emulsions stabilized with 2D materials such as GO.

Preparing emulsions with h-BN has major interest due to the BN higher biocompatibility and its other unique properties, such as wide band gap, electrical-insulating properties, high thermal conductivity, high stability and resistance to oxidation, compared to other sheet-like materials, e.g. GO. Furthermore, numerous in vitro and in vivo assays have confirmed the toxicity of C-based materials. Alternatively BN possesses a better biocompatibility and a lower cytotoxicity.[34-35,36]

It is known that the droplet size is extremely sensitive to the amount of energy delivered to the biphasic system. This one has a direct relationship with the amplitude and intensity of the ultrasonic device. In order to decouple the influence of the energy delivered to the system with the amount of BN in the droplet size, emulsions formulated with 2 wt% BN and an o/w ratio of 1 were first prepared using different amplitudes (20 to 80 %). Results shows (Table S3) that the emulsion droplet size do not change when different amplitudes are applied to the system. Then, the influence of the power delivered to the system by the same ultrasonic device on the droplet size was also evaluated. It has not big influence in the droplet size in the range 20 to 75 W. For higher power, the mean droplet size is slightly smaller, but it is not really significant. So it can be conclude that the emulsifying process used in this study reached its limit to provide energy to the emulsion to produce smaller droplets with 2 wt% BN. This explains the gap with the linear dependency previously observed for lower BN load. Samples with different BN loads and same o/w ratio were then sonicated under constant

power (40W) (Table S5). The obtained results confirm that the BN load is the main parameter affecting the droplet diameter with this ultrasonic probe used as emulsifying device.

The BN based-emulsions have been stored at ambient temperature for 14 days for studying their stability. We observed that emulsions formulated with o/w ratios ≥ 0.6 displayed two phases, one is the emulsified phase composed of 62 to 85% of volume fraction and the other is the oil phase resulting from the separation and sedimentation of the continuous phase due to its high density (mass density at 20°C is 1045 kg m^{-1}). Above the random close packing (corresponding to a dispersed water volume fraction $\phi_w > 0.66$), the droplets can not move freely and they are trapped by the neighbors leading to emulsion destabilization after few hours preparation (Supporting information, Table S1). It was also observed that the emulsions with higher BN concentration have higher emulsion stability index (ESI), determined from the volume ratio of the emulsified phase after 14 days and emulsion after 3 hours. The emulsion with 2 wt% BN and a o/w ratio of 1 (BN 2wt%_R1) is more stable along the time than the rest of emulsion, and shows an ESI around 94 %. In our system we observed that when the emulsion completely breaks down above the random close packing, there is a separation between two bulk phases: one very clear corresponds to the water phase and the other being whitish. Thereby we suggest that almost all particles are dispersed in the oil phase due the degree of hydrophobiciy of BN. A small part of BN particles could be adsorbed at the flat interface between oil and water.

Other phenomena was also observed by Binks et al. when emulsion stability is limited by coalescence phenomenon, destabilization occurs such as rapid film growth in hydrophilic tubes induced by the coalescence of spherical particles-stabilized emulsion drops with a flat oil-water interface separating the bulk oil and water phases.[37]

In our case, the emulsions are stabilized by multilayers of 2D material which inhibit the coalescence. Thus, we could propose two hypotheses to explain that emulsions are not stable above the close packing. The first one is based on that sheet-sheet interaction may promote multilayer film formation. In this case, the first layer packs imperfectly at the interface, leaving bare patches of liquid-liquid (L-L) interfaces that can interact with subsequent layers in a diffuse interfacial zone. For atomically thin plates, the second layer lies very close (within 1 nm) to the L-L interfaces, and on this length scale, thermal molecular fluctuations allow the contact between the layer and both dispersed and continuous phases. In this way, the layers could contain interstitial spaces and then subsequent layers are too far from the interface to interact energetically with both liquid phases. There are two possible deposition pathways: First, the so-called "sequential close packing" route is characterized by an ordered layer-by-layer deposition. Second, a "random ballistic deposition" which has an irrespective prior coverage can take place. In the case of GO, it has been shown that at equal number of material layers, the stabilization energy is lower for the random deposition than close packing. This may explain the instability of emulsion.[9]
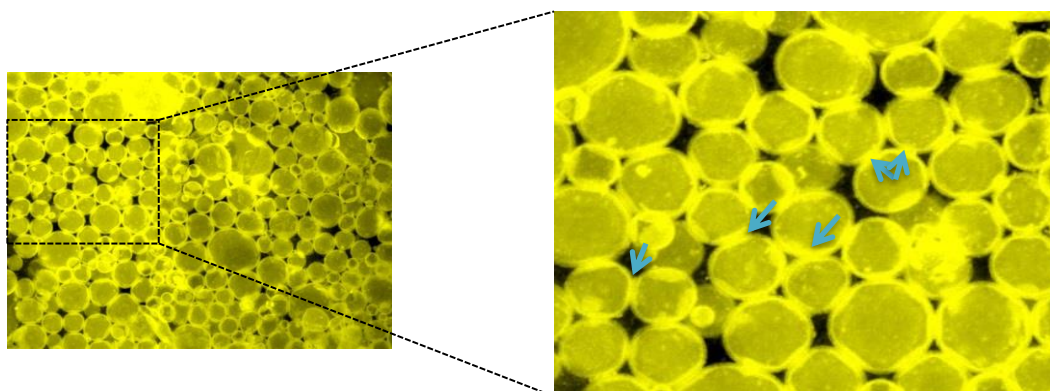

Figure 3. Epifluorescence images of Pickering emulsion BN 2wt%_R1 showing droplet deformation due to particle jamming.

11

In the second hypothesis, we consider a stabilization mechanism called 'droplet bridging'. The emulsions prepared by ultrasonic probe display long-term stability when the dispersed phase volume fraction is well below the random close packing ($\varphi = 0.65$). Partially hydrophobic particles with contact angles somewhat greater than 90° tend to stabilize water-in-oil emulsion where particles slightly protrude from droplets surface to maintain the equilibrium contact angle; this also facilitates efficient packing and steric barrier against coalescence. Particles concentration also plays an important role in the surface coverage. In fact, when coverage is very high, significant droplet deformation could be observed due to jamming of the particles at the droplet interfaces (**Figure 3**). Although the droplets were in close proximity, their interfaces were not joined because of the high particle coverage. This effect has been observed by Zhang *et al.*[38] using layered double hydroxides particles for the preparation of Pickering emulsions. Moreover, droplets bridging has been observed by Frost *et al.*[39] when ionic liquids are used for Pickering emulsions preparation.
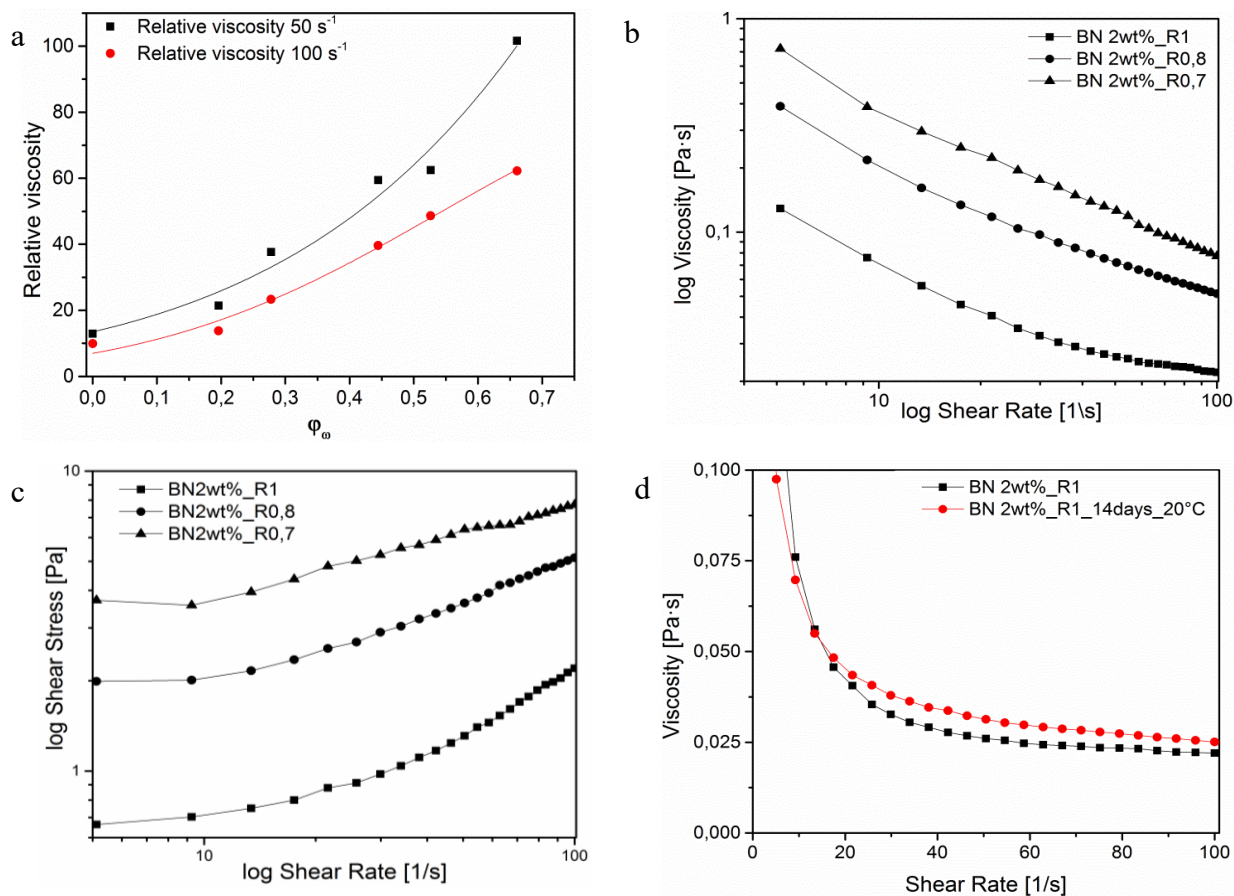
Figure 4. a) Relative viscosity curves in function of water volume fraction (ϕ_w) for emulsions formulated at 2 wt% BN concentration at shear rate 50 s^{-1} and 100 s^{-1} (Lines are eye-guides). For values of ϕ_w up to 0.66 the emulsions broke down. b) Viscosity curves of emulsion with 2 wt% h-BN concentration and different o/w ratios (R=0.7 to 1); c) Flow curves of emulsion with 2 wt% h-BN concentration and different o/w ratios (R=0.7 to 1) d) Viscosity curves of freshly prepared BN2 wt _R1 emulsion, and after 14 days.

By rheological measurements, it is also possible to study the emulsion stability. For that purpose, the effect of varying the water volume fraction (ϕ_w) was investigated by concentrating the emulsions at constant particle concentration using a rotational rheometry

13

technique. **Figure 4**a shows the relative viscosity (ratio between the apparent viscosity of the emulsion and the oil phase viscosity) as a function of the water volume fraction. Our system behaves as the literature predicts, increasing the viscosity when rising the ϕ_w. It is observed that increasing ϕ_w increases the relative viscosity from 12.9, corresponding to low volume fraction (< 0.05), to 101.6 for high volume fraction (0.66) when the shear rate is 50 s^{-1}. The same behavior was found when the shear rate was 100 s^{-1}, the relative viscosity increasing from 9.9 ($\phi_w = 0.05$) to 62.3 ($\phi_w = 0.66$). This fact may be due to the increase of water content and to the possibility that droplets tend to pack closer, adding a significant contribution to the emulsion viscosity. We observed also that w/o emulsions stabilized with exfoliated h-BN formulated with ϕ_w above 0.66 and 2 wt% BN concentration are not stable anymore after preparation or after a few hours and broke down due to the fact that maximum random close packing has been reached for our system.[38, 40] The present results thus show that the maximum packing fraction for w/o emulsion made with ethyl benzoate and BN is close to 0.64, as described in the literature for monodisperse spherical drops. The aim of the study is to use this emulsion as a potential soft template for the preparation of new porous materials. In this case, the inner phase will give the porosity volume and the continuous phase will form the material matrix. If the continuous phase volume is too limited, it will give weak mechanical properties to the solid material. However, it should be noted that the maximum total porous volume reached with the present emulsion to make for instance a membrane would be ca. 64%. The preparation of porous nanocomposites materials from medium internal phase emulsions has been already reported in the literature. Pickering emulsions containing only 60% of disperse phase could lead to open porous polymer foams with low densities and high degrees of pore interconnectivity. [41]

The rheological behavior of pure ethyl benzoate, pure water, and of the obtained emulsions was analyzed by measuring the viscosity in function of the shear rate at 20 °C. The measurement was carried out within the 10 min following emulsification where the emulsions are stable, the duration of experiment was around 4 min and no phase separation was observed after the analysis. **Figure 4**b shows the viscosity curves obtained for the BN emulsions formulated at 2 wt% of BN and different O/W ratios. In this study, standard cone-and-plate geometry with 50 mm diameter and a 1° cone angle was used. The maximal acceptable droplet diameter for this type of geometry is defined by this equation:

$$d \leq a/10 \tag{2}$$

The gap set at the center of the cone (a) has a value of 101 μm so the diameter of droplet must be below 10 μm, and our droplets meet this condition with a 6 μm diameter. At any given shear rate, the emulsions have a higher viscosity than pure phases (Figure 3b), especially at low shear rates due to the even dispersion of h-BN in the water and oil mixture, acting as a stabilizer. The emulsions display a typical shear-thinning flow behavior, characterized by decreasing the viscosity as the applied shear rate increases, approaching to a constant value at high shear rates. At low shear rates, the measured emulsion viscosity is higher, indicating that at rest the droplet close-packing is responsible of viscosity. When a higher shear rate is applied, the droplets start to be organized into layers or strings, and the rheogram displays a decrease in viscosity. The measurements were performed three times using the same emulsion to ensure the repeatability of the test. The results show (Supporting information, Table S2) that the test could be repeated without changes in viscosity data. **Figure 4c** shows the curve of shear stress as a function of the shear rate of an emulsion containing 2 wt% of h-BN and different O/W ratios (R=0.7 to 1). The flow curves exhibit a yield stress dependent on the o/w ratio. The reduction of the o/w ratio from 1 to 0.7 corresponds also to an increase of the inner phase volume (+43% v/v of water) and thus to a concentration of the emulsion with a higher

amount of dispersed phase. As a consequence, an increase of the viscosity and of the yield stress is observed. In **Figure 4**d, the viscosity curves of the emulsion containing 2 wt% BN and with an o/w ratio of 1 are shown as freshly prepared and after 14 days. No change in the apparent viscosity is observed after 14 days.

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

SUPPORTING INFORMATION. An experimental section, additional AFM and SAXS analyses and a stability Table are supplied as Supporting Information.

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TABLE OF CONTENTS GRAPHIC