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Design of alumina monoliths by emulsion-gel casting: understanding the monolith structure from a rheological approach

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Abstract

Multimodal porous cellular alumina structures (monoliths) were prepared by an emulsion-gel casting technique using eco-friendly and inexpensive lipids such as corn oil, castor oil, margarine and their mixtures as the dispersed phase. The monoliths obtained showed a good mechanical stability, exhibiting compressive strengths in the range of 8-50 N.mm⁻². Mercury intrusion porosimetry analysis showed that the monoliths produced presented porosities ranging from 28% to 60% and average pore sizes within 0.2-3.2 μm. The formation of the porous networks was interpreted based on combined droplet coalescence, flocculation and Ostwald ripening effects. The presence of such effects along the emulsion storage time led to changes in their viscoelastic and morphological properties, which were found to correlate with structural descriptors of monoliths after sintering (e.g. average pore sizes and porosity). These correlations open up the possibility to anticipate the final structure of the monoliths and adjust emulsion-gel conditions to produce customized cellular structures with fine-tuned porosities and pore sizes, envisaging their application in membrane processes or chromatography.

Keywords: alumina monoliths; emulsion-gel casting; viscoelastic properties; porous structure; chromatography

1. Introduction

Macroporous ceramics find applications in a wide variety of areas due to a combination of favourable properties like low thermal conductivity, low density, high porosity and high chemical tolerance [1]. Techniques that enable tuning of porosity, pore morphology and distribution are of great interest to obtain suitable materials for cutting edge applications like in fabrication of porous separation media (e.g. membranes, chromatography stationary phases) for high temperature processes, sensors for chemical and biochemical processes, catalyst carriers, electrodes for batteries and fuel cells and scaffolds for tissue engineering [1-4].

There are several popular techniques to produce cellular ceramics including partial sintering, replication, use of sacrificial phase, foaming and gel casting to name a few [3, 5, 6]. The choice of the technique determines the morphological properties of the material obtained i.e., pore shape, size and distribution, interconnectivity, tortuosity, permeability and mechanical strength. From the perspective of separation processes, development of hierarchically porous, contiguous materials with well-defined end-to-end interconnectivity is of the essence. Gel-casting has proven to be an effective technique [7-9] to achieve these objectives.

The advantage of gel casting is that it allows the preparation of molded structures with near-finished shape akin to that available in polymer manufacturing [10-11]. The use of molds leads to ease in scaling up. Depending on the additives and molds used a wide variety of shapes can be produced with diverse porosities, ranging from imperviously dense to highly porous structures. In the present work, we use the technique of emulsion gel-casting to produce cellular structures. In simple terms, the technique involves creating an emulsion with the continuous phase being the ceramic powder material in a suspension and a dispersed phase being a suitable pore forming substance [12]. Suitable additives are also added to influence factors like pore size and the stability of the emulsion [10, 13, 14]. This emulsion is like putty and can be put into molds. Once the shape is set, it can be fired in an oven which accomplishes two purposes – burning out the dispersed phase and strengthening/consolidation of the ceramic material. Earlier publications report the preparation of microporous cellular materials through emulsion-gel casting using polymers [15, 16], alkanes [17-19] or other organic solutions as the

dispersed phases. In either case, during the firing process there are toxic gases released, which can cause serious harm to the environment as discussed in detail elsewhere [20].

In a previous work, a detailed study was conducted on the use of an eco-friendly and less expensive - sunflower oil, as the dispersed phase in emulsion gel-casting process [10]. In the said work by Sanches et. al [10], the effect of several parameters like the dispersed phase to continuous phase ratio, the effect of collagen (used as structural stabilizer) and the effect of burnout conditions on the morphology of the cellular ceramics formed were discussed in detail. Considering these perspectives, the goal of this work was to obtain an in-depth comprehension on the influence of the properties of commercially available lipids, used as dispersed phases, on the final hierarchical pore morphology of the sintered structure. We analysed the rheological properties of the emulsions formed with the different lipids and discuss the morphology of the final structure in terms of pore size, porosity, mechanical strength relating them to the properties of the emulsion like droplet size distribution and viscosity. This study is aimed to provide useful guidelines for design of cellular ceramics of alumina with fine porous structures which can be used in a multitude of applications from making membrane supports to monolithic chromatography applications.

2. Experimental

2.1. Materials

-alumina (Alcoa Chimie, CT-3000), Dolapix PC 67 (Zschimmer & Schwarz), Gelatin Porcine Skin (Oxoid LP0008) sodium lauryl sulfate/SDS (Sigma-Aldrich L-6026, stock concentration of 1g. L^{-1}) and commercially available corn oil, castor oil and margarine (41% lipids and 59% water) were used.

2.2 -alumina suspension

-alumina -alumina needed to prepare a -alumina suspension was calculated using the density of reactive alumina powder which was found to be $\sim 3.98\text{ g.cm}^{-3}$. To ensure the formation of a stable suspension with fluid consistency a carboxylic acid based agent, Dolapix PC 67, was added in the concentration of 1% (v/v). Dolapix PC67 is a de-flocculant consisting in an amphiphilic molecule with the same isoelectric point as alumina, which coats the alumina particles such that it does not aggregate to form lumps. The

suspension was stirred at 1000 rpm for 120 minutes to obtain a stable suspension with smooth consistency.

2.3. γ -alumina emulsion

Oil-in-water emulsions were prepared with pre-defined dispersed phase (V_o) to continuous phase (V_s) ratio of 1.5. Different lipids, i.e. corn oil, castor oil and margarine and lipid mixtures, i.e. corn oil + castor oil (1:1 v/v), margarine + corn oil (1:3 and 3:1 v/v) and corn oil + castor oil + margarine (1:1:1 v/v) were used as dispersed phases whereas aqueous γ -alumina suspensions were used as the continuous phase.

γ -alumina solution was added to the dispersed phase under mechanical stirring at 1000 rpm using an overhead stirring motor. Sodium dodecyl sulphate (SDS), an anionic surfactant was added in a concentration of 6% (v/v) and used to stabilize the emulsion. Gelatin (gelatin oxid) [10-12] was added to the dispersed phase heated at 60 °C in a concentration of 5% (w/v relative to the volume of water in the final emulsion) and used as a structural stabilizer.

The emulsion prepared with the consistency of thick foam was then poured into different pre-greased cylindrical molds with dimensions of 5 cm length and 1.1 cm diameter and incubated at 40°C, for 72h. This procedure results in the evaporation of the excess of water and gel hardening, sufficiently to form a contiguous monolithic *green body* (precursor of the monolithic structure), which could then be easily removed from the mold (de-molding).

2.4 γ -alumina

Once the samples were sufficiently hardened, the resulting consolidated *green bodies*, were separated from the mold (de-molded) and then sintered in 2 stages. In the first stage the oil droplets, gelatin and surfactant were removed by increasing the temperature well beyond the smoke point of the oils used i.e., around 1000 °C, followed by an isothermal plateau to completely remove the carbon residues. This stage was carried out at very small heating rate, i.e., 1 °C.min⁻¹ to avoid the *green body* from exploding due to fast burn out of oil resulting in the build-up of gases within which, during escape, might cause cracks or defects in the column [11]. Despite taking these precautions, it was found that columns containing castor oil were quite often hollowed out or cracked after sintering. This was probably because of the gaseous micro environment within the furnace chamber leading to slower

evaporation of the oils entrapped within the samples themselves. In the second stage, the heating was resumed at a rate of 3 °C min⁻¹ until 1550 °C with a 2-hour sintering plateau. Finally, the samples were cooled to room temperature at a rate of 5 °C min⁻¹ to obtain suitable cellular monoliths.

2.5. Characterization of the dispersed phases and emulsions

The apparent viscosity and viscoelastic properties of the emulsions prepared as described above were studied using a controlled stress rheometer (HAAKE MARSIII, Thermo Scientific) equipped with a plate-plate serrated geometry (diameter 30 mm), with a gap of 1 mm. The samples were equilibrated at 20 °C, for 5 min, after which the apparent viscosity was measured using a steady-state flow ramp in the range of shear rate from 10⁻³ to 400 s⁻¹. Mathematical model

Solver tool for fitting the data to Equation 1 using the Levenberg-Marquardt algorithm. Equation 1 results from the simplification of the Carreau model [21] having into account that the second Newtonian plateau (at infinite shear rate) was never reached.

$$\frac{\eta}{\eta_0} = \frac{1}{1 + N \dot{\gamma}^2} \quad (\text{Equation 1})$$

where η is the apparent viscosity (Pa.s), η_0 is the zero shear rate viscosity, τ is the relaxation time constant, $\dot{\gamma}$ is the shear rate and N is a dimensionless constant related to the power law index ($N = (1 - n)/2$).

The interfacial tension of the emulsions was measured by Wilhelmy plate technique (3S Tensio, GBX) equipment at a temperature of 20 °C with a plate of dimensions 2 cm x 2 cm. Droplet analysis and imaging were performed through optical microscopy (Eclipse Ti-U, Nikon) using objectives of 10x and 50x, equipped with a camera for image acquisition. Image analysis was carried out using the ImageJ software [22] and the Sauter mean droplet diameters in each emulsion were calculated.

2.6. Structural characterization of the monoliths

Scanning electron microscopy (SU1510, Hitachi) was used to inspect the microstructural features of the sintered monoliths after carbonizing the sample with graphite. Mercury intrusion porosimetry (Autopore, IV 9500, Micromeriti CS) was used to characterize the pore size distribution, mean pore diameter and average porosity of the samples. Compressive strength upon rupture (LR30K, Lloyd) was measured to infer about the mechanical resistance of the monoliths using samples with

length:width ratio of 2:1 under a cross head with speed of 15 mm.min⁻¹ using about 3 samples per series.

3. Results and Discussion

Monoliths should ideally consist of structures with hierarchical porous networks and well interconnected pores. The formation of such structures by emulsification gel casting processes requires the use of high dispersed to continuous phase ratios, in order to ensure a good balance between droplet flocculation, coalescence and ripening with consequent formation of a series of interconnected droplets. These interconnected structures are ultimately stabilized by a gelling agent entrapping all the components in place to obtain a contiguous *green body* (the monolith precursor), which, upon sintering with a specific temperature cycle, yields a highly porous monolithic structure. The final structure of the monolith will be then defined by the emulsion behaviour/stability (e.g. droplet coalescence, flocculation, ripening) along the aging period (or storage time, period of time before sintering where the emulsion system is allowed to set), and thus is intimately related to the rheological characteristics of the emulsions. Therefore, the capacity to design monoliths with a fine-tuned morphology depends on the ability to predict their final structure based on the evolution of the rheological and morphological parameters of the emulsion-gel at different stages of the aging process [23].

Rheology of an emulsion is greatly influenced by several factors, including interfacial tension, particle interaction and droplet dimension, which may vary along the emulsion storage time. As a first approach, optical microscopy was used to study the evolution of the morphological characteristics of the emulsions prepared with pure corn oil, castor oil and margarine, and different mixtures of these oils along aging, i.e. from the freshly made emulsion (0 hours) to the *green body* obtained after a storage time of 72 h (Figures 1I and 1II). Changes in the size and distribution of droplets are perceptible from comparative analysis of the microscopy images of the samples reflecting varying degrees of flocculation and coalescence along emulsion aging. The increase of the droplet sizes was particularly observed in emulsions prepared with corn oil, margarine and margarine + corn oil (3:1) as may be confirmed through the values listed in Table 1.

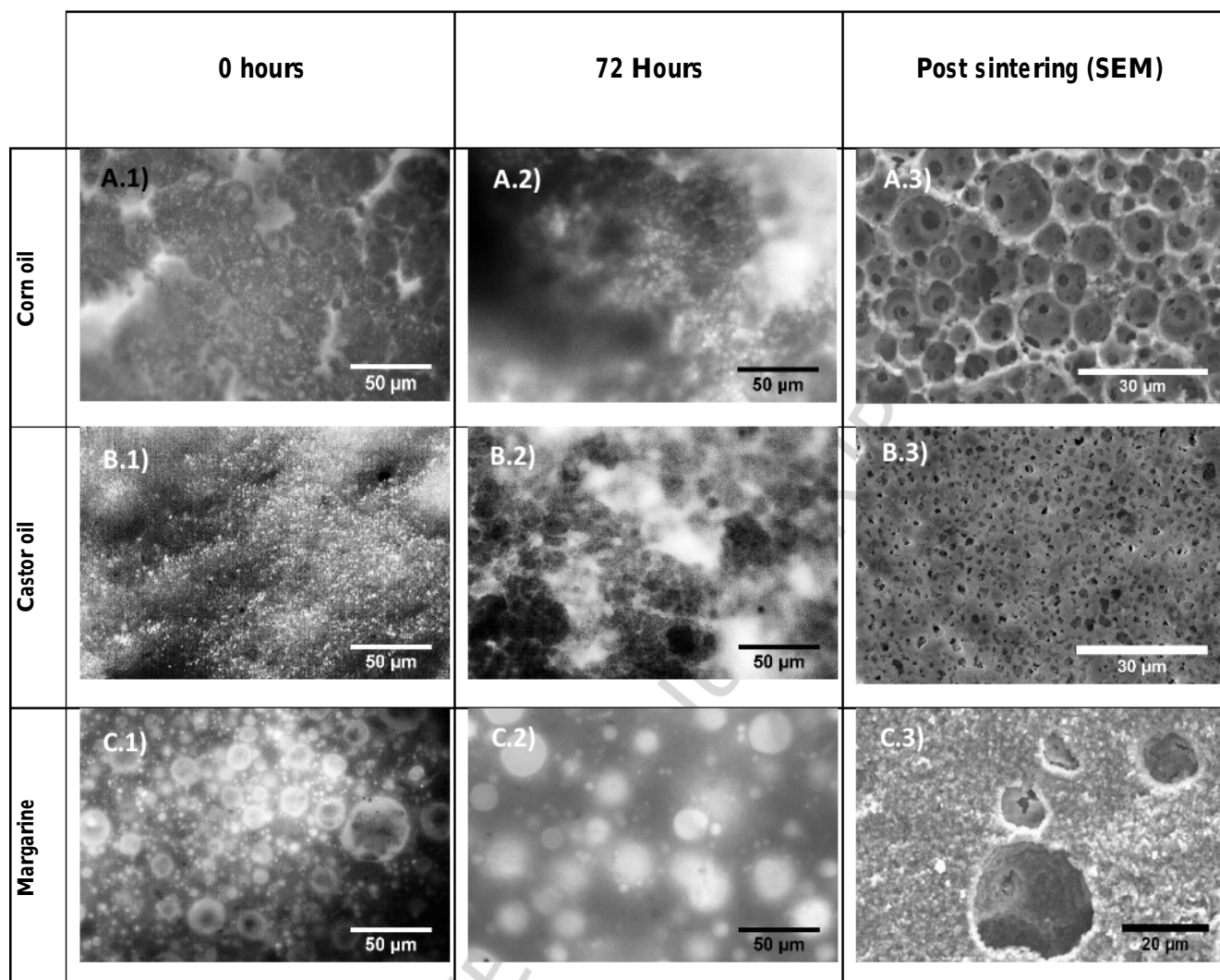


Figure 1. I). Optical microscopy images for emulsions made with A.1) Corn oil at 0 hours, A.2) Corn oil at 72 hours, B.1) Castor oil at 0 hours B.2) Castor oil at 72 hours, C.1) Margarine at 0 hours and C.2) Margarine at 72 hours. SEM images of monoliths (i.e., *green bodies* after sintering) obtained using emulsions prepared with A.3) Corn oil, B.3) Castor oil and C.3) Margarine.

Several studies have shown [13, 24, 25] definitive connections between rheological parameters like viscosity and viscoelastic properties with changes in the emulsion stability expressed by droplet coalescence, flocculation, phase inversion and ripening effects [23].

From this perspective, the variability of the rheological properties of the emulsion-gel along the storage time was studied. Viscosity *versus* shear rate profiles were determined for single lipid emulsions prepared with corn oil, castor oil and margarine and emulsions prepared with mixtures of these lipids.

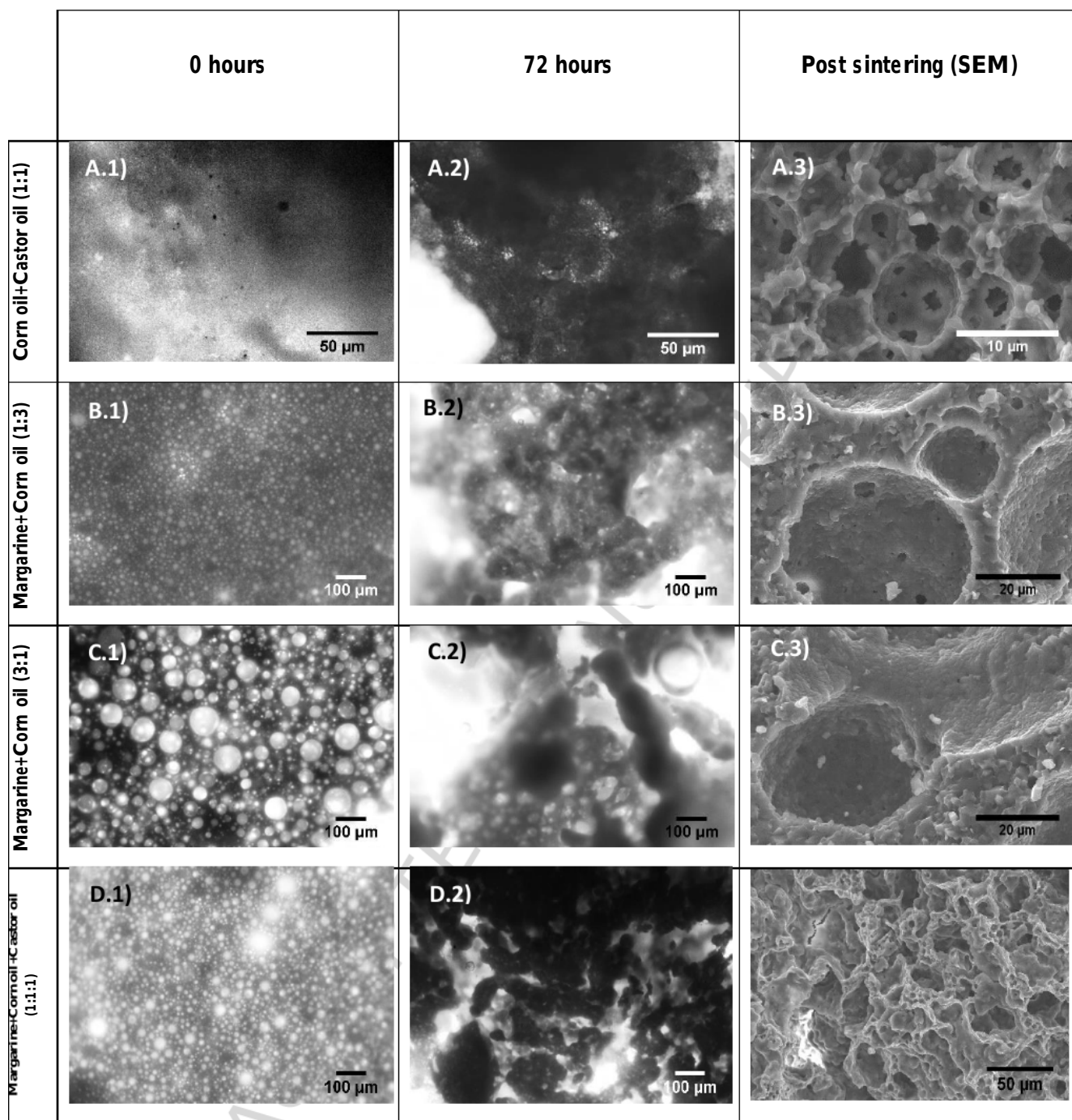


Figure 1. II) Optical microscopy images for emulsions made with A.1) Corn oil + Castor oil (1:1) at 0 hours, A.2) Corn oil + Castor oil (1:1) at 72 hours, B.1) Margarine + Corn oil (1:3) at 0 hours B.2) Margarine + Corn oil (1:3) at 72 hours, C.1) Margarine + Corn oil (3:1) at 0 hours, C.2) Margarine + Corn oil (3:1) at 72 hours. D.1) Margarine + Corn oil + Castor oil (1:1:1) at 0 hours and Margarine + Corn oil + Castor oil (1:1:1) at 72 hours. SEM images of monoliths (i.e., *green bodies* after sintering) obtained using emulsions prepared with A.3) Corn oil + Castor oil (1:1), B.3) Margarine + Corn oil (1:3), C.3) Margarine + Corn oil (3:1) and D.3) Margarine + Corn oil + Castor oil (1:1:1).

As shown in Figure 2 all the prepared emulsions are non-Newtonian as is apparent from the shape of the viscosity-shear curves, i.e. the emulsion systems depict a shear thinning profile, characterized by the decrease of viscosity at higher shear rates preceded by a Newtonian plateau at lower shear rate values. The non-Newtonian behaviour of the emulsions is observed at both emulsion stages analysed, i.e. immediately after emulsification (0 hours) and after 72 hours of storage.

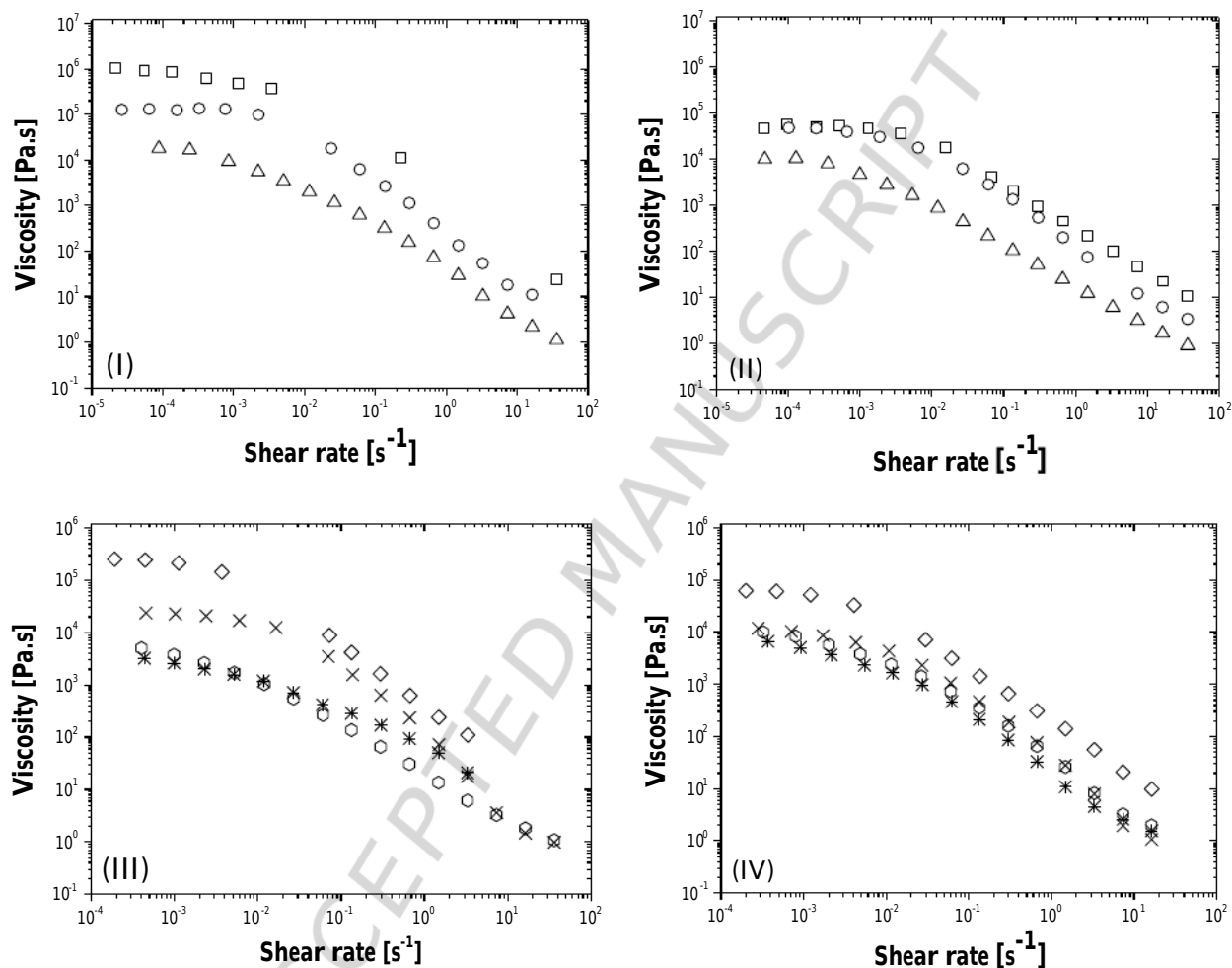


Figure 2. Viscosity vs. shear rate profiles

Corn oil (1:3) [x], Margarine + Corn oil (3:1) [], Margarine + Corn oil + Castor oil (1:1:1) [] for 0 hours IV) Corn oil (1:1:1) [], Margarine + Corn oil + Castor oil (1:1:1) [] after 72 hours.

The plateau region (Newtonian plateau) observed at lower shear rates indicates a limited disruption of the structure of the emulsion at these shear regimes, evidencing the stability of the emulsions. However, as the shear rate increases there is a rapid transition from the Newtonian regime to a shear-

thinning behaviour, indicating that both continuous and dispersed phases are flowing, which may lead to significant changes in droplets dimension, particularly at the higher shear rates tested.

To better understand the aging behaviour, data were fit to the simplified Carreau model, as expressed by Equation 1. It was found that the data fit well to this equation ($r^2 > 0.9$), as shown in Figures S.1 and S.2 in Supplementary Information (S.I.). The power law index (or flow index parameter), N , obtained from the fit was <1 for all samples (Table S.1 in S.I.), corroborating the shear thinning behaviour of the emulsions. The relaxation time constant λ (s), which was also obtained from the fitting, is an indicator of the transition from Newtonian to shear-thinning regime whereas its reciprocal, i.e. $1/\lambda$, represents the shear rate at which this transition takes place. Therefore, a decrease of $1/\lambda$, upon storage (as observed for emulsions prepared with single oils, i.e. corn and castor oils) may be ascribed to the loss of structural cohesion of the emulsions and associated to the increase of the droplet size (coalescence effects).

The droplet size also influences the apparent viscosity, η_{app} , of the emulsions obtained from the value of viscosity at the Newtonian plateau. Higher droplet sizes are commonly associated to lower viscosities. This relation is clearly observed in Table S.1 (in S.I.), which shows that emulsions with lower droplet sizes, such as that obtained from pure castor and corn oils or the mixture of these two oils, are those that also exhibit higher apparent viscosities. Instead, the emulsions prepared with dispersed phases containing margarine showed lower apparent viscosities and larger droplet sizes.

The presence of droplet coalescence effects may thus be inferred by comparative analysis of the changes of the Newtonian plateau viscosity obtained for freshly prepared emulsions and after storage (72 hours) as shown in Figure 3 and Table S.1 (in S.I.). Correlations between droplet coalescence and changes in the viscosity were clear for emulsions made of single oils. The decrease in the apparent viscosity observed with storage for emulsions made from corn oil and margarine, may be ascribed to the droplet coalescence taking place along with other minor effects [23].

Droplet coalescence, and its relation to changes in the apparent viscosity, was not that clear in the case of emulsions prepared using oil mixtures as the disperse phases. The droplet coalescence observed in emulsion prepared using margarine + corn oil (3:1) was followed by an increase of the apparent viscosity with storage while emulsions prepared with margarine + corn oil (1:3) and margarine + corn

oil + castor oil (1:1:1) displayed a decrease of the droplet size after 72h. The absence of droplet coalescence observed in these latter cases seems to indicate a balance in the distribution of the droplets of different oils present in the emulsion minimizing the droplet coalescence.

Table 1. Time relaxations, λ (s) and average droplet diameter ($d_{3,2}$) (μm) of the emulsions used to produce the cellular alumina structures.

0 hours		
Dispersed phase		Average droplet diameter ($d_{3,2}$) [μm]
Corn oil	414.22	1.80 \pm 0.12
Castor oil	350.16	0.90 \pm 0.19
Margarine	2932.42	8.20 \pm 0.8
Corn oil + Castor oil (1:1)	194.92	1.30 \pm 0.23
Margarine + Corn oil (1:3)	193.2	10.10 \pm 1.1
Margarine + Corn oil (3:1)	443.77	12.40 \pm 1.2
Marg. + Corn oil + Castor oil (1:1:1)	998.97	11.30 \pm 1.8
72 hours		
Corn oil	296.56	3.40 \pm 0.21
Castor oil	102.30	1.10 \pm 0.16
Margarine	2993.85	14.00 \pm 1.2
Corn oil + Castor oil (1:1)	233.52	1.30 \pm 0.08
Margarine + Corn oil (1:3)	202.19	8.70 \pm 1.5
Margarine + Corn oil (3:1)	248.37	15.20 \pm 2.2
Marg. + Corn oil + Castor oil (1:1:1)	233.27	10.30 \pm 1.63

These results show that there is no unequivocal relationship between changes of apparent viscosity and droplet size evidencing that besides the droplet dimension, other factors, such as the presence of surfactants and the effect of alumina particles, could explain the heterogeneity of the behaviours found in the different emulsions systems studied and later on the distinct monolithic structures, as shown in the third column of Figure 1 I and Figure 1 II.

Viscoelastic tests were performed to further understand the effect of droplet distribution on the stability and the final microstructure of the sintered samples. Frequency sweeps were performed to evaluate the viscoelastic properties of emulsions. The sto

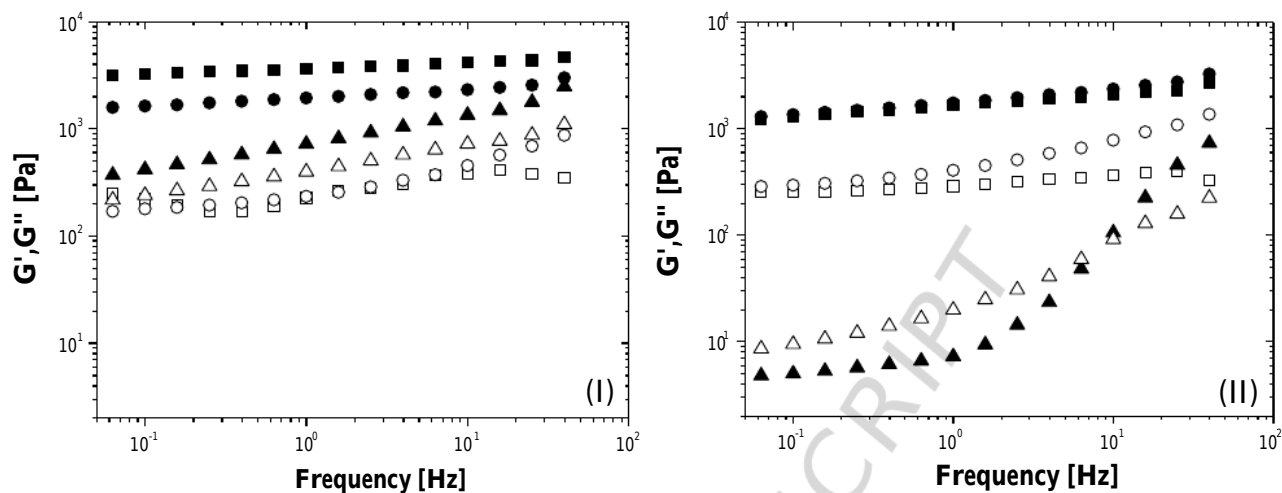


Figure 3. Oscillatory viscoelastic profiles for emulsions made with I) Corn oil (■ - G' , □ - G''), Castor oil (● - G' ,

○ - G''),

Margarine (- - -)

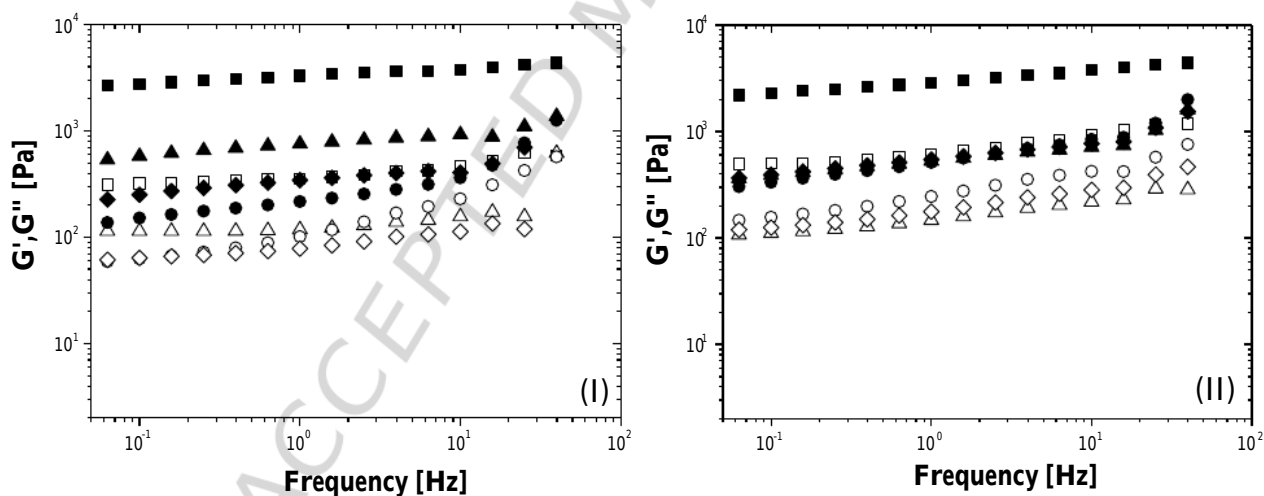


Figure 4. Oscillatory viscoelastic profiles for emulsions made with I) Corn oil + Castor (■ - G' , □ - G''),

Margarine + Corn oil (1:3) (- - -)

oil + Castor oil (1:1:1) (□ - G' , □ -

○ - G'')

Most of the emulsions (except those containing margarine) followed a gel like behaviour with the

range. Such behaviour is commonly seen in highly flocculated or nearly coalesced emulsions [13, 24].
 observed (a plateau region) for most of the tested samples, which has been related to the formation of an elastic structural network which confers a high stability to the emulsion [8, 25]. This characteristic progressively disappears as the content in margarine increases and it is absent for emulsions made with pure margarine.

The reason for such behaviour is that margarine is a pre-existing emulsion, made of 59% water, including surfactants, additives and flavouring agents and has only about 41% of lipids. This drastically alters the volume fraction of the dispersed phase and consequently the distribution of the oil droplets present in the final alumina emulsion-gel. After 72 hours of storage, on applying an oscillatory stress, this emulsion showed a highly viscous behaviour (liquid-like) at lower frequencies, in contrast to all the other samples, with a G_N^0 observed at higher frequencies (10 Hz). This behaviour suggests the presence of fluid emulsions composed of a weak network of entangled molecular chains and weak droplet interaction, as a result of intense structural changes, possibly involving droplet coalescence and Ostwald ripening effects with consequent phase separation [23].

value of the plateau modulus (G_N^0) which can be seen in Table S.1 (in S.I.) [26] as is the case of corn oil containing emulsions.

Over the 72-hours period, it was also apparent that G_N^0 for the pure corn oil and margarine systems decreased significantly; while for castor oil and the mixtures of corn oil (3:1) and margarine + corn oil + castor oil (1:1:1) indicating that these systems are stable. This stability is also confirmed by the absence of droplet coalescence effects along the emulsion storage, as evidenced by the negligible changes in droplet size as shown in Table 1. These emulsions seemed to have achieved a balance between the surfactant necessary for stabilizing the emulsion and the volume fraction of oil droplets present, reaching a stabilized emulsion with homogeneously dispersed droplets.

which means that the viscous component was gaining dominance over the elastic component, envisaging that with longer storage the de-stabilization of the emulsion may occur eventually showing the mechanical spectra of a predominantly viscous behaviour.

It is interesting to note that, in addition to

, the emulsion prepared with pure margarine exhibit a higher dependence of G' and G'' on the oscillatory frequency ω . This is indicative of a decrease of the emulsion cohesion, possibly due to the presence of limited flocculation but significant Ostwald ripening and coalescence, meaning that larger droplets are indeed formed but they are not interconnected. As explained before, this is probably due to the effect of the composition of margarine, which reduces the proportion of the dispersed phase (oil) in the emulsion, while affecting the emulsion stability. This effect is also observable in the other emulsions containing margarine, prepared with mixtures of oils, though it is somewhat mitigated due to the presence of castor and corn oils, decreasing the volume fraction of margarine in the emulsion. However, significantly larger droplet sizes are also observed in these mixtures, albeit interconnected.

Attempts to correlate rheology and microstructural parameters of high internal phase ratio emulsions may be found in the literature. Princen and Kiss [27] proposed an equation that related the low-strain storage modulus (G_N^0) and the Sauter mean droplet diameter ($d_{3,2}$), for highly concentrated poly dispersed emulsions as:

$$G_N^0 \propto \frac{\gamma}{d_{3,2}^3} \quad (\text{Equation 2})$$

This equation was applied to the data points obtained for the emulsion systems studied in the present work, by using the plateau modulus, G_N^0 (corresponding to the low-strain storage modulus) as [28]. By this relationship, for a system with a constant dispersed phase volume

interfacial tension and inversely proportional to the Sauter mean droplet diameter as seen in Figure 5 I and II. Though the proportionality varies with several other factors, there seems to be a general trend indicating the validity of the above relationship for the emulsions systems studied in the present work.

Studies were conducted for characterization of the microstructure of the *green bodies* after sintering combining information from SEM (Figures 1 I and II 3rd column) and mercury intrusion porosimetry analysis (Figures 6 I and II). According to the SEM images depicted in Figure 1 I and II all the samples appear to be highly porous with multimodal porosity and pore sizes.

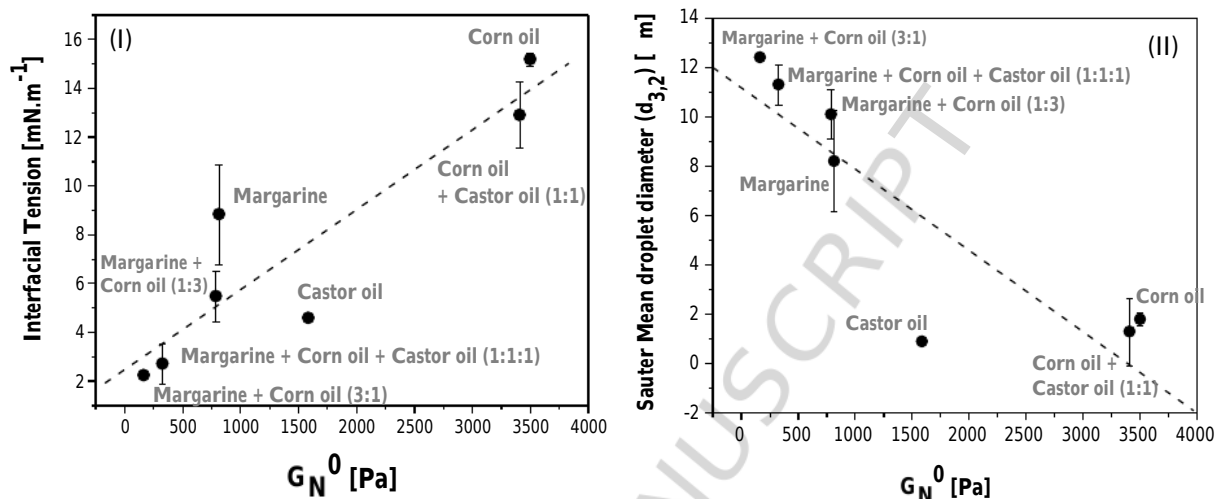


Figure 5. I) Interfacial tension vs. plateau modulus II) Sauter mean droplet diameter vs. plateau modulus for the prepared emulsions.

A typical monolithic structure, showing a hierarchical porous networks combining large cavities (formed by the burnout of the oil droplets) with smaller interconnecting pores (formed by the points where the droplets were contacting) was particularly evident for *green bodies* produced from pure corn oil, pure castor oil and the mixture of corn oil + castor oil (1:1).

The samples obtained from margarine containing emulsions (Figures 1 I - C.3 and Figure 1 II - B.3, C.3 and D.3) show dense surfaces with scattered defects corresponding to positions occupied by the larger droplets before sintering. Such structural differences were also confirmed by mercury porosimetry analysis which showed samples with low porosities of 32% (Figure 6 I) and a small average pore sizes of 200 nm (Figure 6 II), still amplified by the presence of large cavities (defects). As previously discussed, the use of margarine as a dispersed phase component lead to emulsions with weak structures, containing fewer droplets in a viscous flowing fluid unable to sustain suspended matter, where the aggregation of alumina particles is likely to occur, explaining the denser structure of the monoliths obtained.

The addition of corn oil as an emulsion component led to *green bodies* which appear to have some degree of interconnectivity by minute pores (Figures 1 I A.3, Figure 1 II - A.3, B.3, D.3 and E.3), with increased porosities (ranging 40% - 55 %) and average pore sizes, reaching particularly high

The impact of corn oil and margarine is also clear by analysis of the pore size distribution (PSD) profiles of the respective monoliths. Most of the monoliths exhibit two well defined bands located in different pore size microscale regions. Monoliths prepared using pure corn oil and margarine present bands located e predominance in each

Furthermore, monoliths prepared with emulsions containing both lipids (corn oil and margarine)

region remains in the same position, with maximum at 0.1-

However, and in contrast to that observed for monoliths prepared with pure corn oil, the contribution of the pore sizes in the smaller microscale is significant, explaining the lower average pore sizes observed for monoliths obtained with margarine + corn oil emulsions (Figure 6 II).

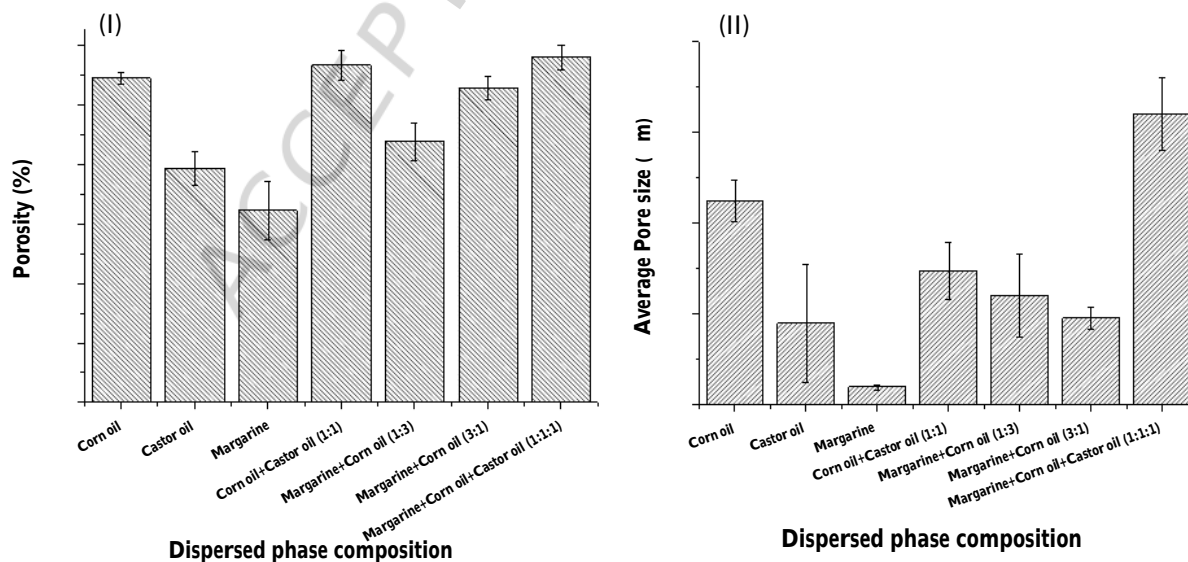


Figure 6. I) Values of porosity and **II)** average pore sizes of the monoliths prepared with different oils, after sintering, measured by mercury intrusion porosimetry.

The monoliths obtained with castor oil emulsions also depicted structures with small porosities of 40 % and average pore sizes of $0.1 \mu\text{m}$. In this case, the pore size distribution profile (Figure S.3 in S.I.) shows that there is no predominance of pores with a specific pore size, rather a wider distribution of pore sizes is observed.

The structural characteristics of these monoliths are associated with the small and highly stable droplet sizes observed in the emulsions obtained with pure castor oil (Table 1). Identical trend is observed for all the *green bodies* produced with other emulsions containing castor oil. Indeed, samples prepared from emulsions with corn and castor oils result in monoliths with high porosities resembling those obtained with pure corn oil but with lower average pore sizes due to the higher initial droplet size stability due to the presence of castor oil (Table 1). This effect is also clear by the relative

porosity of the monoliths prepared with corn oil + castor oil emulsions (Figures S.3 and S.4 in S.I.). However, one should bear in mind that the analysis of porous morphology based on mercury intrusion porosimetry only takes into account the presence of open pores permeable to Hg, which does not preclude the presence of closed pores in the monoliths. The presence of closed pores is suggested through microscopy images, especially observable for margarine-based emulsions systems (Fig.1 II B, C and D). Nevertheless, it is important to note that for most applications, such as those involving fluid flows only through-pores are significant.

Furthermore, correlations between some rheological and morphological properties of the emulsions and the final structural characteristics of monoliths were determined. The plots in Figure 7 show that the average pore sizes present a proportional tendency towards the interfacial tension between the phases of the emulsion. Also, a linear correlation was found between the pore sizes and the changes of plateau modulus (G_N^0) and the droplet size along storage. These correlations indicate that the average pore size of the monolith increases with the decrease of plateau modulus and with the increase of the droplet size. The observed variations of these parameters are concordant with the presence of droplet coalescence effects with storage. Hence, these correlations confirm that the formation of monoliths with larger pore sizes benefit from conditions that destabilize the emulsions inducing droplet coalescence effects, ultimately leading to the increase of the droplet size with storage.

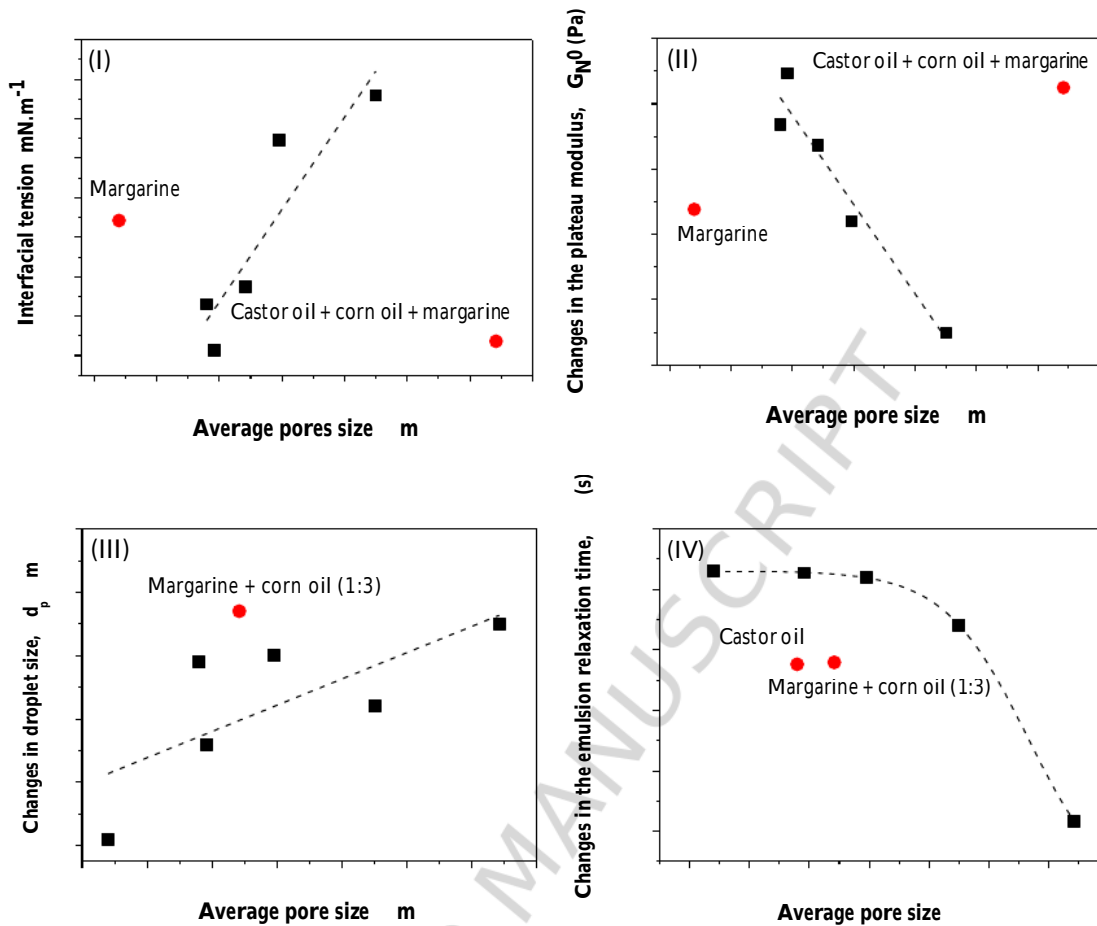


Figure 7. Correlation of the average pore sizes of the monoliths with the I) interfacial tension, II) changes in G_N^0 and III) changes in droplet size (d_p) and IV) changes in the emulsion relaxation time (τ) with storage.

In contrast a non-linear correlation was found between the average pore sizes and changes in the degree of dependence between the average pore size of the monolith and changes of the emulsion relaxation time is insignificant at low pore size range, as expressed by a plateau observed in this region. However, a transition from the steady regime (represented by a plateau at lower pore sizes) to The formation of monoliths with higher average pore sizes seems to be associated with the reduction of the emulsion relaxation time with storage. This relation may also be understood from the point of view of the structural characteristics of the emulsion, since a decrease of relaxation time indicates a

loss of structural cohesion which is generally associated with an increase of the droplet sizes and thus larger pore sizes.

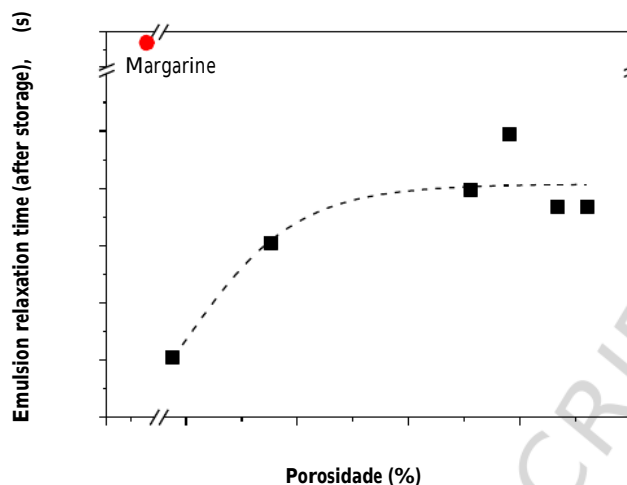


Figure 8. Correlation of the relaxation time of the emulsions after storage (72h) with the porosity of the monoliths.

Similar analysis was performed aiming to identify possible relationships between the emulsion properties and the monolith porosity. The porosity of monoliths seemed to exhibit a linear dependence N^0) with storage period and with the droplet size (Fig.S.5. in S.I.). However, in all cases, these correlations are mainly verified for emulsions containing margarine as component of the dispersed phase. The porosity of monoliths produced from emulsions prepared using corn oil and castor oils appear as outliers of these correlations. These results suggest that such correlations do not express a real dependence of the porosity on these emulsion parameters, but much likely a predominant and consistent effect of margarine on the monoliths structure, yielding monoliths with denser structures and thicker pore walls as observed in SEM images (Fig. 1 E.3, F.3, G.3).

The porosity of the monoliths was actually found to correlate with the emulsion relaxation time (Figure 8) observed after storage. Similarly, to that observed for the average pore sizes, a non-linear two-step relationship was found between the porosity and the emulsion relaxation time. The porosity of monoliths is positively dependent on the emulsion relaxation time, increasing with the increase of the relaxation time in the low porosity range (up to ~45%), and becomes independent from monolith porosity at values higher than 50%.

Mechanical strength is an important requirement for prospective applications of highly porous monolithic columns. Thus, compressive strength testing was carried out. The corresponding results, shown in Figure 9, are within the range reported for cellular ceramics [7-9, 29, 30]. The higher the porosity the weaker the column is expected to be.

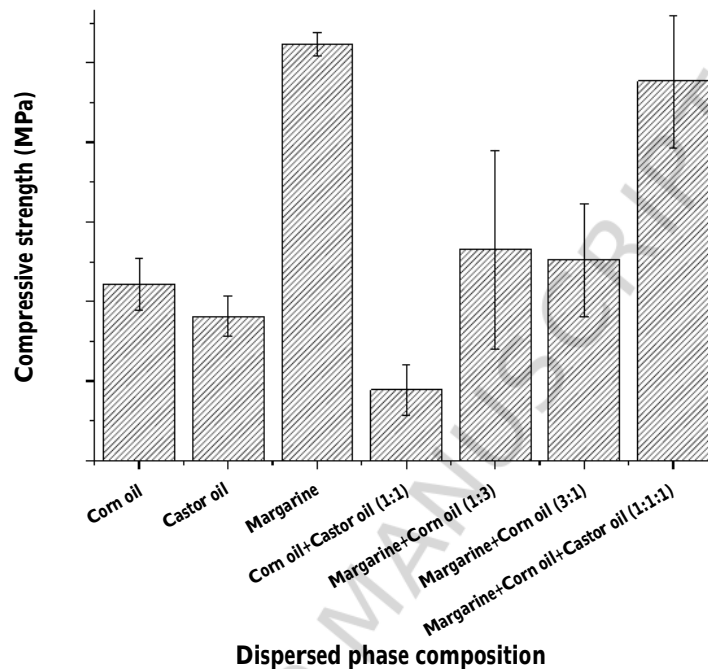


Figure 9. Measured compressive strength upon rupture for the monoliths prepared with different oils.

In concordance with this, the monolith columns made with margarine had the highest compressive strength due to a low porosity. Monolithic columns with higher porosity such as those prepared using emulsions containing castor oil and castor oil + corn oil mixtures showed the weakest compressive strength values. Surprisingly the monolithic columns prepared with emulsions containing margarine + castor oil + corn oil as the dispersed phase showed to have quite a high compressive strength, despite the high porosity. As suggested by the SEM image in Fig. 1 II D.3, monoliths prepared with margarine + castor oil + corn oil (1:1:1) emulsions seems to combine the multi-modal porosity resulting from the use of castor and corn oils with the high pore wall thickness due to the presence of margarine as an emulsion component, which may explain the high compressive strength shown by these monoliths.

4. Conclusions

Mechanically stable and highly porous cellular ceramics can be produced by emulsion gel casting with alumina suspension as the continuous phase and eco-friendly lipids as the dispersed phase, which

constitutes a viable alternative to the use of toxic and more expensive dispersed phases, e.g. alkanes. The structural characteristics of the monoliths may be tuned by suitable selection of the lipids (or lipid mixtures) forming the dispersed phase, since they dictate the behaviour of the emulsion-gel along aging (storage period). In this regard, storage and behaviour along storage may provide important insights about droplet coalescence, flocculation and ripening events occurring along emulsion aging and eventually explaining the final microstructure of the sintered green bodies. Emulsions prepared from pure corn and castor oils or a mixture with equivalent weight proportions of these led to *green body* structures resembling the typical monolith morphologies, i.e. high porosities (up to 58%), well interconnected pores and multimodal porous sizes - . Contrastingly, margarine emulsions led to *green bodies* with dense structures (low porosities and average pore sizes) and scattered large cavities (defects). Corn oil reduces emulsion stability, prompting more intense droplet coalescence and flocculation effects along aging, leading to the formation of *green bodies* with a more perceptible hierarchical porous structure, improved porosities and higher average pore sizes. The sintered *green bodies* produced also depict good mechanical resistance exhibiting compressive strengths in the range of 8 - 50 N.mm⁻². It is also important to highlight that it is possible to scale up the preparation of monoliths by emulsion-gel casting processes as long as a mixing system with appropriate dimensions is used, along with a proportional increase in the chemical components while maintaining the geometry and aspect ratio of the system. Furthermore, it was demonstrated in this work that some rheological and morphological properties of the gel-emulsions (i.e. interfacial tension, droplet size, relaxation time and storage modulus) are correlated with monolith structural descriptors, i.e. the average pore size and porosity. The correlations established provide the possibility to anticipate the final microstructural features of the monoliths based on easy measurable emulsion-gel properties. The design of monoliths with fine-tuned morphologies is regarded as an important aspect since it directs the production of porous medium, for chromatography and membrane based separations, in a way to fulfil the requirements of a wide range of purification processes, privileging the efficiency of separation processes.

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Data accessibility statement

The data described in the present work will be available upon request by email to cmp@fct.unl.pt.

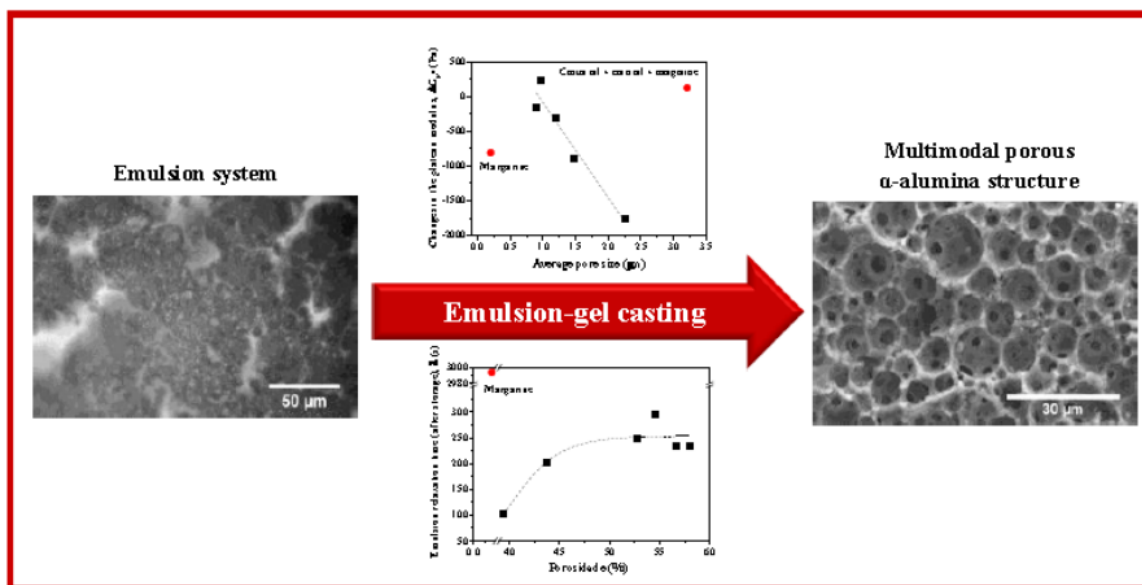
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Graphical Abstract



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Highlights

Multimodal porous alumina cellular structures were produced by emulsion-gel casting using non-toxic dispersed phases

Formation of porous network interpreted based on droplet coalescence, flocculation and Ostwald ripening effects

Correlations were found between monolith structural descriptors and the change of viscoelastic and morphological properties of emulsions along storage

Pore size distribution of sintered monoliths are favoured by the presence of droplet coalescence effects

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