Morphology of latex and nanocomposite adsorbents prepared by freeze-casting†

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Freeze-casting liquid dispersions of solid particles is a useful alternative for synthesizing porous solids, thus creating lightweight and mechanically resistant materials for various applications. This work describes and discusses different morphologies obtained by freeze-casting poly(styrene-acrylic) latex aqueous dispersions, either pristine or foamed, and compares them with those prepared by the addition of nanoclay. The surface area and dye sorption capacity of freeze-cast latex–clay nanocomposite monoliths are much higher than those of the freeze-cast latex only and the pore morphology is also different in these solids. The freeze-cast polymer displays an interesting morphology including a fishbone shape unprecedented in non-crystalline solids cast from aqueous media. Quite differently, the latex–clay nanocomposite exhibits only lamellar pores with irregular features on their walls. These differences are assigned to the stiffening role of the clay lamellae in the rubbery polymer, reducing the extent of particle aggregation and coalescence and thus preserving voids. Dispersion foaming prior to freeze-casting produces additional features in the solids but without making a positive contribution to the surface area and dye sorption capacity. These results are understood considering pore templating by ice crystal growth and the templating effect of clay particles on fine ice morphology.

A great variety of methods have been utilized to obtain porous and/or aligned materials including gel casting,18 gas bubbling,11 dense gas foaming,12 spray-drying,13 electrospinning,8 layer-by-layer15 and eutectic growth19 but the freeze-casting process is simple and environmentally friendly.17

The freeze-casting process, based on the lyophilization of a frozen suspension within a mold, enables the formation of porous structures which replicate ice crystals formed under steep temperature gradients resulting in materials with oriented pores.18-21 This produces singular permeation properties coupled with a high specific surface area, in addition to mechanical strengthening in a specific direction due to the anisotropic pore structure.19-22 Moreover, several factors can be used to control the pore size, such as the use of additives,17 the solidification rate, the use of different solvents and polymers23 and solid content of the initial suspension.18,23,24

Because of its versatility, freeze-casting has been applied to a wide range of materials from polymers to ceramic suspensions,17,25-27 metals and their composites28 targeting mechanically resistant18,29 and/or absorbent/adsorbent lightweight materials.10-32 However, reports about using freeze-casting in order to shape structured adsorbents are sparse and focus solely on the use of zeolites.31,32 Similarly, there are few reports on polymers with clay nanocomposites synthesized by freeze-casting, targeted for strengthening ceramics.17,25,27

Layered silicates (clays) such as sodium montmorillonite are easily available and have been widely used in polymer matrices to improve the thermal, mechanical and solvent resistance of

Introduction

Currently, efficient removal of dyes from wastewater is essential since their discharge into water bodies is strictly prohibited worldwide and affects both aquatic life and water quality.1 Commonly used methods for dye removal include adsorption, photocatalysis, dye coagulation/floculation, membrane filtration, photodegradation and biodegradation. Among these, adsorption is widely used due to its low cost, high efficiency and simplicity.2

Several porous materials have been employed as adsorbents, such as activated carbon and carbon nanotubes,3 clays,4 hybrid aerogels,4 and natural and synthetic polymers and their composites.5-7 Polymer materials are used to design structured porous and surface morphology and are found in a wide range of applications, from tissue engineering6 to automotive parts and process intensification.8

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†Electronic supplementary information (ESI) available: (1) Description and picture of the home-made apparatus; (2) pictures showing water resistance and no significant dimensional changes before and after two years of water immersion; (3) plots showing water sorption by the freeze-cast foamed latex and nanocomposite monoliths. See DOI: 10.1039/c4ta05743k
nanocomposites. Furthermore, clays are used to adsorb water soluble pigments and dyes from major sources of environmental pollution (textiles, printing, dyeing, etc.).

Gawryla and Schiraldi used different water-soluble synthetic polymers (poly(vinyl alcohol), poly(acrylic acid), poly(ethylene oxide) and poly(ethylene glycol)) to improve the mechanical strength of sodium montmorillonite aerogels, with densities typically from 0.01 to 0.1 g cm$^{-3}$. They obtained freeze-cast lightweight highly absorbent nanocomposite aerogels. These aerogels have a lamellar structure resulting from the alignment of clay particles along the ice crystal faces, which opens up the possibility of obtaining nanocomposites with good compressive strength, since clay lamellae can orient forming columns.

Besides the polymer materials mentioned above, latex was used only to produce natural rubber latex (NR) nanocomposites with a range of clay contents by freeze-casting. In these cases, clay contributed a regular layered morphology.

The present work also describes freeze-cast clay–polymer nanocomposites but using a latex with $T_g$ in the room-temperature range which is much higher than that of natural rubber. Morphologies templated by ice are thus preserved at room temperature.

**Experimental section**

**Materials**

Sodium montmorillonite (NaMMT) was acquired from Southern Clay Products (cation exchange capacity = 102 mequiv. per 100 g clay). Methylene blue (MB) dye was from Synth. The poly(styrene-butyl acrylate-acrylic acid) latex (P(S-BA-AA)), with 32% dry weight, $T_g = 51 \pm 1 ^\circ C$, 55 nm particle diameter ($\theta$) and $-10 \pm 2$ mV zeta potential ($\zeta$), was prepared in this laboratory as reported by Keslarek et al.. Other samples of styrene-acrylate were poly(styrene-butyl acrylate) (P(S-BA)) commercial resins, Acronal 295 D (53% dry weight, $T_g = 25 \pm 1 ^\circ C$, $\theta = 100$ nm, $\zeta = -80 \pm 2$ mV) and Denvercril RA 193 (51% dry weight, TMFF = 18 $^\circ C$, $\theta = 55$ nm, $\zeta = -11 \pm 2$ mV), supplied by BASF (São Paulo, Brazil) and Denver (São Paulo, Brazil), respectively. Milli-Q deionized water was used throughout.

**Composite preparation**

NaMMT was dispersed in water with continuous stirring using a blade propeller at 1000 rpm for 24 h to yield a 2.65% w/w clay dispersion. The nanocomposite containing 6% clay (relative to total solids in dry samples) was prepared by mixing 7.7 g clay dispersion with 10 g latex. The mixture was slowly homogenized for 10 min at room temperature, using a magnetic stirrer to yield an aqueous precursor dispersion containing 1.15% w/w clay. The latex and its nanocomposite were also foamed using a blade propeller at 1500 rpm for 10 min, yielding samples with about twice the volume of the liquid samples. Each suspension (1.0 mL) was transferred to cylindrical glass molds (4.0 cm length, $\theta = 1.1$ cm), immediately dipped into liquid nitrogen and kept for 10 min (although freezing time was only 1 min). The bottom of the molds came into contact with liquid nitrogen first, in order to induce unidirectional freezing. The molds were placed within 250 mL round bottom glass flasks previously cooled by immersion in liquid nitrogen and subsequently mounted on a home-made freeze-drying apparatus (described in the ESI, Fig. S1†), operating at 90 mmHg for 6 h.

Larger monoliths required for apparent density determination and compression tests were prepared by pouring 20.0 mL of each suspension into $\theta = 50$ mm glass Petri dishes, frozen in the same way and freeze-dried (freeze-dryer Terroni, model LB 300 TT (São Carlos, SP)) at low pressure (0.001 mmHg) for 24 h. For the sake of comparison, the latex and its nanocomposite were air-dried at 60 °C. The schematic illustration of experimental steps for sample preparation is shown in Fig. 1.

**Scanning electron microscopy (SEM)**

Microscopy and microchemical analyses were done on a JEOL JSM-6360 LV scanning electron microscope, using Secondary Electron Imaging (SEI) and Backscattered Electron Imaging (BEI). Energy Dispersive X-ray Analysis (EDX) was done on the same microscope as a Noran System Six microanalysis system. A Supra 55VP ZEISS field emission SEM was also used. Monolith sections were cut at room temperature using a razor blade, placed on a carbon sample holder and coated with a thin carbon layer, using a MED 020 Sputter (BalTech).

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**Fig. 1** Preparation of freeze-cast and air-dried (ad) poly(styrene butyl acrylate lacrylic acid) latexes and their nanocomposites.
Average pore size and surface area

At least 9 features (pore size, lamellar spacing and/or lamellar thickness) were measured from SEM micrographs using the Image Pro Plus 4.0 software. The average pore size and surface area were also determined from nitrogen adsorption experiments using an ASAP 2010 apparatus from Micromeritics.

Density and porosity

The apparent density and porosity of dry monoliths were calculated using a pycnometer and distilled water as the immersion fluid. Samples between 0.4 and 0.65 mm³ were weighed in an analytical balance (Mars-220 AM; \(d = 0.0001\) g) and immersed at room temperature in a weighed 50 mL pycnometer pre-filled with water. Assays were performed in triplicate for each sample.

Adsorption tests

Ca. 0.15 g of each freeze-cast adsorbent was added to 4 mL of 300 mg L⁻¹ MB aqueous solution and left under constant stirring by inversion (18 rpm), at 25 °C for 1 h. The same procedure was repeated using 0.009 g clay as the adsorbent, but in this case, the flasks were centrifuged for 10 min at 2500 rpm, in order to separate clay particles from the supernatant after contact. The supernatant absorbance at 665 nm was measured using a UV-Vis spectrophotometer (Pharmacia). Triplicate assays were made for each sample.

Compression tests

Cylindrical specimens (\(Ø = 5.5\) mm and thickness between 4 and 5 mm) were subjected to uniaxial compression under 1–400 g weights. The load was gradually increased until the specimens collapsed and the resulting deformation was measured with a digital Mitutoyo micrometer. The compressive modulus was calculated from the linear elastic range (strain < 15%) of the stress-strain curve. The comparison of stress values is presented at 50% strain. Assays were performed in triplicate for each sample.

Results and discussion

General features of samples

The freeze-cast monoliths have similar features (Fig. 2a), and they are easy to handle but they undergo permanent deformation by compression. Reflectance (1 – transmittance) values of the samples were 0.98 for the freeze-cast monolith and 0.43 for an air-dried sample with the same weight per unit area. The opacity is due to light scattering by the air-filled pores. As expected, the non-porous polymer film (Fig. 2b) is translucent.

Fishbone morphology development

The SEI micrograph of cut surfaces of the freeze-cast latex shows a complex dendritic/fishbone morphology (Fig. 3a) of oriented anisotropic pores which is unusual in amorphous polymers although it resembles “shish-kebab” structures found in semicrystalline polymers. This morphology is observed throughout the monoliths meaning that dendritic ice crystals are easily grown and do not stop growing until the limits of the glass mold are reached, characterizing a steady state growth.

The fishbone morphology is unprecedented in freeze-cast monoliths prepared from common amorphous polymers in aqueous media but similar structures were obtained using more complex systems: quasiternary polyethylene/hexamethylbenzene/adamantine eutectic and also isotactic polypropylene and pentaerythrityl tetrabromide eutectic, 1,2,3,4,6-pentaacetyl \(\beta\)-D-galactose (BGAL) dissolved in liquid carbon dioxide, porous silicon carbide (SiC) ceramics produced by freeze-casting polyacarbolosine/camphene solution and poly(\(\alpha\)-lactic-co-glycolic acid) scaffolds prepared by using 1,4-dioxane as solvent.

The BEI micrograph (Fig. 3b) shows a lamellar morphology with fishbone structures on their faces and rather a uniform gray tone, evidencing low component segregation, during the
formation of this elaborate morphology. Based on these micrographs we can infer that during sample freezing, lamellar ice crystals grow along the temperature gradient while smaller side branches grow at an angle. The formation of dendrites on lamellar ice crystals occurs under very high cooling rates and results from the balance between two directions of ice crystal growth: one parallel to the temperature gradient and the other along the preferred direction of crystal growth, determined by interfacial energies.\textsuperscript{24}

**Morphological transitions**

In addition to the fishbone morphology, the freeze-cast latex shows a variety of pore morphologies templated by different ice crystal habits (planar, columnar, lamellar) formed by time-dependent crystal transitions, as previously reported for directional freeze-casting in ceramic and polymer materials.\textsuperscript{18,24,43,48–51} Such transitions of ice were clearly evidenced by observing the SEM images of freeze-cast hydroxyapatite\textsuperscript{43} and alumina suspension,\textsuperscript{24} and can be triggered by a Mullins–Sekerka instability.\textsuperscript{52} Other instabilities related to the size and concentration of particles, in addition to solidification kinetics, may also influence this process, but it is not clear at this point which of these mechanisms is dominant.\textsuperscript{18,24}

A representation of the morphological transitions of the ice crystal is shown in Fig. 4. Three distinctly different ice structures are formed due to different temperature gradients at different locations within the sample, following previous reports.\textsuperscript{24,43,51,54} According to this mechanism, as the ice front advances, the temperature gradient is reduced and ice crystals undergo transitions that are time-dependent, which are spatially registered in the sample.\textsuperscript{18,21,24,43}

Initial stages of sample freezing close to the container walls produce particles entrapped in the first frozen zone. Then, the interface moves progressively forming columnar and lamellar ice structures, excluding particles and yielding elongated and layered pores, respectively.\textsuperscript{18,41} This is also observed in the present work. A cellular pore morphology (Fig. 5) is observed near the glass wall while an elongated pore morphology (Fig. 6a) is observed up to 2 mm away from it.

Subsequently, morphological sidebranching instability takes place substituting lamellar pores for a dendritic shape.\textsuperscript{24,55} This transition occurs under very high cooling rates and it results

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**Fig. 4** Scheme of morphology changes during latex freezing.

**Fig. 5** SEI micrographs of freeze-cast poly(styrene-butyl acrylate-acrylic acid) show (a) flat walls formed in contact with the container walls and cellular pores and (b) magnification of cellular pores of the region outlined in black in (a).
from the balance between two directions of ice crystal growth: one parallel to the temperature gradient and the other along the preferred direction of crystal growth, determined by interfacial energies.\textsuperscript{24} Thus, the morphological diversity observed in this work is explained by ice crystallization at different temperatures and temperature gradients, depending on the distance from the container walls. The same latex dried at 60 °C imaged under higher magnification (Fig. 6b) shows fewer pores on its surface (probably templated by air bubbles), with an average diameter of 0.24 ± 0.05 μm and thus much smaller than the pores obtained by freeze-casting.

Morphology after clay addition

Clay introduces significant changes in pore morphology with the prevalence of lamellar architecture (Fig. 7a) carrying small pores (Fig. 7b and c) and the absence of fishbone morphology. The surface area is about 80 ± 20 times higher while the average pore size is 1/140 that of the plain polymer (Table 1). On the other hand, foamed samples do not show significant changes in surface area due to clay addition.

Differences between average pore sizes determined from BET and SEM micrographs (Table 1) also indicate the existence of a second level porosity in non-foamed samples, as recently observed in a work of Hunger and co-workers,\textsuperscript{36,57} in which BET measurements confirmed the existence of nanoporosity indicated in SEM micrographs of freeze-cast chitosan/gelatin/alumina composites.

Similar lamellar structures were obtained in porous alumina ceramics freeze-cast from aqueous dispersion.\textsuperscript{24} The authors assigned it to homogeneous ice nucleation coupled with particle exclusion by the advancing solidification front forming a lamellar or columnar ice morphology, while roughness on the walls was assigned to ceramic particles trapped in between the ice dendrites.\textsuperscript{24} In two other publications, separate parallel lamellae were also observed in the microstructure of freeze-cast glycerol-plasticized casein scaffolds with and without clay, respectively.\textsuperscript{36,57}

When a polymer-clay nanocomposite is dried under air, lamellae of the clay tend to align parallel to each other, creating extensive domains stabilized by electrostatic adhesion.\textsuperscript{33,58} Transmission Electron Microscopy (TEM) pictures of both poly(styrene-co-butyl acrylate-co-acrylic acid) latex and natural rubber and its clay nanocomposites were previously published by this group and show exfoliated clay lamellae together with some very small tactoids, for both polymers. TEM micrographs never show void formation or ruptured film areas in the polymer-clay platelet interface, evidencing strong polymer–particle adhesion.\textsuperscript{33,58} Clay interacts strongly through ionic bridges formed by the ions trapped between the latex particles and the clay platelets.\textsuperscript{19} When the sample is freeze-cast, a lamellar morphology prevails because clay particles line-up parallel to the ice crystal faces during freezing, from aqueous precursor dispersion with clay concentration higher than 0.7% (w/w).\textsuperscript{29,38,59} Below this concentration, added clay did not self-assemble\textsuperscript{29} and in our case, clay concentration (1.15% w/w) in the aqueous precursor dispersion was sufficient to produce this morphology. Furthermore, clay platelets act as barriers to...
propagation of ice crystal growth due to their stiffening effect and large aspect ratio.\textsuperscript{24} Details of dendritic crystals like their fine branches are thus lost and fishbone features are not observed. The same effect on the otherwise interdendritic spaces was previously observed with alumina particles of different sizes.\textsuperscript{18,21}

Deville and co-workers also observed that the growth pattern produces roughness/dendrites on only one side of lamellae,\textsuperscript{24} directly related to the morphology of the solvent crystal.\textsuperscript{18} However, in the present work, the roughness of the freeze-cast nanocomposite (Fig. 7a) and the fishbone morphology of the freeze-cast latex (Fig. 3) have been obtained from the same solvent and observed on both sides of lamellae.

BEI micrographs of nanocomposites (Fig. 7b, c and 8) show some brighter domains that correspond to areas with a higher average atomic number. X-Ray energy-disperse spectroscopy identified carbon, oxygen, sodium, aluminum, silicon and sulfur in these spots, while the elemental maps revealed that some spots are composed predominantly of oxygen, sodium and sulfur elements while others contain oxygen, aluminum and silicon. This information evidences that aggregates contain respectively sodium sulphate (from the latex polymerization initiator, sodium persulfate) and sodium montmorillonite.

**Morphology of the foamed latex**

The cut surfaces of monoliths obtained from the foamed latex shows interconnected spherical cavities distributed throughout

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
Sample & Morphology & SEM micrographs & Lamellar spacing (µm) & Lamellar thickness (µm) & Average pore size (μm) & BET analysis & \\
\hline
& & & & & & & \\
Latex & Cellular & — & — & 2.7 ± 1.2 (100) & 0.51 ± 0.21 (2) & — & 331.0 ± 5.0 (2) \\
& Elongated & — & — & 7.3 ± 3.9 (36) & — & — & — \\
& Lamellar & 7.0 ± 1.1 (19) & 2.5 ± 0.7 (19) & — & — & — & — \\
& Fishbone & — & — & 4.3 ± 1.6 (20) & (6.5 ± 1.6) 10 (20) & 5.1* & — \\
& & Lamellar & 67.4 ± 1.5 (9) & 13.2 ± 1.6 (10) & 2.0 ± 0.29 (17) & 4.2 ± 1.3 (17) & — & — \\
Latex + NaMMT & Roughness & — & — & 9.7 ± 2.8 (10) & 3.2* & — & — \\
& Cavities & — & — & 2.3 ± 0.65 (11) & (9.7 ± 2.8) 10 (15) & — & — \\
& Fishbone & — & — & (3.4 ± 1.5) 10 (20) & — & (3.4 ± 1.5) 10 (20) & — \\
Foamed latex & & Lamellar & 3.8 ± 1.8 (19) & 2.3 ± 0.65 (11) & (6.5 ± 1.6) 10 (20) & 3.2* & — \\
& & Cavities & & & 2.0 ± 0.29 (17) & 4.2 ± 1.3 (17) & — \\
& & & & & & & — \\
Foamed latex + NaMMT & & Lamellar & & & 2.0 ± 0.29 (17) & 4.2 ± 1.3 (17) & — \\
& & Cavities & & & 9.7 ± 2.8 (10) & 3.2* & — \\
& & & & & & & — \\
& & & & & & & — \\
\hline
\end{tabular}
\caption{Structural properties of freeze-cast samples\textsuperscript{a}}
\end{table}

\textsuperscript{a} Numbers inside the parentheses indicate the number of replicates. Superscripts F and L indicate foam and liquid regions for the same sample. — Not applicable. * Measurements without replicates. ** Not measured.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig8.png}
\caption{X-Ray spectrum, BEI micrograph and the corresponding EDX elemental distribution maps of the freeze-cast poly(styrene-butyl acrylate-acrylic acid)–clay nanocomposite. Note the correspondence between bright spots in the BEI image and dotted areas in elemental maps. Al and Si accumulate together, as well as Na and S.}
\end{figure}
(Fig. 9) containing smaller pores with fishbone morphology on their walls. The addition of the clay dispersion to the foamed latex decreases the foam stability and the liquid drains faster, leaving residual foam at the top and liquid at the bottom of the glass mold.

The SEM micrograph of the cut surface in Fig. 10a shows the contact area between foamed and drained liquid regions. The former (with the circled area) contains rounded structures while the latter (with a square) is similar to Fig. 6a. The cavities templated by air bubbles in Fig. 10b show smaller lamellar pores, similar to the frozen nanocomposite without foaming. Akin foam morphologies were obtained by using the styrene–divinyl benzene polymer to obtain a material with 90 vol% porosity and high relative water adsorption, with potential use as a soil additive in agroprocess intensification, but by using a more complex procedure.9

Results obtained using commercial latexes

The results presented so far in this report refer to the P(S-BA-AA) latex obtained in this laboratory and its nanocomposites, but both lamellar and fishbone morphologies were also obtained with two commercial styrene-acrylic latexes (Fig. 11 and 12).

Dye adsorption

Adsorbate removal by freeze-cast monoliths ranged from 3.1% (foamed latex) to 99.8% (foamed latex + NaMMT) (Fig. 13). For the sake of comparison, a nanocomposite film prepared by
casting and a clay dispersion, both with the same amount of clay contained in freeze-cast nanocomposites, were used as adsorbents.

Clays are good adsorbents because of the existence of several types of active sites on the surface, which include Brönsted and Lewis acid sites besides ion exchange sites. Latex samples with clay show almost the same capacity to adsorb dyes as the clay dispersion itself, showing that the freeze-cast nanocomposites may be used as convenient, pelleted adsorbents, with great application potential in dye removal from aqueous solution (ESI, Fig. S2 and S3†).

The mechanical strength and water stability of the monoliths can probably be improved by cross-linking, but this was not attempted in this work.

Dye removal using the cast nanocomposite film increases from 57% to 81% by increasing the contact time from 1 to 4 h, while dye removal reaches 99% using freeze-cast nanocomposites, after 1 h. According to previous publications, when a nanocomposite film is prepared by casting, positive counterions of the styrene-acrylic latex or natural rubber particles form ionic bridges, responsible for strong adhesion between clay and latex particles that (both) contain excess negative charges. These strong cation binding sites account for MB adsorption. The interaction between the filler and the latex matrix is electrostatic. Since strong binding sites are formed at clay–polymer interfaces, we expect that adsorption capacity increases with filler volume fraction. This is an important question to be answered by future (and extensive) work.

Following the previous work of Braga et al. and our own observations in the laboratory, dye desorption from the casting and a clay dispersion, both with the same amount of clay contained in freeze-cast nanocomposites, were used as adsorbents.

Fig. 12 SEM micrographs of freeze-cast porous poly(styrene butyl acrylate) from Denver show cross-section perpendicular to the ice front (a) and roughness details of the region outlined in black (b).

Fig. 13 Removal of aqueous methylene blue solution (300 mg L⁻¹) with time in the presence of clay dispersion (2.25 mg mL⁻¹) and different freeze cast adsorbents (35 mg mL⁻¹). The air-dried sample is indicated by ad.

Fig. 14 (a) Compressive stress–strain data for all samples and (b) triplicate measurements for the foamed poly(styrene-buty1 acrylate-acrylic acid)/clay nanocomposite. Continuous lines are just connecting the experimental points.
The freeze-casting process is slow and incomplete. Dye molecules are trapped at the clay–polymer interface benefiting from a strong electrostatic attraction and also from polymer hydrophobicity that is absent at clay-only adsorption sites.

Although the removal of MB by clay dispersions and different clay nanocomposites have been previously studied, freeze-cast nanocomposites are the first examples of effective lamellar adsorbents prepared from common amorphous polymers and clay. These results reveal the great potential of freeze-casting in the field of water remediation. In structured adsorbents, lamellar structures with sufficient small spacing and width (<0.2 mm) are promising structures with enhanced mass transfer compared to pellets, monoliths or foams with the same density.

**Compression tests**

The compression results (Fig. 14) show an initial linear elasticity due to elastic cell wall bending when the strain is less than 15%. Increasing strain causes plastic deformation and finally, densification. These deformation steps are also observed during compression of polymeric foams like epoxy, foamed latex rubber and cellulose nanowhisker reinforced acrylic foams synthesized by freeze-casting.

Comparing the nanocomposite (porosity = 79%) with the foamed latex (porosity = 81%) (Table 2) we can infer that an additional improvement in compressive stress for non-foamed samples could be assigned to their anisotropic lamellar structure while foamed samples have only random isotropic cavities.

A similar behaviour has been observed in a recent study by Xu and co-workers, in which acrylic foam samples reinforced with cellulose nanowhiskers (CNW) were prepared by both directional and non-directional freeze-casting. Improvements in mechanical properties along the loading direction of freeze-cast samples were attributed to reinforcement by CNWs added to the reduction of cell size and cell alignment.

**Conclusions**

Freeze-cast latex and latex–clay nanocomposites are low density porous solids with various pore morphologies (fishbone, lamellar, cellular) templated by ice crystals. The fishbone complex morphology is assigned to ice crystallization along the freezing temperature gradient combined with the formation of side branches growing normal to the temperature gradient. Hierarchical solid foams carrying dendritic and lamellar pores along the walls of cavities that are in turn templated by air bubbles were also obtained. The formation of complex porous structures produces a water-insoluble porous nanocomposite that can be used as a dye sorbent as effective as exfoliated clay in water. This is the first example of nanocomposite adsorbents prepared by freeze-casting.

**Acknowledgements**

L.L.S. thanks the CNPq fellowship. This is a contribution from the INCT Inomat, a project supported by Brazilian agencies MCTI/CNPq and Fapesp. We would also like to thank Ziarat Shah for synthesizing the P(S-BA-AA) latex.

**Notes and references**


**Table 2** Density, porosity and stress–strain data for freeze-cast and air-dried samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (g cm&lt;sup&gt;–3&lt;/sup&gt;)</th>
<th>Porosity (%)</th>
<th>Stress at 50% strain (kPa)</th>
<th>Compressive modulus (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latex</td>
<td>0.3438 ± 0.0005</td>
<td>66.2 ± 0.9</td>
<td>119 ± 7</td>
<td>23.4 ± 3.3 (10)</td>
</tr>
<tr>
<td>Latex + NaMMT</td>
<td>0.211 ± 0.003</td>
<td>78.5 ± 0.3</td>
<td>43 ± 5</td>
<td>85 ± 3</td>
</tr>
<tr>
<td>Foamed latex</td>
<td>0.183 ± 0.003</td>
<td>81.4 ± 0.9</td>
<td>27 ± 4</td>
<td>64 ± 4</td>
</tr>
<tr>
<td>Foamed latex + NaMMT</td>
<td>0.101 ± 0.007</td>
<td>89.9 ± 0.7</td>
<td>5 ± 1</td>
<td>15 ± 4</td>
</tr>
<tr>
<td>Latex/a-d&lt;sup&gt;b&lt;/sup&gt;</td>
<td>≈ 1</td>
<td>≈ 0</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>Latex + NaMMT/a-d&lt;sup&gt;b&lt;/sup&gt;</td>
<td>≈ 1</td>
<td>≈ 0</td>
<td>a</td>
<td>a</td>
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<sup>a</sup> Not measured. <sup>b</sup> Air-dried samples are indicated by a–d.