

Preparation and Foaming of Nanocomposites in Supercritical CO₂

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In this study poly(D,L lactic acid)/clay nanocomposites were prepared and porous microcellular materials were fabricated using supercritical carbon dioxide as foaming agent. The morphology of the produced porous polymer/clay systems was investigated using scanning electron microscopy (SEM). Image processing of the samples uncovered the relation of the final cellular structure with the alkylammonium type and the cation exchange capacity (CEC) of the modified clay used as the nanofiller.

INTRODUCTION

An alternative, yet well established, technique in foaming of polymers is that of using supercritical fluids (SCF). The main advantage of this technique over others is that it entails an environmentally friendly blowing agent, which is also nontoxic, non-flammable, and chemically and thermally stable, such as CO₂. All of these characteristics make SCF a most favourable choice as a processing medium for foaming polymers. Various polymer–gas systems have already been studied [1,2] and, most recently, a variety of nanocomposite systems has been also investigated [3-5]. Most of these studies report on the effect of the filler – such as clays – on the transport of gases in polymers in relation with the supercritical conditions (temperature and pressure dependence) used and/or the filler's loading in the nanocomposite. However, less attention has been paid on the effect of the nanofiller's modification and its surface chemistry on the final porous structure, which is the objective of this study.

MATERIALS AND METHODS

The biodegradable aliphatic polyester poly(D,L lactic acid) (PDLLA) (12% content in D-lactide stereoisomer) was the polymer matrix used and was purchased by Galactic with $M_n=68000$ and $M_w/M_n=2.8$. The nanoclay used for the modifications was sodium montmorillonite (NaMMT) (CEC = 92.6 meq/100 g clay) by Southern Clay Products (Texas, USA). All the amines, dichloromethane (CH₂Cl₂) and triethylene glycol (used for the density measurements of the porous materials) were obtained from Sigma-Aldrich without any further purification. CO₂ was obtained from Air Liquide Méditerranée (>99.98% purity).

Modification of sodium montmorillonite has been performed via an ion-exchange reaction with alkylammoniums resulting in two different series of clay products. One series of modified montmorillonite were prepared using alkylammonium surfactants where the number

of carbon atoms in the attached chains was differing (4, 8, 12, 16 and 18C-ammonium), while the alkylammonium concentration was kept equivalent to 1.5 times the CEC of the clay. The other series was prepared by using only hexadecylammonium for the modification and by varying the modification level from 50 to 200% of the clay CEC. Further details on clay modification were reported on a previous study [6].

Two series of nano-hybrid films were subsequently fabricated from a poly(DL-lactic acid) solution loaded with 3 wt% of organically modified montmorillonite from the two previously prepared series. The fabrication of nanocomposite materials was conducted according to the solution casting routine as described in reference [7]. Following the same procedure two more samples of pure polymer and polymer with 3 wt% of unmodified (sodium) montmorillonite (NaMMT) were also prepared for comparison reasons. All samples were, subsequently, formed in compression-molded discs (at 90 °C and 100 bar) in order to obtain the same uniform thickness (0.75 mm) for foaming treatment and characterization.

The effect of the surfactant type and its organic cation concentration during clay modification on the final porous structure was investigated through a series of experiments where all the other parameters were kept constant as summarized in Table 1. Clay loading, saturation pressure and temperature constant values were chosen according to previous studies focused on the role of these parameters on the porous structures of a similar system i.e. neat and nanocomposite poly(L-lactic acid) [5,8].

Table 1: Experimental conditions for the supercritical treatment of the two series of nanocomposites.

Parameters	1st series of nanocomposites: alkylammonium type varying	2nd series of nanocomposites: CEC varying
% CEC	150	50, 75, 100, 150 and 200
CH ₃ (CH ₂) _{n-1} NH ₃ Cl (Surfactant)	n=4, 8, 12, 16, 18	n=16
Clay content, wt%	3	3
Pressure, bar	150	150
Temperature, °C	45	45

The microcellular porous structures of pure and nanocomposite poly(DL-lactic acid) here were prepared with the batch foaming technique (pressure quench) using supercritical CO₂ as blowing agent. The compression-molded discs were placed in the high pressure vessel under CO₂ atmosphere at 150 bar and 45 °C for at least 4 hours in order to allow CO₂ to be sorbed into the polymer matrix and the sample to be saturated. Then, the system was quenched in a supersaturated phase by rapid depressurization (in less than 10 s). The experimental apparatus is presented in Figure 1 as well as the phenomena that take place for the evolution of the final porous structure.

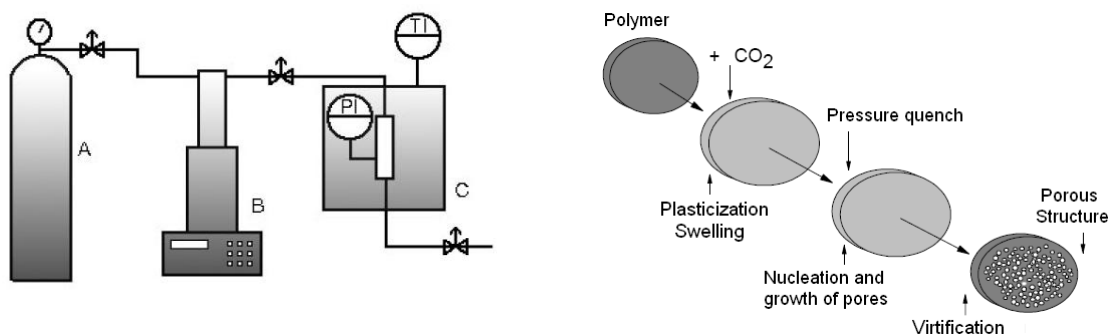


Figure 1: At the left is the schematic diagram of the experimental apparatus: (A) CO₂ tank; (B) syringe pump; (C) pressure vessel and at the right an overview of the procedure.

The morphology of the nanohybrids was investigated by X-ray diffraction analysis (XRD) using a Rich. Seifert 3003 TT diffractometer with Ni-filtered CuK α radiation ($\lambda=0.154$ nm). The scanning range of interest was varied from $2\theta=1.5^\circ$ to 10° with a step of 0.01 and a measuring time of 15 s per step. The porous samples were freeze-fractured in liquid nitrogen and their cross-sections were examined by Scanning Electron Microscopy (SEM) (JEOL, mod. JSM-840A). All surfaces were coated with graphite to avoid charging under the electron beam. The image processing was performed using an image analyzer with the appropriate software (Image J). Samples were examined under the microscope and two magnifications ($\times 400$ and $\times 750$) were recorded from a representative area of each sample in order to determine the average pore sizes. The densities of the foamed samples were measured by the buoyancy method (ASTM D-792) with triethylene glycol as the reference liquid.

RESULTS

XRD patterns of the alkyl-modified clays and the corresponding PDLLA nanocomposites are displayed in Figure 2 (I&II). Note that all of these systems contain equal amounts of the inorganic nanofiller by weight (3 wt%) which was calculated after NaMMT and all modified clays were subjected to thermogravimetric analysis.

The basal spacing (i.e. the distance between two successive plane layers) of the natural mineral (NaMMT) is getting larger as the C atoms of the surfactant and the % CEC increases. The initial peak at 7.35° (corresponding to $d_{(001)} = 1.2$ nm) of the NaMMT (not shown here) was replaced by a peak sifted at lower 2θ values (larger d-spacings) for all the modified clays. A comparison between the clay and the corresponding nanocomposite also illustrates peaks at lower 2θ values, indicating that the polymer chains diffuse into the silicate galleries expanding the clay structure. The second peak that is detected in the X-ray diffractograms of some nanocomposites is attributed to the (002) plane.

The XRD analysis, through comparison of the PDLLA composite materials alone (Figures I(b) and II(b)), indicates that the more the carbon atoms of the surfactant and the higher the modification level (% CEC) of the clay, the better the dispersion in the polymer matrix (larger d-spacings). This, in turn, corresponds to more nucleation sites as it is shown next.

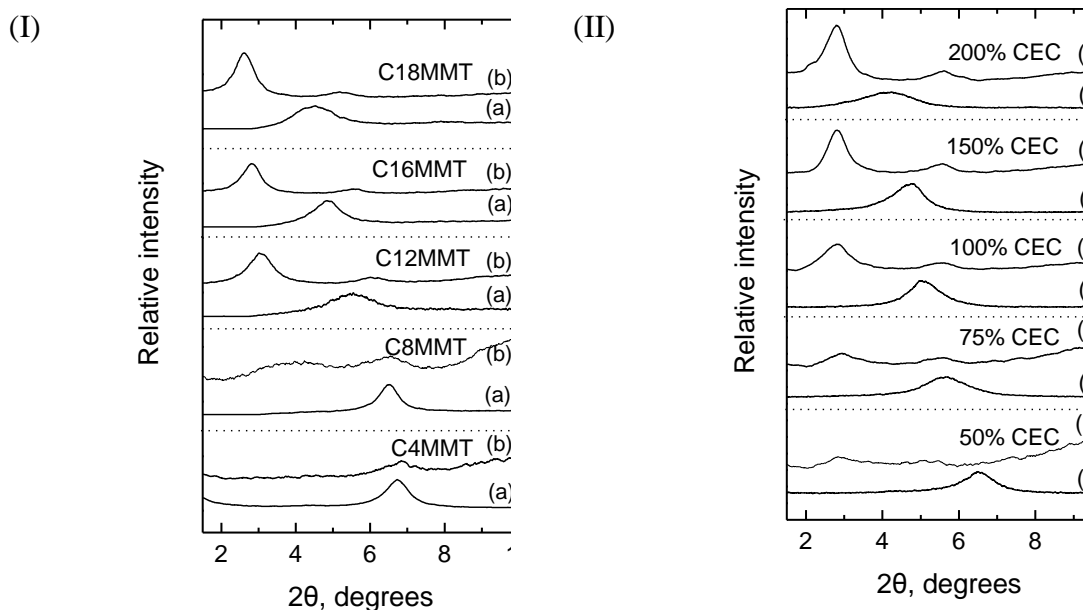


Figure 2: XRD patterns of the 1st (I) and the 2nd (II) series of clays (a) and nanocomposites (b)

The cross section morphology of porous nanocomposites is given at the SEM micrographs of Figures 3 and 5. The average pore size of the nanocomposites together with that of the pure PDLLA and PDLLA/NaMMT for comparison reasons are given in Figures 4a and 6a. Clearly the addition of nanofillers changes the size of the pores. The average pore diameter decreased from 20.2 μm (neat polymer) to 5.7 μm for the nanocomposite with the larger surfactant (PDLLA/ C18MMT) and 8.5 μm for the higher modification level (200% CEC). Furthermore, the average pore size decreases with increasing the carbon chain of the surfactant and with increasing the modification level (CEC) of the clay compared to pure PDLLA or even to PDLLA/NaMMT.

Surface chemistry, which in our case entails both the surfactant size and amount exchanged with Na ions on the surface of montmorillonite platelets, apparently plays a role in the differences observed in Figures 3-6. Nanoparticle surface chemistry affects the final pore morphology, hence, the nucleation and growth of pores. Generally, the addition of clay nanoparticles in polymers has been shown to cause heterogeneous nucleation [5,9,10,11], since the dispersed clay particles act as nucleating sites. As more bubbles start to nucleate the amount of gas available for growth is divided into more cells and, thus, foams with smaller pore diameters and increased pore density are induced. The key phenomenon that causes heterogeneous nucleation is the interfacial tension between gas nuclei and the metastable hybrid polymer phase. The energy cost due to the introduction of the surface is less when CO_2 nuclei are formed on the surface of the organically modified clay than in the polymer bulk phase. Similar observations were found for silica/PMMA nanocomposites [11]. Due to this effect, fluorination of the silica nanoparticle surface led to decreased pore size and it was showed that fluorination of the nanoparticle reduced the critical free energy of nucleation.

Consequently, the production of structures with increased cell density and smaller cell size shown in Figures 3-6 can be attributed to the surface chemistry, which affects the dispersion of nanoparticles in the PDLLA matrix (as suggested from the XRD analysis) and the MMT interaction with supercritical carbon dioxide. The former leads to more sites

available for heterogeneous nucleation, because, even if the same nominal nanoparticle concentration is used in all nanocomposites, their effective concentration is higher once the nanoparticles are better dispersed depending on the clay surface chemistry. As a consequence, more heterogeneous nucleation sites are available for better dispersed samples (larger surfactants and higher modification levels), leading to a reduction of pore size and increase of pore density (Figures 4 and 6). The interaction of clay platelets with supercritical carbon dioxide, on the other hand, affects the interfacial tension between gas nuclei and the metastable hybrid polymer phase.

The strong affinity between CO_2 and the carbonyl groups of PDLLA, intercalated in the clay galleries, may reduce the gas-particle interfacial tension and, thus, the contact angle, which would lead to a reduction in nucleation free energy and a large increase of the nucleation rate similar to the case of PMMA/clay nanocomposites [12]. More CO_2 is likely to be attracted on the clay surface with larger interlayer distance - where more PDLLA chains are diffused - to form nuclei. The combined effect of these factors, which are inter-related, is an increased pore density and smaller pore size of the nanocomposite materials compared to pure PDLLA and PDLLA/NaMMT materials.

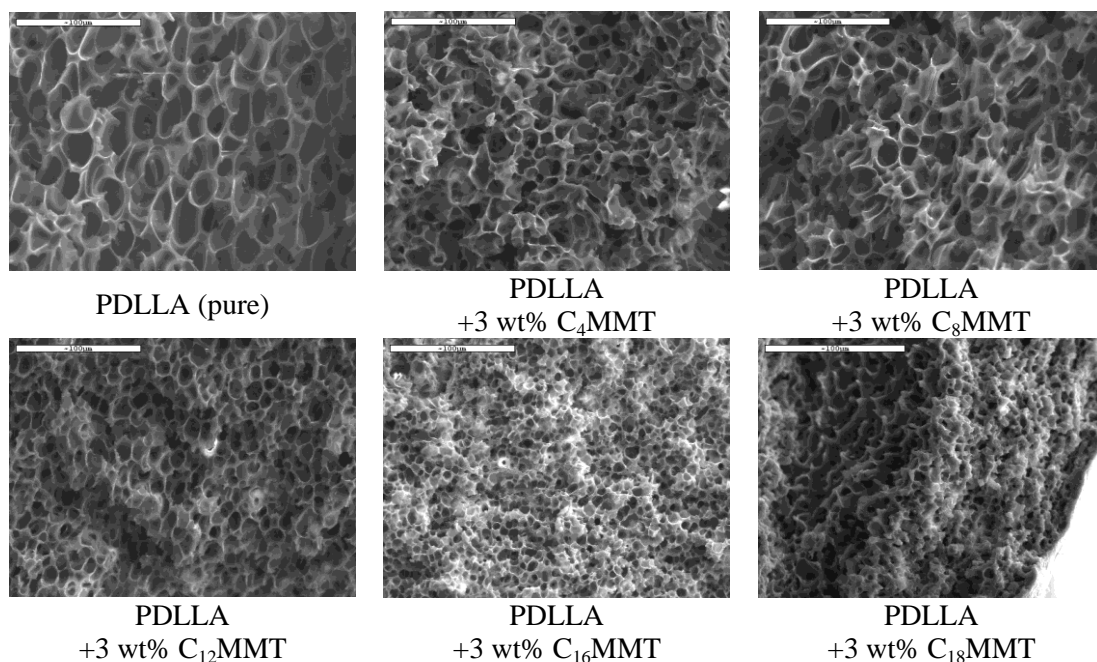


Figure 3: Surfactant type effect. Cross-sections of pure and nanocomposite PDLLA with various alkylammonium surfactants (scale bar: 100 μm).

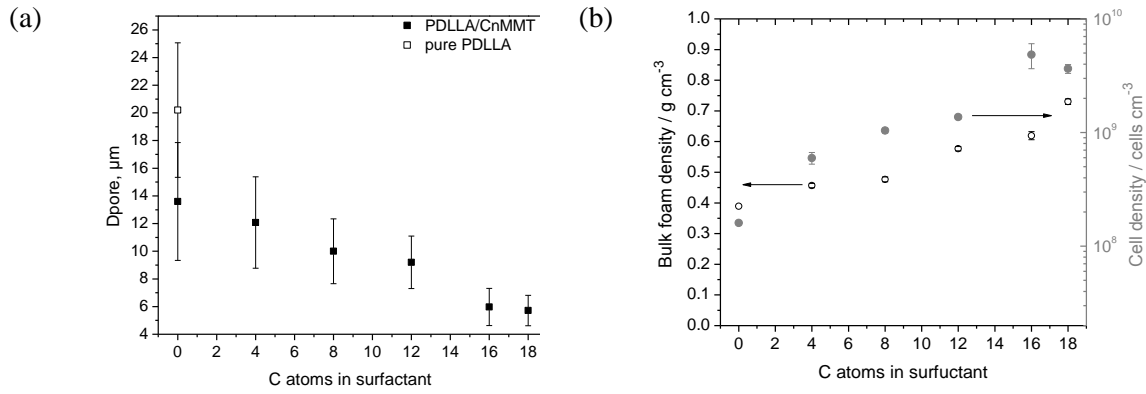


Figure 4: Surfactant type effect at the average pore diameter (a), the bulk foam density and the pore density (b).

Another measured parameter is the bulk foam density of the samples. Figure 4b depicts the impact of the surfactant's carbon chain on the bulk foam density, which seems to be slightly increasing from 0.4 to 0.7 g/cm⁻³. When a similar comparison is made to infer on the effect of clays with various CECs on the bulk foam density, differences between the samples does not lead to a consistent trend of increase or decrease rather than a region of contiguous values of 0.55-0.59 g/cm⁻³ (Figure 6b). In contrast to pore diameter and density, the foam density was not dramatically influenced by the increase of the C atoms of the surfactant or the CEC of the clay indicating a similar weight reduction compared to the bulk (unfoamed) PDLLA. Previous works that report on the effect of nanoparticle loading on polymer's foam properties, also suggest that addition of the nanoparticles do not significantly affect the bulk foam density [4,5].

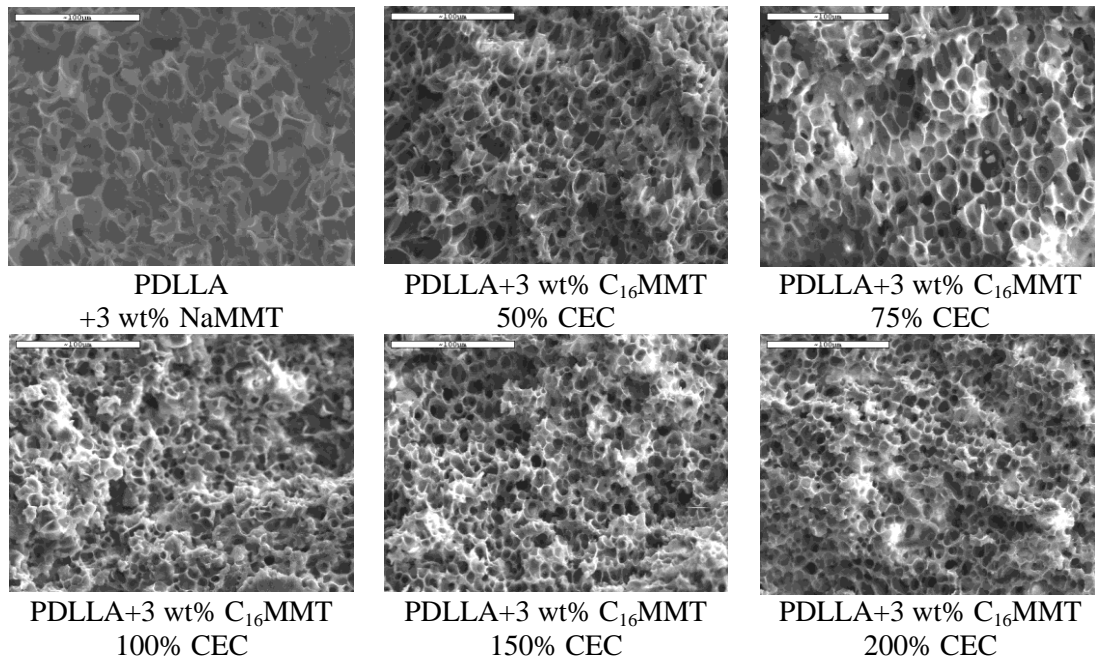


Figure 5: Organic cation concentration effect. Porous morphologies of pure and nanocomposite PDLLA at various modification levels (scale bar: 100 μm).

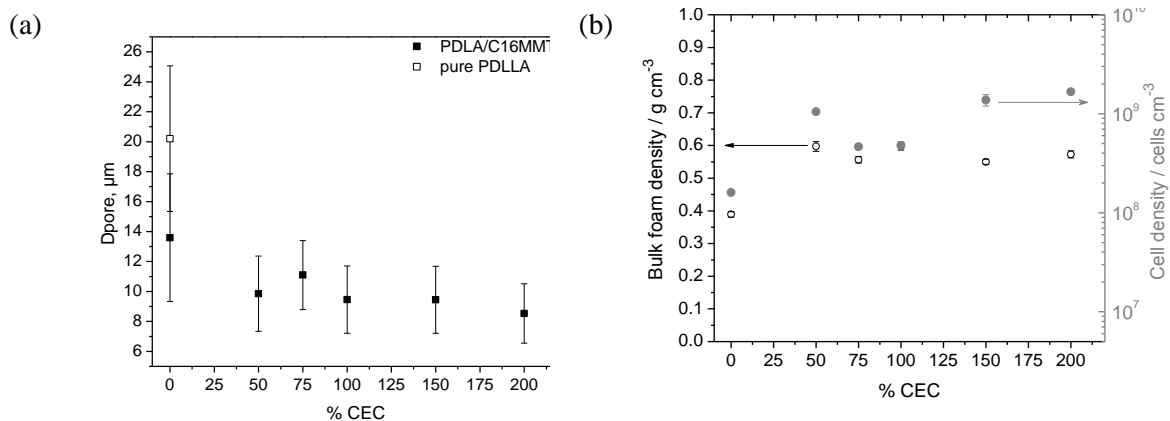


Figure 6: Effect of clay CEC on the average pore diameter (a), the bulk foam density and the pore density (b).

CONCLUSION

Poly(D,L lactic acid), PDLLA, and PDLLA/clay nanocomposites containing 3 wt% of inorganic loading but different types of alkylammoniums (with carbon chain atoms: 4 – 18) and different modifications levels (cation exchange capacities) were foamed using supercritical carbon dioxide via pressure quench. Clay dispersion in PDLLA matrix was investigated by XRD analysis and SEM imaging was used to monitor the porous morphology of the materials. The surface chemistry of the clay found to have profound effects on the structure evolution. The addition of organically modified MMT lead to heterogeneous nucleation and greatly reduced cell size and increased cell density, but had no significant effect on the bulk foam density of the porous nanocomposites at least when the clay's CEC was varying. In such a complex process, the final pore size reflects the net effect of several factors and a number of hypotheses were explored as potential explanations. In conclusion, control of the foam cell morphology can be realized by adjusting the interaction between CO₂ and the clay surface. The more the C atoms of the alkylammonium used and the higher the modification level (CEC) of the clay, the smaller the pore diameters and the larger the pore density that can be obtained.

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