Sub-microcellular polymeric foams based on 1-vinyl-2-pyrrolidone and butyl acrylate with tuned thermal conductivity

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ABSTRACT

Sub-microcellular polymers have been produced by ScCO₂ foaming, based on 1-vinyl-2-pyrrolidone (VP) and butyl-acrylate (BA). Three different copolymers were prepared, varying the compositions of VP and BA, following a simple radical polymerization process using an UV initiator. The samples a good foaming behavior and also excellent flexibility and handleability, with expansion ratios between 1.53 and 1.72, and cell sizes in the microcellular range (below 5 µm). However, it was observed that the gas distribution and, consequently, the cellular structure inside the polymer foams was highly-dependent on the VP and BA proportions, leading to very different thermal conductivity values, even for similar volume gas fraction values. These results were related to the copolymer nanostructuration, which seems to have an influence in the final pore structure, thus opening the possibility of designing microcellular foams with similar macroscopic characteristics but different thermal conductivity values.

KEYWORDS: sub-microcellular foams; 1-vinyl-2-pyrrolidone; butyl acrylate; thermal conductivity; supercritical carbon dioxide

INTRODUCTION

Cellular materials are two-phase materials in which a gas phase is dispersed in a solid phase. The interest in cellular materials derives from their unique combination of low-weight together with thermal, acoustical and mechanical properties. For this reason, cellular materials have been used for decades in several applications, such isolation, packaging or filtering.¹²³

Cellular polymers are a special kind of cellular materials, in which the solid phase is formed by a polymer. Cellular polymers or polymer foams are especially interesting due to their versatility, easy production and the possibility of tuning specific properties in terms of the cellular structure. During the last three decades, special efforts have been carried out to improve the processing processes to obtain high-performance cellular polymers, throughout the reduction of density and/or the control of the morphology.⁴

The main production route to obtain well-controlled polymeric foams involves the use of inert gasses, specially CO₂, that is employed in the supercritical state to obtain the polymeric materials in the microcellular range.⁵ The low critical conditions of supercritical CO₂ (ScCO₂) (31.1 °C and 73.8 bar) offers many advantageous
properties, like a tuneable solvent power, plasticization of glassy polymers and higher diffusion rates.\textsuperscript{6,7} To produce a microcellular structure using ScCO\textsubscript{2}, a polymer is saturated with CO\textsubscript{2} in the supercritical regime, for a fixed time period and temperature. After saturation, the sample is depressurized to atmospheric pressure at a constant temperature, taking advantage of the swelling and plasticization of the polymer, which reduce the glass transition temperature ($T_g$), allowing gas expansion. In this method, the microstructure is controlled by changing the processing temperature and depressurization rates.\textsuperscript{8,9}

Microcellular foams, with average cell sizes in the range of 1–10 µm, and cell densities on the order of $10^9$–$10^{15}$ cells·cm$^{-3}$, present outstanding properties, especially high thermal isolation characteristics. For this reason, the study of the thermal conductivity, heat transfer mechanisms and the theoretical modelling associated has gain great importance in the last years. Different authors, such as Solórzano et al.\textsuperscript{10}, Reglero Ruiz et al.\textsuperscript{11}, Antunes et al.\textsuperscript{12} or Shanqiu et al.\textsuperscript{13} have analyzed the different contribution of the Heat Transfer Mechanisms (HTM) (convection, radiation, and conduction) for different cellular materials and polymer foams, depending on the relative density and thermal properties of the solid phase. Finally, Forest et al.\textsuperscript{14} recently published a very extensive analysis of the state of the art in the same topic, including also the description of the preparation of micro/nano-cellular polymers using ScCO\textsubscript{2}, and more recently, several works of Notario et al.\textsuperscript{15,16} are focused on the analysis of the Knudsen effect in nanocellular polymers, which allows reducing drastically the thermal conductivity, obtaining super-isolating materials.

Taking into account the importance of the cellular polymers in thermal applications, different investigation lines explore commercial and easy-available polymers or copolymers that can be foamed under ScCO\textsubscript{2}, with controlled porosity and defined cellular structure, in order to determine their isolation ability throughout thermal conductivity measurements. Following this research line, the copolymers based in poly(vinyl pyrrolidone-co-butyl acrylate) (VP/BA) have recently showed a great attention due to several reasons. They are commercially available, cheap, versatile, and can be easily polymerized obtaining material in the form of films (up to 100 µm thickness) or bulk samples (up to several mm thickness). Especially interesting are the research works presented by Vallejos et al. and Trigo-López et al.\textsuperscript{17,18}, designing colorimetric cation responsive water soluble polymers films employing VP/BA copolymers. In their works, the sensory materials responded with a colour change to the presence in water of different cations such as Fe(III), Co(II), Cu(II), and Sn(II). Also, different investigation lines have been developed to analyze some properties of these specific polymers, such as the analysis of the molecular dynamics of poly(vinyl pyrrolidone) or the relaxational study of films based in VP/BA by using dielectric and dynamic mechanical spectroscopy (Redondo-Foj et al.).\textsuperscript{19,20}

Previous publications demonstrate the increasing interest attracted by these blends in several fields of polymer science. However, there is a lack of studies concerning their foaming ability, which has not been considered up to date. In addition, structuration of the copolymers in the resulting blend is also important to comprehend the foaming behavior. In this sense, several authors have analyzed the interaction of the CO\textsubscript{2} with the different nanodomains in the random copolymer structure, and its influence in the foaming behavior and in the final cellular structure.\textsuperscript{21,22,23} Finally, the importance of the relation between nanostructuration and foaming behavior is emphasized in recent works of Forest et al.\textsuperscript{24} and Pinto et al.\textsuperscript{25}, which are specially focused in the possibility of controlling the foam morphology throughout the structuration of the blend, in which the CO\textsubscript{2} molecules are placed in designed polymeric nano-domains, leading to nanocellular foams.
Bearing these ideas in mind, we propose to analyze the thermal conductivity of VP/BA copolymers, including in the study the relation between the nanostructuration and foaming behavior. In our work, three different VP/BA copolymers with different proportions (50/50, 60/40 and 70/30 % molar feed ratio of each monomer) will be bulk polymerized in a simple way, obtaining samples with 1.5 mm thickness. High Resolution Scanning Electron Microscopy (HR-SEM) and Differential Scanning Calorimetry (DSC) analysis will be performed to determine the nanostructuration and glass transition temperature of each polymer. Then, samples will be foamed under \( \text{ScCO}_2 \) and the cellular structure will be determined. Finally, thermal conductivity measurements will be performed using the Transient-Plane Source method, comparing the values obtained in the solid and foamed samples.

**EXPERIMENTAL**

**Materials**

All materials and solvent were commercially available and used as received. The following materials were employed: 1-vinyl-2-pyrrolinone (VP) \( (\rho \approx 1.04 \text{ g cm}^{-3}, \text{Aldrich >99%}) \), butylacrylate (BA) \( (\rho \approx 0.89 \text{ g cm}^{-3}, \text{Aldrich >99%}) \) and 2,2-dimethoxy-2-phenylacetophenone (Fotoi) (Aldrich >99%).

**Copolymer samples preparation**

The three different materials (M1, M2 and M3) were prepared by radical copolymerization of the hydrophilic monomer VP, the hydrophobic monomer BA, with different (VP/BA) proportions (50/50, 60/40, 70/30 % molar feed ratio), using Fotoi (0.156 wt. %) as ultraviolet photo-initiator. Afterwards, the bulk radical polymerization reaction was carried out in a silanized glass mould (1.5 mm thick) in an oxygen-free atmosphere overnight at RT. No crosslinking agent was used. The chemical composition and structure of the samples is presented in Figure 1.

**DSC experiments**

DSC measurements were carried out in a DSC Q200 TA Instruments equipment. Samples were tested using a three cycles procedure. First, samples were cooled down to -80 °C at 10 °C min\(^{-1}\). Then, after 5 min of stabilization, samples were heated up to 250 °C at 20 °C min\(^{-1}\). Finally, and also after 5 min of stabilization, in the last cycle the temperature was again cooled down to RT at 10 °C min\(^{-1}\). All the tests were performed under \( \text{N}_2 \) atmosphere (flow rate 50 ml min\(^{-1}\)). Mass of the samples was fixed at approximately 15 mg in each test. Three different tests were performed, with no variability in the thermal transitions observed. Glass transition temperature \( (T_g) \) in a miscible copolymer is defined by the well-known Fox Equation:

\[
\frac{1}{T_g} = \frac{\phi_1}{T_{g,1}} + \frac{1-\phi_1}{T_{g,2}}
\]

where \( T_{g,1} \) and \( T_{g,2} \) represents the glass transition values of the copolymer, first and second copolymer, respectively, and \( \phi_1,2 \) are the molar fractions of each copolymer. The determination of the glass transition temperature values as a function of composition for binary copolymers give us information about the miscibility of the monomers employed. In general, observation of a single glass transition region for all the copolymers is used for establishing full miscibility or the existence of one-phase mixture. In our compositions, glass transition temperatures of the polymers were about 100 to 120 °C (VP) and -40 to -50 °C (BA).

**High Resolution-SEM observations**

Nanostructuration of solid samples was determined by high-resolution electron microscopy FEI Quanta 200 F model (HR-SEM), in the Unidad de Microscopía del Parque Científico of the University of Valladolid (UVA). Samples were treated by a water solution of 2
wt. % phosphotungstic acid (PTA) and 2 wt. % benzyl alcohol. After 10 min at 60 °C samples were rinsed three times on a drop of distilled water. After this treatment the selective staining of poly(butyl acrylate) by PTA reveals the nanostructuration, and, on the contrary, the presence of an unique single phase.

ScCO\textsubscript{2} foaming procedure and cellular structure characterization

Foaming experiments took place in a high pressure vessel (model PARR 4681), provided by Parr Instrument Company. Saturation pressure was controlled using an accurate pump (model STF-10), provided by Supercritical Fluids Technologies Inc. A single-step foaming process was performed. Samples were introduced in the pressure vessel and saturated at 30 MPa and 60 °C for 24 h. These conditions were selected after carrying out different foaming tests at three different temperatures (RT, 40 °C and 60 °C), and two different saturation pressures (10 MPa and 30 MPa). It was observed that foaming only occurred at high temperature (60 °C) and pressure (30 MPa), thus selecting these foaming parameters to perform the experiments. After reaching a fully saturated sample the pressure was released in 5 s using an electronic valve. Then, samples were removed quickly from the pressure vessel, determining the mass of the samples to estimate the quantity of CO\textsubscript{2} absorbed during the saturation step. This method, although is not highly accurate to determine the exact quantity of CO\textsubscript{2} absorbed, can give us a brief idea of the CO\textsubscript{2} sorption ability of the samples. For each sample, three different SEM micrographs were analyzed. Samples were frozen in liquid nitrogen, fractured and gold coated in vacuum to assure the electrical conductivity of the samples. Images were taken using a scanning electron microscopy model JEOL JSM-6460LV.

Finally, foams were tempered at RT for several hours to assure that all the gas diffusion process was finished, and density was measured using an Archimedes density measurement kit.

Cellular structural characterization was carried out throughout the determination of the average bubble radius and cell density, that were measured using the Image\textsuperscript{®} software from SEM images. For each sample, three different SEM images were analyzed. Samples were frozen in liquid nitrogen, fractured and gold coated in vacuum to assure the electrical conductivity of the samples. Images were taken using a scanning electron microscopy model JEOL JSM-6460LV.

The Image\textsuperscript{®} software accounts for the number of bubbles in each image and the average radius. The number average radius $\bar{R}$ is calculated from Equation 2:

$$\bar{R} = \frac{\sum_{i=1}^{N} n_i R_i}{\sum_{i=1}^{N} n_i}$$

where $N$ represents the bubble count. The total cell number $N_c$ in the sample was calculated using Equation 3, which accounts for the 3D extrapolation starting from a 2D image:

$$N_c = \frac{6(1-\frac{\rho_c}{\rho_s})}{\pi R^3} V_f$$

where $\rho_s$ and $\rho_c$ are the solid and foam core density, respectively, and $V_f$ is the void fraction. Solid density can be easily determined using the mixture law. In the case of the foam density, the solid outer skin was removed prior to measurements.

Thermal conductivity measurements

Thermal conductivity was determined using the Transient Plane Source method (TPS). In thermal transient methods, a heat pulse or heat flux in the form of a step-wise function is generated within the specimen, and the time/temperature response resulting is analyzed, deriving thermal parameters of the sample. An example of this method is the Transient Plane Source technique employed in this work. In the TPS technique, the TPS sensor, consisting of an electrical conducting pattern of thin nickel foil (10 µm) in the form of double spiral, which resembles a hot disk, embedded in insulating layer made of kapton (70 µm), behaves both as heat source and temperature sensor. A heat pulse is generated heating the sensor, recording the resistance
variation at the same time $R(t)$, according to Equation 4.

$$\Delta T(t) = \frac{1}{\alpha} \left( \frac{R(t)}{R_0} - 1 \right) \tag{4}$$

where $\alpha$ is the thermal expansion coefficient, $R_0$ is the initial resistance and $\Delta T(t)$ is the temperature variation. Using this method, thermal parameters of the sample, such as thermal conductivity and thermal diffusivity, can be obtained from previous information solving the heat conduction Equation. To perform the experiments, the sensor is sandwiched between two samples of the same material, and a heat pulse is generated during a short time. Radius of the sensor, as well as experimental parameters such as output power and measurement time must be selected, and vary with the materials studied. The transient plane source is a technique versatile, fast, and offers simple and quick thermal measurements in a wide variety of materials.

In our experiments, a sensor with radius $R = 3.189$ mm was employed. Five measurements of each material were carried out, to minimize the variability of the results. To perform the experiments, the solid outer skin of the foamed samples was removed mechanically using a polishing machine, and the sensor was sandwiched between 6 samples of the same material (3 on each side), to avoid the border effects.

RESULTS AND DISCUSSION

Solid material characterization

A picture of one of the samples extracted from M1, taken over a squared notebook to show transparency (dimensions 15 x 15 mm$^2$ and 1,5 mm thickness) can be found in supporting information (SI, figure S1).

The obtained samples were all transparent, flexible and easily manageable. Total surface of each material was 100 x 50 mm$^2$. Eight samples were cut from each material, with dimensions 15 x 15 mm$^2$ and 1,5 mm thickness, as shown in Figure 2. Two of these samples were used to perform the DSC and HR-SEM measurements, and the rest of the samples were employed in the foaming process and in the thermal conductivity characterization.

The DS thermograms obtained are presented in SI, figure S2, showing a singular behavior in material M1, whereas materials M2 and M3 present similar transitions. Having a look at DSC results, it can be observed that all materials an unique broad glass transition peak, appearing at 5 $^\circ$C, although this transition is weaker in M3. This value is in good agreement with the theoretical glass transition of a single phase material obtained from Equation (1). Calculated value for glass transition temperature from Equation (1) was about 0 $^\circ$C, taking as $T_{g,VP} \approx 393$ K, $T_{g,BA} \approx 228$ K, $\varphi_{VP} = \varphi_{BA} = 0.5$ ($T_g$ values of the polymers measured using the same procedure).

Conversely, materials M2 and M3 do not present the glass transition about 5 $^\circ$C, but they present one slight transition about 60 $^\circ$C, which may be due to molecular relaxations related to the thermal history of the material. In fact, this transition disappeared after the first heating cycle of the samples. In addition, in material M3 it is observed an additional transition close to 120-125 $^\circ$C, that could be due to the presence of a certain quantity of 1-vinyl-2-pyrrolidone copolymer, that does not form a single phase with the butyl-acrylate. Finally, in all the materials is observed that degradation begins at 160-170 $^\circ$C. These results will be next verified throughout the HR-SEM observations of the nanostructuration (see Figure 2).

FIGURE 2 HR-SEM images of the solid samples (bar scale 500 nm) - a) M1 ; b) M2 ; c) M3

HR-SEM pictures show a very different structuration behavior of the samples, depending on the proportions of VP and BA. In sample M1, (50VP/50BA), no structuration of the polymers is observed, and blend is constituted of a one single phase. However, in sample M2, (60VP/40BA), both polymers are not completely
miscible, with an ordered structure of nano-spheres dispersed in the matrix. Size of these nanodomains is about 50 nm. Finally, the structuration is more significant in sample M3 (70VP/30BA), in which the domains dispersed in the polymer matrix have a more irregular shape, with bigger sizes than in the case of sample M2. Also, due to the relative proportion and the immiscibility observed, in material M3 this dispersed second phase can detected in the DSC measurements, whereas in samples M1 and M2 this detection does not occur.

**Microcellular foam characterization**

After the characterization of the solid samples, supercritical CO$_2$ foaming was performed using the experimental parameters previously described. Figure 3 presents the SEM micrographs of the foamed materials.

FIGURE 3 SEM micrographs of the samples – a-b) M1 ; c-d) M2 ; e-f) M3

As it is observed in SEM micrographs, the three copolymers present a very different cellular morphology, although all the cellular structures are homogeneous and lie in the microcellular range (less than 10 µm), demonstrating the foaming ability of VP/BA system. However, the addition of butyl-acrylate seems to be a critical factor that tunes the cellular structure into different morphologies. In material M1 (50VP/50BA), the cellular morphology presents isolated closed cells, with diameters between 1 and 2 µm (Figure 3a). When the content of BA decreases to 30 %, in material M3 (70VP/30BA), the foam shows a completely different morphology in which micro granules seems to be packed, surrounded be channels that fill all the structure (Figure 3e). Finally, the most interesting cellular structure appears in material M2 (60VP/40BA). Figure 3d shows an homogeneous microcellular open-cell structure, with interconnected cells (diameter less than 5 µm). Although the formation of this open-cell structures in batch ScCO$_2$ foaming processes is unusual, some other examples have been reported by Martín-de León et al. concerning the production of PMMA nanocellular foams. As it can be seen in Figure 3c, a solid outer skin of about 50 µm was observed in all the samples.

These results can be connected to the nanostructuration of the solid samples (see Figure 2). It can be deduced that in sample M1, the one-single phase leads to isolated closed cells (Figures 3a and 3b), whereas in sample M3 the irregular nanodomains of BA causes the morphological structure in which no pores are presented (Figures 3e and 3f). In the case of material M2, the nanostructuration of BA into nano-spherical domains dispersed in the VP matrix originates a well-defined open-cell microcellular structure (Figures 3c and 3d). The CO$_2$ molecules, which are mainly dissolved by the acrylate groups of the BA, are located in the low-$T_g$ region formed by the nano-spherical domains of BA. Then, during depressurization, the decrease of the temperature causes that cell growth is limited by the high-$T_g$ of the dispersed matrix of VP, thus limiting their size and leading to the structure observed in Figures 3e and 3f. It is important to remark that all the samples present a good flexibility, which increased with the content of BA. In terms of expansion ratio, despite the different cellular morphologies, all the materials presented a similar behavior (see photographs of the foamed samples in SI, figure S3). Detailed values of the physical parameters of the foamed samples are listed in Table 1.

**TABLE 1 Physical parameters of the foamed materials**

<table>
<thead>
<tr>
<th>Material</th>
<th>% wt. CO$_2$</th>
<th>$\rho_f$ (g·cm$^{-3}$)</th>
<th>ER</th>
<th>$V_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>21.2</td>
<td>0.56</td>
<td>1.72</td>
<td>0.58</td>
</tr>
<tr>
<td>M2</td>
<td>18.5</td>
<td>0.61</td>
<td>1.60</td>
<td>0.62</td>
</tr>
<tr>
<td>M3</td>
<td>14.3</td>
<td>0.65</td>
<td>1.53</td>
<td>0.65</td>
</tr>
</tbody>
</table>

In Table 1, expansion ratio (ER) is the ratio between the solid and the foam density. For precise calculations, solid density was calculated using the mixture’s law applied for the composition of each material (Equation 5):
\[ \rho_S = A \cdot \rho_A + B \cdot \rho_B \]  

(5)

, where A and B represent the molar fraction of each co-monomer, and \( \rho_A, \rho_B \) are the density of each co-monomer (1.04 g·cm\(^{-3}\) for VP and 0.89 g·cm\(^{-3}\) for BA). Theoretical density values obtained for each material are \( \rho_{M1} = 0.96 \text{ g·cm}^{-3} \), \( \rho_{M2} = 0.98 \text{ g·cm}^{-3} \) and \( \rho_{M3} = 0.99 \text{ g·cm}^{-3} \). To compare, the experimental density values for each sample were \( \rho_{M1} = 0.98 \text{ g·cm}^{-3} \), \( \rho_{M2} = 1.01 \text{ g·cm}^{-3} \) and \( \rho_{M3} = 1.03 \text{ g·cm}^{-3} \). Volume gas fraction \( V_f \) was calculated as the inverse of \( ER \). It is important to remark that as it can be seen in SEM micrographs (Figure 5c), samples presented a solid outer skin (about 50 µm thickness), and density values presented in Table 1 are obtained without removing the solid outer skin (\( \rho_s \)). On the other hand, for the cellular structure calculations using the ImageJ® software, this skin will not be taken into account, thus obtaining the density of the foamed core (\( \rho_c \)).

The results show that CO\(_2\) uptake increases with BA content, which confirms the good affinity for the CO\(_2\) of acrylate-based polymers.\(^{33}\) However, the expansion ratio of the samples, after the CO\(_2\) desorption process up to equilibrium state, is similar in all the materials. This phenomenon is explained as follows: CO\(_2\) uptake measurements are carried out just after depressurization, and when samples are at RT, after several minutes, a significant part of the absorbed gas has diffused out of the sample, leading to the expansion ratios showed in the Table (between 1.5 and 1.7, see Figure 6). Density of the samples are in the range of expected values obtained in CO\(_2\) supercritical foaming process (between 0.55 and 0.65 g·cm\(^{-3}\)).

As said before, the cellular structure was analyzed using the ImageJ® software. To account the number and average diameter of the cells, SEM micrographs are first binarized, as it is shown in Figure S4 in SI. Then, the software calculates the number of bubbles (bubble count), and the average bubble radius \( \bar{R} \). To obtain the cell density, \( N_c \) from Equation 3, the foam core density is measured after removing the solid outer skin. Table 2 presents the average morphological parameters obtained from three different SEM micrographs of each material.

<table>
<thead>
<tr>
<th>Material</th>
<th>Bubble count</th>
<th>( \bar{R} ) (µm)</th>
<th>( \rho_c ) (g·cm(^{-3}))</th>
<th>( N_c ) (cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>195</td>
<td>2.12</td>
<td>0.49</td>
<td>( \approx 3.68 \times 10^7 )</td>
</tr>
<tr>
<td>M2</td>
<td>1213</td>
<td>4.17</td>
<td>0.53</td>
<td>8.51 \times 10^4</td>
</tr>
<tr>
<td>M3</td>
<td>N/A</td>
<td>N/A</td>
<td>0.58</td>
<td>N/A</td>
</tr>
</tbody>
</table>

In the case of material M1, the Equation 3 gives no realistic results for the cell density \( N_c \) (4.37 \times 10^9 cm\(^{-3}\)), which is highly superior to the experimental observation, according to SEM micrographs (see Figures 3a-b). A more realistic, but not extremely accurate approximation is considering the total surface of the SEM micrograph using for bubble count (Figure 3b) to obtain the number of cells per cm\(^2\) (surface density, \( \sigma \)), and extrapolate to 3D to obtain an estimation of the number of cells per cm\(^3\) (volume density, \( N_c \)). The extrapolation can be carried out using the Equation (6):

\[ N_c = \sigma^{3/2} \]  

(6)

The obtained value using this procedure is indicated in Table 2 (\( N_c \approx 3.68 \times 10^7 \text{ cm}^{-3} \)).

In the case of material M2, the calculations are in good agreement with observations, with value of cell density in the range of 10^8 cm\(^{-3}\), in the sub-microcellular range. Finally, material M3 does not present a classical cellular structure with well-defined cells, but a more intricated morphology in which the gas is retained in channels between the packed micro-granules of polymer. For this reason, in this case it is difficult the calculation of morphological parameters.

**Thermal conductivity results**

The obtained values for thermal conductivity are listed in Table 3, for solid samples and also for
foamed samples. First, measurements in solid samples were performed, then samples were foamed according to the previously exposed procedure, and finally the thermal conductivity values of foamed samples were determined. In both cases, the same experimental set-up was used (see experimental section).

TABLE 3 Experimental thermal conductivity values obtained for solid and foamed samples

<table>
<thead>
<tr>
<th>Material</th>
<th>$\bar{\rho}$ (g·cm$^{-3}$)</th>
<th>$\lambda$ (W·(m·K)$^{-1}$)</th>
<th>std ($\lambda$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOLID</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1</td>
<td>0.96</td>
<td>0.202</td>
<td>0.0027</td>
</tr>
<tr>
<td>M2</td>
<td>0.98</td>
<td>0.189</td>
<td>0.0006</td>
</tr>
<tr>
<td>M3</td>
<td>0.99</td>
<td>0.188</td>
<td>0.0027</td>
</tr>
<tr>
<td>FOAM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1</td>
<td>0.49</td>
<td>0.131</td>
<td>0.0025</td>
</tr>
<tr>
<td>M2</td>
<td>0.53</td>
<td>0.152</td>
<td>0.0011</td>
</tr>
<tr>
<td>M3</td>
<td>0.58</td>
<td>0.101</td>
<td>0.0015</td>
</tr>
</tbody>
</table>

Values for thermal conductivity present, in all the cases, a low standard deviation, indicating the accuracy of the measurement method. In solid samples, thermal conductivity varies in a very narrow range, between 0.189 and 0.202 W·(m·K)$^{-1}$. This low variation can be explained because solid samples present the same density (0.96-0.99 g·cm$^{-3}$), and this is the main parameter influencing the thermal conductivity. Concerning the foamed samples, a reduction of thermal conductivity values is observed in all the cases respect to solid samples (values of thermal conductivity vary between 0.101 and 0.152 W·(m·K)$^{-1}$). The highest thermal conductivity value is observed in sample M1, due to the gas mobility inside the open-cell structure. In the case of foamed samples, the density values correspond to the foamed core $\rho_f$. Experimental values in this work are in the range with data reported by other authors for microcellular foams based in other polymers. For example, Reglero Ruiz et al.$^{34}$ described values of thermal conductivity between 0.055 and 0.062 W·(m·K)$^{-1}$ for (methyl methacrylate)−(butyl acrylate)−(methyl methacrylate) microcellular foams and Notario et al.$^{15}$ described values between 0.059 and 0.107 W·(m·K)$^{-1}$ for poly(methyl methacrylate) sub-micro cellular foams. An illustrative graph can be traced representing, for each material, the ratio between foamed and solid conductivities $\lambda_f/\lambda_s$ and gas volume fraction $V_f$ (Figure 4).

FIGURE 4 Relative thermal conductivity as a function of gas volume fraction

Figure 4 shows an interesting comparative graph between the three materials. It was expected that increasing the gas volume fraction $V_f$ decreases the thermal conductivity, considering that the solid density only varies slightly in our samples. This is clear in sample M3, which presented the closed-cell structure seen in the SEM micrographs (see Figure 3d), with a reduction respect to M1 about 16 % (from 0.65 to 0.54). However, in sample M2, this value increases greatly (about 60 % respect to M2), and this could be due to the open-cell structure observed in the SEM micrographs (see Figure 3f). Thus, it is demonstrated that the influence of the cellular morphology in the thermal behavior is predominant, and much more important that the gas content represented by the gas volume fraction. To resume, varying the monomer proportion in these copolymers tunes to very different cellular morphologies and thermal conductivity values, with practically the same gas volume fraction and expansion ratios.

CONCLUSIONS

In this work, the thermal conductivity of microcellular foams based in 1-vinyl-2-pyrrolidone and butyl acrylate is analyzed. Samples with different VP/BA proportions were prepared, in a simple radical polymerization process using an ultraviolet photo-initiator. Solid amorphous samples were nanostructured, showing nanodomains of different geometries when varying the BA proportion. Then, foaming was carried out in a supercritical CO$_2$ batch process, obtaining samples with similar expansion ratios (between 1.53 and 1.72), but very different cellular structures. The
determination of the thermal conductivity was carried out using the Transient Plane Source Method (TPS), observing that the values were highly dependent on the cellular morphology (values varied between 0.10 and 0.15 W·(m·K)$^{-1}$). It was also detected that proportion 60VP/40BA presented an open-cell microcellular structure, with the lowest thermal conductivity values, and also a very good flexibility. Thus, the foaming of this material, which is also currently being used in sensory applications, could improve the sensory behavior respect to the solid, specially concerning the water absorption capability. For this reason, this study can be considered the starting point to deep analyze the foaming behavior, and also the mechanical and thermal characteristics of these copolymers.

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REFERENCES AND NOTES


GRAPHICAL ABSTRACT

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Sub-microcellular polymeric foams based on 1-vynil-2-pyrrolidone and butyl acrylate with tuned thermal conductivity

ScCO$_2$ foaming of copolymer blends of 1-vynil-2-pyrrolidone and butyl-acrylate produces microcellular foams with similar expansion ratio but tuned cellular morphology and thermal conductivity values.