Ionic liquids as foaming agents of semi-crystalline natural-based polymers

Ana Rita C. Duarte,*a,b Simone S. Silva,a,b João F. Mano,a,b and Rui L. Reis,a,b

Received 23rd December 2011, Accepted 23rd April 2012
DOI: 10.1039/c2gc16652f

In this work, the ability to foam semi-crystalline natural-based polymers by supercritical fluid technology is evaluated. The application of this technique to natural polymers has been limited due to the fact that they are normally semi-crystalline polymers, which do not plasticize in the presence of carbon dioxide. This can be overcome by the use of plasticizers, such as glycerol, which is a commonly used plasticizer, or ionic liquids, which have recently been proposed as plasticizing agents for different polymers. Following the green chemistry principles, the main aim is, hereafter, the design and development of new 3D architectures of natural-based polymers, combining ionic liquids (IL) and supercritical fluid (SCF) technology. A polymeric blend of starch, one of the most abundantly occurring natural polymers, and poly-e-caprolactone, a synthetic polymer, which is a biodegradable aliphatic polyester commonly used in an array of biomedical applications (SPCL), was processed by supercritical fluid foaming, at different operating conditions, namely pressure (10.0 up to 20.0 MPa), temperature (35 up to 60 °C) and soaking time (30 min up to 3 h). The ionic liquid tested in this work was 1-butyl-3-methylimidazolium acetate ([bmim]Ac). The interactions between SPCL and [bmim]Ac or glycerol were analysed by Fourier transform infrared spectroscopy, differential scanning calorimetry and by mechanical tests, using both tensile and compressive modes. Morphological analysis, porosity, interconnectivity and pore size distribution of the matrixes were evaluated and the morphology was analyzed by scanning electron microscopy and by micro-computed tomography. To our knowledge the use of ionic liquids as foaming agents is reported here for the first time. The results obtained suggest that this approach can further promote the development of composite polymer–IL materials, particularly for catalysis, chromatography, extraction and separation purposes.

Introduction

The application of polymeric foams is extremely widespread, from the automotive to the chemical industry or biotechnology. Insulation, lightweight materials supports for catalysis, membranes for process separations, controlled release systems and three dimensional matrixes for tissue engineering and regenerative medicine are some examples which have been reported in the literature.1–3 The large number of applications can be further expanded by the production of polymer composite matrixes.

Biodegradable polymers made from renewable resources constitute an important material innovation as they decrease our dependence on petroleum resources and reduce the amount of waste material, while yielding a product that provides similar benefits to those of traditional plastics. Such materials can be produced by simple modification of natural macromolecules (e.g. chitosan from chitin or derivatives of cellulose) or may be obtained from polymerization of natural-origin monomers (e.g. polylactides). Several naturally derived polymers, such as cellulose, starch, chitosan, chitin, alginates and other polysaccharides, hold the potential to be used in applications where synthetic polymers have traditionally been the materials of choice.4,5 However, natural-based polymers have great limitations in processability particularly due to their unusually high crystallinity, which limits their solubility and their high melting temperature, often higher than the degradation temperature. Conventionally, polymer foaming techniques include: thermally induced phase separation (TIPS), in which the foaming agent is dissolved in the polymer and upon heating phase separation occurs leading to the creation of a porous structure; a chemical foaming agent (CFA), in which this agent is mixed with the polymer and upon heating it degrades into a gaseous component leading to the formation of a porous structure; and casting and leaching, in which the polymer is dissolved in an organic solvent and a solid porogen is added to induce porosity in the structure being afterwards leached out. All these methods require, however, the use of organic solvents or high temperatures. The development of novel processes that are able to overcome the drawbacks of these technologies and that are at the same time able to comply with the principles of sustainable development is a major challenge.6

Supercritical fluid foaming is an alternative technique widely used for the preparation of 3D porous structures, particularly

*3B’s Research Group – Biomaterials, Biodegradables and Biomimetics, University of Minho, Headquarters of the European Institute of Excellence on Tissue Engineering and Regenerative Medicine, AvePark, 4806-909 Taipas, Guimarães, Portugal. E-mail: aduarte@dep.uminho.pt
Simone S. Silva, João F. Mano and Rui L. Reis
a,b
†ICVS/3B’s PT Government Associated Laboratory, Braga/Guimarães, Portugal
from thermoplastic polymers. In this technique the polymer is exposed to carbon dioxide, which plasticizes the polymer by reducing its glass transition temperature ($T_g$). On venting carbon dioxide by depressurization, the thermodynamic instability causes supersaturation of CO$_2$ dissolved in the polymer matrix, and hence nucleation of the cells occurs. The main requirement for the success of supercritical fluid foaming is the solubility of carbon dioxide in the polymer as this will ultimately dictate the ability to lower its $T_g$ and therefore plasticize the polymer. 

This is the main reason why, so far, semi-crystalline natural-based materials could not be processed by this technique. The possibility to use a plasticizer or a foaming agent may help to overcome this; however, this compound would have to be removed from the structures in a subsequent processing step.

Plasticizers are low-molecular-weight compounds, which, when blended with polymers, will decrease the intermolecular forces of the polymeric network, increasing the flexibility of the matrixes and/or decreasing its melting temperature. Glycerol, for instance, is a commonly used plasticizer in many different industrial applications. Glycerol is a colourless, water soluble high-boiling point liquid with characteristics that make it interesting for the purpose of this study and therefore it was used as the control foaming agent.

 Ionic liquids represent green recyclable alternatives to the conventional organic solvents and are defined as salts that are liquid at room temperature. The first IL was synthesized in 1914, but it was only in the late 70s and 80s that important advances in the field emerged. The enormous potential arises from particular characteristics of these liquids, namely their physico-chemical properties (viscosity, density, hydrophilicity and solubility) which can be tuned by the combination of different cations and anions. Additionally they present negligible vapour pressure, good thermal and chemical stability, high ionic conductivity and a large electrochemical window. Ionic liquids have been explored in polymer science in a number of different ways, in particular they can be used as solvents or catalysts. The solubility of polysaccharides in ILs has opened a new window of opportunities for polymer processing, especially naturally-derived polymers. Ionic liquids have also been reported to have plasticizing properties on some polymers, e.g., synthetic polymers such as PVC, PMMA and the natural polymer starch.

While glycerol is an inert plasticizer, ionic liquids in contrast may add interesting features to the porous matrixes as they can play a role as performance additives. For example on micro-extraction and separation technologies, as well as in chromatography the presence of an ionic liquid within the stationary phase, with different functions, e.g. as extractants, desorption solvents or mediators, may be used for process improvement. The presence of an ionic liquid dispersed in a solid matrix can also be used for catalysis purposes.

In this sense, processes able to take advantage of supercritical fluid technologies coupled with ionic liquids (IL) have received much attention from the scientific community. In this work we suggest for the first time the use of ionic liquids as foaming agents. The capacity to plasticize polymers can be further exploited to prepare porous matrixes, creating at the same time a composite structure which can take advantage of the presence of the ionic liquid.

## Materials and methods

### Materials

A commercial blend of corn starch and poly-e-caprolactone (SPCL), 30 : 70 wt%, in granular form was used to perform the experiments. The ionic liquid used was 1-butyl-3-methylimidazolium acetate ([bmim]Ac) obtained from Sigma Aldrich. Glycerol (gl) was purchased from Vaz Pereira. Carbon dioxide (99.998 mol%) was supplied by Air Liquide. All reagents were used as received.

### Compression moulding

SPCL samples in the presence of the ionic liquid or glycerol have been prepared by compression moulding (Table 1). Rectangular boards (187 × 120 × 3 mm) of SPCL and the blends of SPCL + IL and SPCL + gl were processed using a Moore hydraulic press (UK) at 80 °C, 8 MPa for 15 min.

### Supercritical fluid foaming

The porous matrixes were prepared by SCF foaming at different operating conditions ranging from 10.0 up to 20.0 MPa and 35 up to 60 °C. In each experiment a cylindrical sample of SPCL, SPCL IL or SPCL gl was loaded in the high pressure vessel. The vessel was heated by means of an electric thin band heater (OGDEN) connected to a temperature controller, which maintained the temperature within ±1 °C. Carbon dioxide was pumped into the vessel using a high pressure piston pump (P-200A Thar Technologies) until the operational pressure was attained. The pressure inside the vessel was measured with a pressure transducer. The system was closed for different time periods, 30 min, 1 or 3 h, to allow the plasticization of the polymer. Afterwards the system was slowly depressurized.

### Characterization

#### Infrared spectroscopy (FTIR-ATR).

The infrared spectra of SPCL, SPCL IL and SPCL gl were obtained in the absorption mode, using a Fourier transform infrared (FTIR) spectrometer (Shimadzu-IR Prestige 21) equipped with an attenuated total reflection (ATR) system with a resolution of 4 cm$^{-1}$ at 32 scans, in the spectral region of 4400–800 cm$^{-1}$.

#### Mechanical tests

**Tensile:** Mechanical tensile tests were performed in an INSTRON 5540 (Instron Int. Ltd, High Wycombe, UK) universal testing machine with a load cell of 1 kN. The dimensions of the specimens used were 50 mm length, 4 mm width and 3 mm thickness. The load was placed midway between the supports.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[bmim]Ac (wt%)</th>
<th>Glycerol (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPCL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPCL IL</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>SPCL gl</td>
<td></td>
<td>30</td>
</tr>
</tbody>
</table>

---

---

---
with a span \(L\) of 10 mm. The crosshead speed was 1:5 mm min\(^{-1}\). For each condition, the specimens were loaded until the core break.

**Compressive.** Compressive mechanical properties of the materials prepared by compression moulding were measured using an INSTRON 5540 (Instron Int. Ltd, High Wycombe, UK) universal testing machine with a load cell of 1 kN. Compression testing was carried out at a crosshead of 2 mm min\(^{-1}\), until a maximum reduction in sample height of 60%. The compressive modulus is defined as the initial linear modulus on the stress–strain curves.

The data presented for both tensile and compressive tests are the result of the average of at least five measurements.

**Scanning electron microscopy (SEM).** Samples of the polymeric matrixes prepared were observed by a Leica Cambridge S360 Scanning Electron Microscope. The matrixes were fixed by mutual conductive adhesive tape on aluminum stubs and covered with gold palladium using a sputter coater.

**Micro-computed tomography (micro-CT).** The inner structure, porosity and interconnectivity were evaluated by micro-computerized tomography using Scanco 20 equipment (Skyscan 1702, Belgium) with penetrative X-rays of 53 keV. The X-ray scans were acquired in high-resolution mode. A CT Analyser® was used to visualize the 2D X-ray section images of the scaffolds.

**Statistical analysis.** Statistical analysis of the data was conducted using one-way ANOVA with Bonferroni’s post test by using GraphPadPrism version 5.0 for Windows (GraphPad Software, San Diego, http://www.graphpad.com). Differences between the groups with \(p < 0.05\) were considered to be statistically significant.

**Results and discussion**

Our major interest is the possibility of processing these materials using a green and environmentally friendly technology. In the case of the thermoplastic polymers, 3D structures can be obtained by supercritical fluid foaming. This is a good alternative to conventional processes as no organic solvents or chemicals are used. The modification of natural polymers and the preparation of thermoplastic natural-based materials are therefore of critical importance for the success of supercritical fluid foaming. These materials were prepared by compression moulding of SPCL and the plasticizing agent into 3 mm thick plates, which were further processed.

Compression moulded samples were analysed using different techniques in order to understand the interactions between the ([bmim]Ac) ionic liquid and the polymer. Glycerol was used in order to establish a comparison as it can be considered a model plasticizing agent\(^{29}\).

FTIR spectra, in attenuated total reflectance (ATR) mode of the compressed moulded samples of SPCL, SPCL IL and SPCL gl samples, were acquired and are shown in Fig. 1.

Attention should be given to the peaks at 900–1200 cm\(^{-1}\), which include the characteristic peaks of starch and poly-ε-caprolactone (Fig. 2a).

The ionic liquid characteristic peaks, namely the imidazolium cation and the acetate carboxylate (C=O and C–O), were identified according to the literature at 1173 cm\(^{-1}\) and 1578 and 1379 cm\(^{-1}\), respectively\(^{30}\).

The analysis of the spectra suggests that [bmim]Ac has stronger interactions with starch, rather than with poly-ε-caprolactone. Of particular relevance is the peak at 1080 cm\(^{-1}\), which is attributed to the C–O bond stretching in the C–O–H groups of starch. In Fig. 1a the intensity of this peak is rather low, probably due to the absence of ionic liquid. However, this is not the case when [bmim]Ac was blended with the polymer (Fig. 2i). This peak is absent in the case of the SPCL gl matrix, which indicates that no
interaction occurs between the two. Ning and coworkers\textsuperscript{31} have studied the effect of a different ionic liquid, 1-allyl-3-methylimidazolium chloride for corn starch. Upon spectroscopic analysis of the spectra obtained by FTIR, particularly looking at the C–O group of starch (1150 cm\(^{-1}\)) the authors concluded that [AMIN]-Cl has weaker interactions with starch than glycerol due to the change to lower frequencies of this peak. In contrast, and similarly to the results presented by Sankri and coworkers,\textsuperscript{26} the use of [bmim]Ac in our experiments promoted an increase in hydrogen bonding which indicates stronger interactions between the ionic liquid and polymer rather than glycerol and the polymer. A significant reduction in hydrogen bonds between the ionic liquid and starch was observed in the case of both [bmim]Cl and [bmim]Ac plasticization.

According to the study presented by Hanke et al.,\textsuperscript{32} each ion pair of the ionic liquid forms complex interactions with the solute. This is due to the fact that the ionic liquids present strong interactions between the charged ions. In the case of [bmim]Ac the ions will interact with the C–O–H group of starch; while the acetate will interact with the hydrogen atom, the bmim will interact with the oxygen atom. As a result the C–O–H group of starch will not be able to form any other hydrogen bonds, decreasing the hydrogen bond intensity and hereafter promoting the mobility of the polymer chains. Besides, the ILs containing acetate ion (Ac\(^–\)) are characterized by stronger hydrogen bonding acceptability (basicity).

The peak at 1020 cm\(^{-1}\) corresponds to the C–O bond in the C–O–C of starch and has been reported in the literature to be characteristic of amorphous starch. The crystalline state could be identified by a band at 1047 cm\(^{-1}\).\textsuperscript{33} The FTIR-ATR spectra collected from all the samples suggest the presence of more amorphous domains of starch in the samples SPCL IL rather than in SPCL or SPCL gl. Additionally, in the presence of [bmim]Ac there is a shift of this band towards lower frequencies.

The broad peak in the region 3000–3600 cm\(^{-1}\) is associated with the stretching vibration mode of the hydrogen bonded O–H groups (Fig. 2ii). The intensity of this peak is noticeably higher in the samples where [bmim]Ac was present, indicating an increase in the hydrogen bonds, which is not the case when glycerol is present in the samples.

Such an interpretation suggests that ionic liquids have greater interactions with SPCL than glycerol.

**Mechanical properties**

Tensile and compression tests were performed in the compression moulded matrixes before foaming in order to evaluate the effect of ionic liquid and glycerol in the plasticization of the polymer. Mechanical properties were evaluated in both tensile and compressive modes. A summary of the results obtained is presented in Table 2.

The results of the mechanical tests confirm the plasticization of the samples. The Young modulus is statistically different in the case of SPCL and SPCL IL, in both tensile and compression tests. Besides, SPCL IL samples show a higher elongation at break, which is statistically different from SPCL gl. These results also indicate the strong plasticizing effect of IL. Similar results were observed by Sankri et al.,\textsuperscript{26} where thermoplastic starch samples plasticized by 1-butyl-3-methylimidazolium chloride showed a much higher elongation at break than the glycerol plasticized starch samples.

<table>
<thead>
<tr>
<th>SPCL</th>
<th>253.7 ± 12.9</th>
<th>10.8 ± 1.2</th>
<th>11.6 ± 0.5</th>
<th>6.1 ± 0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPCL IL</td>
<td>197.1 ± 14.3</td>
<td>12.3 ± 2.3</td>
<td>9.1 ± 0.6</td>
<td>2.7 ± 0.4</td>
</tr>
<tr>
<td>SPCL gl</td>
<td>217.8 ± 11.4</td>
<td>7.2 ± 1.5</td>
<td>6.9 ± 0.9</td>
<td>5.9 ± 0.9</td>
</tr>
</tbody>
</table>

**Supercritical fluid foaming**

The effect of the presence of [bmim]Ac and glycerol on the processing of the SPCL was evaluated under different operating conditions. Fig. 3 represents a cross-section image of the matrixes prepared.

A more detailed study on the morphology of the materials developed was carried out by analysis of the 2D images provided by micro-computed tomography. Table 3 shows the inner morphology of the matrixes prepared at different pressures in comparison with the raw material.

Plasticization takes place when the gas is dissolved in the polymer and it affects three different characteristics of the polymers, particularly viscosity, gas diffusivity and interfacial tension.\textsuperscript{34} The enhancement of carbon dioxide solubility in the matrix was promoted by the addition of [bmim]Ac. There is a considerable decrease in viscosity upon carbon dioxide dissolution, which may be comparable to the decrease observed when CO\(_2\)-free IL is heated. This should be greater for the systems with the IL rather than glycerol. It is in fact the differences in the viscosity and gas diffusivity that are related to the solubility of carbon dioxide that explain the differences in porosity obtained. Unlike the ionic liquid, glycerol is soluble in carbon dioxide to some extent and this may be the reason for the differences observed.

The operating variables which mostly affect the process are pressure, temperature and soaking time. A comprehensive study on the effect of these variables was designed and the morphological properties, namely the porosity and interconnectivity, of the materials produced were calculated. The interconnectivity of the scaffold is calculated according to the formula

$$I = \frac{[(V_{total\ pore} - V_{total\ pore\ disconnected})/V_{total\ pore}] \times 100}{\text{where the volume of the disconnected pore volume for the disconnected pore volume which was defined to be higher than 50 \mu m}}$$

Fig. 4 summarizes the results obtained.

**Pressure effect**

The effect of pressure on the morphology of the matrixes was evaluated at 40 °C and during 30 min soaking time. Fig. 5

---

*Green Chem.*
shows the relationship between pressure and porosity of the materials.

The polymeric blend SPCL did not present any morphological changes concerning porosity and interconnectivity, when processed at different pressures. However, differences were observed between SPCL and the samples containing either ionic liquid or glycerol, even at lower pressures. This indicates that the presence of the plasticizing agent is fundamental for the enhancement of the foaming process. The same conclusion is valid for values of interconnectivity of the samples.

**Table 3** Morphological characteristics (porosity and interconnectivity, IC) of the materials processed under different operating conditions (soaking time, ST; pressure and temperature)

<table>
<thead>
<tr>
<th>Operating parameters</th>
<th>SPCL</th>
<th>SPCL IL</th>
<th>SPCL gl</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST (h)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>10.4</td>
<td>10.2</td>
<td>28.4</td>
</tr>
<tr>
<td>40</td>
<td>15.9</td>
<td>21.7</td>
<td>24.3</td>
</tr>
<tr>
<td>45</td>
<td>17.2</td>
<td>35.2</td>
<td>29.5</td>
</tr>
<tr>
<td>55</td>
<td>5.2</td>
<td>29.1</td>
<td>36.1</td>
</tr>
<tr>
<td>60</td>
<td>8.8</td>
<td>25.0</td>
<td>34.9</td>
</tr>
<tr>
<td>15</td>
<td>17.3</td>
<td>32.0</td>
<td>36.1</td>
</tr>
<tr>
<td>20</td>
<td>16.7</td>
<td>35.9</td>
<td>34.9</td>
</tr>
<tr>
<td>40</td>
<td>17.3</td>
<td>21.9</td>
<td>40.9</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>41.1</td>
<td>29.3</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>4.9</td>
<td>25.9</td>
</tr>
</tbody>
</table>

**Fig. 4** Representative micro-CT 2D images of the cross-section of SPCL, SPCL IL and SPCL gl, processed under different operating conditions.

**Temperature effect**

The effect of the processing temperature on the morphology of the materials was evaluated at 10.0 MPa. The variation of porosity as a function of operating temperature is illustrated in Fig. 6. Statistical differences were observed between SPCL and both SPCL IL and SPCL gl.

From Fig. 5 it is possible to conclude that especially when using IL there is a value of temperature which maximizes the porosity of the samples. At 45 °C and 10.0 MPa, the highest
values of porosity were obtained. This is due to the melting behavior of the samples. The melting temperature of poly-ε-caprolactone is $\sim 60 ^\circ C$, as confirmed by the DSC analysis (data not shown). Therefore, approaching this temperature the samples tend to melt, collapsing the structure, which is translated into the lower porosity observed.

Furthermore, while the samples loaded with glycerol do not present significant changes with increasing temperature, the samples in which the plasticizer was [bmim]Ac show a significant enhancement in the foaming process.

### Soaking time effect

The analysis of the 2D images of the matrices prepared suggested that carbon dioxide diffusion into the bulk of the blend is one of the parameters which influence the final morphology of the samples. The effect of soaking time on the samples processed at 40 °C and 20.0 MPa (Fig. 7) demonstrated that there is a slight increase in the porosity as the soaking time increases, nonetheless this effect is not as pronounced as expected. Increasing soaking time would allow the diffusion of more carbon dioxide molecules into the bulk of the samples, which would ultimately result in higher porosity. This fact was not observed, which may indicate that the equilibrium value of carbon dioxide sorption in the samples is achieved after 1 h.

### Effect of the presence of ionic liquid

The analysis of the operating conditions on the morphology of the matrices obtained provides more insights on the effect of [bmim]Ac in the supercritical fluid foaming process. These findings suggest that not only the interactions between polymer and ionic liquid are important but also the interactions between ionic liquid and carbon dioxide. The solubility of carbon dioxide in 1-butyl-3-methylimidazolium acetate was determined by Shiflett et al., who observed a high solubility of CO₂ in the ionic liquid. Specific solvation interactions between the IL and carbon dioxide studied by Carvalho et al. explain the high solubility by the strength of interaction of CO₂ with the anion. In this particular case the interaction results from an acid–base interaction between the acid carbon of carbon dioxide and the carboxylate of the anion, which results in the chemisorption that takes place in the ionic liquid. Furthermore, imidazolium-based room temperature ionic liquids are a singular group of IL which have been reported for their particularly high absorption of carbon dioxide.

This can explain the differences observed between the samples processed in the presence of IL or gl. While glycerol acts merely as a plasticizing agent, the ionic liquid establishes interactions with both the polymer and carbon dioxide, promoting the decrease in the viscosity, which enhances the supercritical fluid foaming process. Advantages can hereafter be taken from the impregnation of a polymeric matrix with an ionic liquid, especially considering particular applications in which it is desirable to have the ionic liquid dispersed in the matrix.

### Conclusions

The presence of an ionic liquid blended with a semi-crystalline natural-based polymer has proven to be essential for the possibility of foaming that particular polymer. This effect was
comparable to the effect of glycerol but may add interesting features to the materials. The ionic liquid has been demonstrated to be an efficient plasticizer promoting the gas foaming of the semi-crystalline natural-based polymer. FTIR-ATR spectroscopy has shown some interactions between the ionic liquid and the polymeric blend, which explains the plasticization effect. Mechanical properties, both tensile and compressive tests, have also demonstrated the plasticizing effect of [bmim]Ac. Depending on the supercritical foaming conditions, particularly pressure, temperature and soaking time, the morphology of the 3D matrixes obtained can be finely tuned.

The application of porous materials covers a wide range of fields. From their use in biomedical applications as drug delivery devices or 3D scaffolds to catalytic substrates or stationary phases in extraction and separation processes, a number of applications can be envisaged.

The use of ionic liquids in the preparation of porous structures may also see exciting perspectives, mainly due to the fact that ionic liquids may promote catalysis of certain reactions involving gaseous reactants and products. Other applications include, for instance, the use of these materials in sorptive microextraction techniques, in which the ILs may play a role as extractants, solvents, mediators or desorption solvents. The materials developed may also be applied in gas sequestration as suggested by Jones promoting, for instance, the capture of carbon dioxide, and other flue gases.

Acknowledgements

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007–2013) under grant agreement no. KBBE-2010-266033 (project SPECIAL). S. S. Silva would like to thank the Portuguese Foundation for Science and Technology (FCT) for her post-doctoral fellowship (SFRH/BPD/45307/2008).

References