

# On the development of a facile approach based on the use of ionic liquids: preparation of PLLA (sc-PLA)/high surface area nano-graphite systems

Lorenza Gardella,<sup>a</sup> Davide Furfaro,<sup>a</sup> Maurizio Galimberti<sup>b</sup> and Orietta Monticelli\*<sup>a</sup>

Received 6th May 2015,

Accepted 3rd June 2015

## Introduction

Poly lactide (PLA) is one of the most promising bio-based (the monomer can be derived from renewable sources), biodegradable and biocompatible polymers for various end-use applications, exhibiting properties comparable to those of the traditional oil-based thermoplastics.<sup>1</sup> Unfortunately, its poor thermal processability, low crystallization rate and inherent brittleness, together with hydrophobicity and lack of reactive functional groups along the polymer backbone, constitute a major limitation for its wide application in both industrial and biomedical fields.<sup>2,3</sup> As a consequence, considerable research effort has been made over the last few decades to improve the PLA performance and make it competitive with the tradi-

tional, consumable polymers. These attempts mainly include addition of plasticizers<sup>4</sup> and/or nucleating agents,<sup>5</sup> blending<sup>6-8</sup> and reactive blending<sup>9,10</sup> with other polymers, copolymerization<sup>11</sup> and incorporation of fillers/nanofillers.<sup>12-15</sup> In particular, concerning the development of PLA nanocomposites based on graphene/graphite, which is the object of our study, the addition of the carbon nanofiller was found to improve the crystallization rate of the polymer, it acting as a nucleating agent.<sup>16-18</sup> Moreover, as demonstrated by Pinto *et al.*<sup>19</sup> PLA/graphene nanocomposites showed improved mechanical and gas barrier properties with respect to the neat polymer matrix. The dispersion of the nanofiller in PLA was generally carried out by using the solution-mixing approach. Such a method implies the preliminary dispersion of the layered carbon filler in a solvent able to promote exfoliation and dispersion of the graphene layers as well as solubilization of the polymer. Furthermore, in order to promote specific interactions of the nanofiller with the polymer, graphene oxide (GO), which contains hydroxyl and epoxy groups on the basal planes and

<sup>a</sup>Dipartimento di Chimica e Chimica Industriale, Università di Genova, Via Dodecaneso, 31, 16146 Genova, Italy. E-mail: orietta.monticelli@unige.it

<sup>b</sup>Dipartimento di Chimica, Materiali e Ingegneria Civile "Giulio Natta", Politecnico di Milano, Via Mancinelli, 7, 20130 Milano, Italy

carboxy groups on the hedges, was used. The use of graphene oxide requires the oxidation of graphite, typically performed by using strong acids and oxidating agents,<sup>20</sup> thus achieving the extensive modification of the carbon atom hybridization. Hence, to restore sp<sup>2</sup> based graphene layers, which is fundamental for the electrical and thermal conductivity, subsequent reduction of GO has to be performed. However, it is recognized that the complete reduction of GO can be hardly achieved. Such a top-down procedure thus leads to graphene/graphitic nanofillers with a structure damaged to some extent.<sup>20</sup>

In spite of the significant results (in terms of improvement of polymer properties) obtained by applying the described approaches, for preparing PLA-based composites keeping the benefits connected with the bio-based nature of the polymer, it would be highly desirable to use methods and/or materials with a low environmental impact, besides using a graphitic nanofiller with the sp<sup>2</sup> hybridization of the carbon atoms preserved. Recently, ionic liquids (ILs) have been proposed as “green” solvents.<sup>21,22</sup> Although, these compounds are not always green, they can be considered low environmental impact molecules. In the polymer field, ionic liquids have been mainly used as polymerization media.<sup>23</sup> The interest in utilizing ionic liquids not only as solvents but also as initiators,<sup>24</sup> catalysts<sup>25</sup> and additives<sup>26–33</sup> has increased over the last few years. In particular, imidazolium based ionic liquids were found to be efficient plasticizers for poly(methyl methacrylate) (PMMA), prepared by *in situ* polymerization in the ionic liquid medium.<sup>26,27</sup> 1-Butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF<sub>6</sub>]) was also applied by Xing *et al.*<sup>28</sup> to modify the properties of poly(vinylidene fluoride) (PVDF). The prepared PVDF/[bmim][PF<sub>6</sub>] blends were found to exhibit excellent mechanical performances with significantly increased ductility and good optical transmittance. Ionic liquids, based on ammonium, imidazolium and phosphonium were also studied as plasticizers for poly(vinyl chloride) (PVC).<sup>29</sup> More recently, 1-butyl-3-methylimidazolium hexafluorophosphate, incorporated into poly(ethylene oxide) by solution casting, was shown to slow down the melt crystallization of the polymer and the spherulitic growth rate.<sup>30</sup> As far as the combination of ILs with PLA is concerned, only a few attempts have been reported so far, mainly regarding phosphonium-based ionic liquids.<sup>31–33</sup>

Apart from the above described applications in polymer science, ionic liquids were also found to be effective stabilizing agents for carbon nanotubes<sup>34,35</sup> and, more recently, they have been used to disperse graphite/graphene.<sup>36–38</sup> Zhou *et al.*<sup>36</sup> obtained a uniform dispersion of graphene sheets by applying a multi-step procedure, which consisted of a preliminary dispersion of graphite oxide (GO) in water, followed by the addition of an IL polymer (PIL) [poly(1-vinyl-3-butylimidazolium chloride)], and finally GO reduction. PIL/graphene was mixed with [bmim][PF<sub>6</sub>] and the resulting system was found to hold a higher conductivity than the pure ionic liquid. A similar procedure was applied by the same authors to prepare graphene nanosheet/polyaniline composites.<sup>37</sup> Indeed, the gels formed by ILs and graphene have been studied as poten-

tial electrolytes for dye sensitized solar cells by Ahmad *et al.*<sup>38</sup> Recently, Zhao *et al.*<sup>39</sup> also highlighted the mechanism by which the  $\pi$ -electron-rich carbon nanomaterials, such as graphene, can be dispersed in ionic liquids. Although the above studies have demonstrated the potentiality of ILs, the methods applied to disperse graphite/graphene in ILs are generally based on GO and on the use of co-solvents or co-dispersing agents. Clearly, the development of easier methods, simultaneously characterized by a low environmental impact, might allow a more wide use of ILs in this field.

In the present study, PLA-based composites were prepared through the simple dispersion of a nanosized graphite in ILs, followed by melt blending the graphite/IL system with poly(L-lactide) PLLA or with the PLLA/PDLA pair (sc-PLA). Nanosized graphite with a high surface area (HSAG), higher than 300 m<sup>2</sup> g<sup>-1</sup>, a low number of stacked graphene layers and a high shape anisotropy was selected.<sup>40</sup> Such a method does not require either the chemical modification of the graphitic nanofiller or the use of solvents or co-dispersing agents.

In particular, the use of ILs in the preparation of PLA-based composite systems is characterized by several advantages: (i) the “green” nature of ILs, (ii) the known capability of ILs to disperse/exfoliate graphite, (iii) the possible involvement of ILs in the modification of PLA properties.

The morphology of the composites was characterized through scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy analysis (EDS) and the thermal properties were studied, as a function of HSAG content, by means of differential scanning calorimetry (DSC).

## Experimental

### Materials

Poly(L-lactide) (PLLA) is a commercial product from Nature Works Co. Ltd, USA (2002 Da,  $M_n = 100\,000\text{ g mol}^{-1}$ ) with a residual monomer content less than 0.3% by mass. For the preparation of composites based on stereocomplex PLA (sc-PLA), poly(L-lactide) (PLLA), PLLA 1010 Synterra (average molecular weight  $1 \times 10^5$ ), and poly(D-lactide) (PDLA), PDLA 1010 Synterra (average molecular weight  $1 \times 10^5$ ), purchased from Purac (The Netherlands) in pellet form, were used as received. The high surface area nano-graphite (HSAG) powder, TC-307 from Asbury, is an ultra-fine powder with a nominal BET surface area of 350 m<sup>2</sup> g<sup>-1</sup>, and particle size distribution from 0.20  $\mu\text{m}$  to 20  $\mu\text{m}$ . Graphite TC-307 from Asbury was used as received.

The following ILs, all purchased from Sigma-Aldrich, were used as received: 1-butyl-3-methylimidazolium iodide ([bmim][I]), 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) and 1-butyl-3-methylimidazoliumhexa-fluorophosphate ([bmim][PF<sub>6</sub>]).

### Preparation of PLLA/IL, PLLA/PDLA/IL (sc-PLA/IL), PLLA/IL/HSAG and PLLA/PDLA/IL/HSAG (sc-PLA/IL/HSAG) systems

Before accomplishing the preparation of the PLLA/IL systems, the polymer was vacuum dried overnight at 40 °C. As shown in

**Table 1** Characteristics of the prepared samples

Sample name	Type of polymer	Type of ILs	HSAG concentration (wt%)	IL concentration (wt%)	IL <sup>a</sup> solubility	$\Delta M^b$ (%)
PLLA/2[bmim][I]	PLLA	[bmim][I]	—	2	+	60
PLLA/5[bmim][I]	PLLA	[bmim][I]	—	5	—	58
PLLA/2[bmim][Cl]	PLLA	[bmim][Cl]	—	2	—	80
PLLA/2[bmim][PF <sub>6</sub> ]	PLLA	[bmim][PF <sub>6</sub> ]	—	2	+	20
PLLA/5[bmim][PF <sub>6</sub> ]	PLLA	[bmim][PF <sub>6</sub> ]	—	5	+	23
PLLA/10[bmim][PF <sub>6</sub> ]	PLLA	[bmim][PF <sub>6</sub> ]	—	10	±	23
PLLA/2[bmim][PF <sub>6</sub> ]/0.04HSAG	PLLA	[bmim][PF <sub>6</sub> ]	0.04	2	+	21
PLLA/5[bmim][PF <sub>6</sub> ]/0.1HSAG	PLLA	[bmim][PF <sub>6</sub> ]	0.1	5	+	23
sc-PLA/2[bmim][PF <sub>6</sub> ]	PLLA/PDLA	[bmim][PF <sub>6</sub> ]	—	2	+	—
sc-PLA/5[bmim][PF <sub>6</sub> ]	PLLA/PDLA	[bmim][PF <sub>6</sub> ]	—	5	±	—
sc-PLA/10[bmim][PF <sub>6</sub> ]	PLLA/PDLA	[bmim][PF <sub>6</sub> ]	—	10	+	—
sc-PLA/2[bmim][PF <sub>6</sub> ]/0.04HSAG	PLLA/PDLA	[bmim][PF <sub>6</sub> ]	0.04	2	+	—
sc-PLA/5[bmim][PF <sub>6</sub> ]/0.1HSAG	PLLA/PDLA	[bmim][PF <sub>6</sub> ]	0.1	5	+	—

<sup>a</sup> + completely soluble, ± partially soluble, — immiscible. <sup>b</sup> Percentage of molecular mass variation compared to the neat PLLA that is  $(M_{\text{system}}/M_{\text{neat PLA}}) \times 100$ .

Table 1, different amounts of ILs were added to the polymer matrix. Indeed, the ionic liquid and the polymer were charged into a glass reactor, namely a laboratory internal mixer provided with a mechanical stirrer (Heidolph, type RZR1), which was connected to a vacuum line and evacuated for 15 min at room temperature, followed by argon purging for 5 minutes. The above operations were repeated at least three times, to avoid humidity coming in contact with the reagents.

The reactor was then placed in an aluminum block oven at 180 °C and, under an inert atmosphere, the polymer system was mixed for 10 minutes at 100 rpm. In the case of the systems based on stereocomplex PLA (sc-PLA), equal amounts of PLLA and PDLA were mixed with the ILs at 230 °C for 10 min at 100 rpm.

For the systems containing the HSAG, the nanofiller, whose concentration was fixed at 2% by mass, was previously dispersed in the IL by using a sonic bath (Model Ney Ultrasonic) at 80 °C for 120 minutes. The composites were prepared by mixing PLLA or sc-PLA with the as-prepared IL/HSAG systems, using the same conditions as for the neat PLA/IL system. Moreover, a sample was prepared by adding the HSAG directly into PLLA and mixing for 10 minutes at 100 rpm.

### Characterization

The variation of PLA molecular mass during the processing was evaluated by measuring the reduced viscosity of chloroform-based solutions containing 1 wt% of the polymer.

A Zeiss Supra 40 VP field emission scanning electron microscope equipped with a backscattered electron detector was used to examine the prepared system morphologies. The specimens were submerged in liquid nitrogen for 30 min and fractured cryogenically. All samples were thinly sputter-coated with carbon using a Polaron E5100 sputter coater.

Differential scanning calorimetric analysis was performed under a continuous nitrogen purge on Mettler calorimetric apparatus, model DSC1 STAR<sup>e</sup> System. Both calibrations of heat flow and temperature were based on a run in which one

standard sample (indium) was heated through its melting point. The samples, having a mass between 2.5 and 6 mg, were heated from room temperature to 200 °C (250 °C for sc-PLA-based systems), then cooled down to room temperature and finally heated to 200 °C (250 °C for sc-PLA-based systems) again. A scanning rate of 10 °C min<sup>-1</sup> was used both on heating and cooling.

Thermal gravimetric analysis (TGA) was performed with a STAR<sup>e</sup> System Mettler thermobalance under a flow of nitrogen of 80 ml min<sup>-1</sup>. The weight loss of the samples (having initial masses of ca. 10 mg) was measured from room temperature to 500 °C at a heating rate of 10 °C min<sup>-1</sup>.

The development of the morphology during melt-crystallization was followed by means of a Leika DMLP polarized optical microscope equipped with a 20× objective lens. The microscope was coupled with a Linkam CSS450 hot-stage to enable a careful control of the thermal history while acquiring optical micrographs with a dedicated digital video-camera. The samples were initially melted and compressed in films of approximately 20 μm thickness by gently squeezing them between microscope glasses. The following temperature protocol was adopted: the samples were annealed for two minutes at 200 °C and then cooled down to 125 °C at 10 °C min<sup>-1</sup>, at which temperature they were isothermally crystallized and the micrographs were taken at a frequency of about 30 s.

## Results and discussion

This work primarily focused on “neat” systems based on PLLA, or an equimolar mixture of PLLA and PDLA (sc-PLA), and ionic liquids (ILs), prepared by melt-mixing the polymer matrices with different kinds of imidazolium-type ILs (Table 1). The behavior of the imidazolium salt was found to be strongly dependent on the anion. Both [bmim][I] and [bmim][Cl] were characterized by a scarce solubility, with the occurrence of phase separation for a concentration of the IL as low as 2–5%

by mass, whereas [bmim][PF<sub>6</sub>] was found to be miscible up to about 10% by mass. Moreover, the decrease of the molecular mass of the polymer was relevant in the presence of [bmim]-[Cl] and [bmim][I] (up to about 80%), but much smaller (about 20%) in the case of [bmim][PF<sub>6</sub>], in all the explored concentration ranges. In the literature, the effect of the anionic counterpart of the ionic liquid was documented for other polymers, such as poly(vinyl chloride) (PVC).<sup>28</sup> It was also reported that ionic liquids can catalyze degradation reactions of polymers and, in particular, the hydrolytic degradation of PLA, which seems to be our case.<sup>31</sup> As such, because of its highest solubility in the polymer matrix as well as minor degradative effects, [bmim][PF<sub>6</sub>] was selected as the ionic liquid for the preparation of the PLA-based systems. Composites were prepared both in the absence and in the presence of high surface area nano-graphite (HSAG), with the ionic liquid promoting exfoliation and dispersion of the HSAG, and their properties were characterized.

The dispersion of the IL in the polymer was studied by SEM analysis. In Fig. 1, the SEM micrograph of the surface of the sample PLLA/5[bmim][PF<sub>6</sub>] is shown together with the EDS spectrum.

In Fig. 1a, the surface of the sample does not show any visible domains on a (sub)micrometric scale, while the concentration of both F and P-elements, belonging to the IL, is constant throughout the surface of the sample. Analysis performed on a large number of samples allowed the observation of an even dispersion of the mentioned elements, up to a content of the ionic liquid of about 5 wt% by mass of the ionic liquid content. It is thus possible to derive that [bmim]-[PF<sub>6</sub>] has a good solubility in the polymer melt up to this concentration.

The thermal properties of the PLLA/[bmim][PF<sub>6</sub>] and sc-PLA/[bmim][PF<sub>6</sub>] systems, as studied by means of DSC, were compared to those of the neat PLLA and sc-PLA. Tables 2

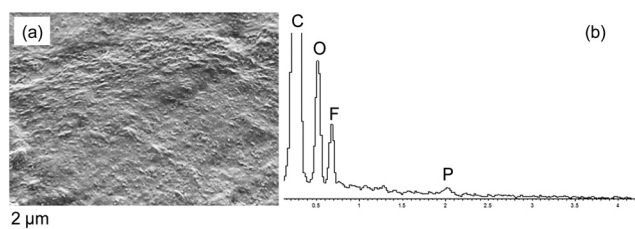


Fig. 1 (a) SEM micrograph and (b) EDS analysis of PLLA/5[bmim][PF<sub>6</sub>].

and 3 show the DSC results for PLLA- and sc-PLA-based systems, respectively. In the second heating scan, only the glass transition temperature ( $T_g$ ) was observed at 63 °C in the case of the neat PLLA, whereas both cold crystallization and melting peaks were visible for the systems containing the IL. This different behavior can be ascribed to the increase of the polymer crystallinity as a consequence of the (slight) reduction of its molecular mass, which was discussed in this section and whose results are shown in Table 1. Nevertheless, in the samples containing the IL and characterized by a similar molecular mass,  $\Delta H_m$  was found to increase by increasing the concentration of [bmim][PF<sub>6</sub>]. Indeed, the degree of crystallinity ( $W_c$ ), calculated on the basis of the melting enthalpy of a 100% crystalline PLA ( $\Delta H_o = 93 \text{ J g}^{-1}$  (ref. 41)), turned out to be 2% and 3% for PLLA/2[bmim][PF<sub>6</sub>] and PLLA/5[bmim][PF<sub>6</sub>], respectively. Indeed, it is possible to infer a nucleating effect of IL, it being already reported for other polymer matrices, such as poly(ethylene oxide).<sup>28</sup> Moreover, it is worth noting that the  $T_g$  of the polymer tends to slightly decrease on increasing the IL content, thus indicating a (small) plasticizing effect of [bmim][PF<sub>6</sub>]. A decrease in  $T_g$  was already reported for other polymer/IL systems,<sup>26-28</sup> the extent of the decrease depending on the solubility of the ionic liquid in the amorphous portion of the polymer, which, in the case of our PLA-based system, seems to be limited.

The study of the thermal behavior of the prepared systems was completed by accomplishing TGA analysis. The TGA results show that the initial degradation temperature ( $T_{\text{onset}}$ ) as well as the temperature related to the maximum degradation rate ( $T_{\text{max}}$ ) diminishes by increasing the concentration of IL in the polymer. The latter decrease turns out to be limited, of about 20 °C for the sample containing the highest amount of [bmim][PF<sub>6</sub>]. It is worth underlining that a moderate enhancement of the PLA degradation rate is interesting for some specific applications, as the acceleration of the hydrolytic degradation is particularly important for product-based PLA used in biomedical applications or to be composted or landfilled.<sup>1</sup>

In the literature, the effect of IL on the polymer thermal stability was evaluated for other matrices also, such as PMMA<sup>27</sup> and PVC.<sup>29</sup> While for the latter polymer a decrease of the degradation temperature, caused by the introduction of IL, was reported, in the case of PMMA an increase of the thermal stability in the [bmim][PF<sub>6</sub>]-based sample was found. Indeed,

Table 2 Thermal properties of PLLA and PLLA/[bmim][PF<sub>6</sub>] systems (second heating scan)

Sample name	$T_g$ (°C)	$T_{cc}$ (°C)	$\Delta H_{cc}$ (J g <sup>-1</sup> )	$T_m$ (°C)	$\Delta H_m$ (J g <sup>-1</sup> )	$T_{\text{onset}}^b$ (°C)	$T_{\text{max}}$ (°C)
PLLA	63	—	—	—	—	344	365
PLLA/2[bmim][PF <sub>6</sub> ]	60	130	1.7	153	1.8	337	364
PLLA/5[bmim][PF <sub>6</sub> ]	57	129	2.7	152	2.9	320	354
PLLA/2[bmim][PF <sub>6</sub> ]/0.04HSAG	59	130	10.0	153	9.9	338	365
PLLA/5[bmim][PF <sub>6</sub> ]/0.1HSAG	58	128	19.0	152	18.6	320	355
PLLA/0.1HSAG <sup>a</sup>	63	129	5.7	153	5.9	—	—

<sup>a</sup> Sample prepared by adding directly the HSAG in PLLA. <sup>b</sup> Initial degradation temperature.

**Table 3** Thermal properties of sc-PLA and sc-PLA/[bmim][PF<sub>6</sub>] systems (second heating scan)

Sample name	$T_g$ (°C)	$T_c$ (°C)	$\Delta H_c$ (J g <sup>-1</sup> )	$T_m^{\text{homo}}$ (°C)	$\Delta H_m^{\text{homo}}$ (J g <sup>-1</sup> )	$T_m^{\text{stereo}}$ (°C)	$\Delta H_m^{\text{stereo}}$ (J g <sup>-1</sup> )
sc-PLA	63	125	37.1	173	25.6	223	37.5
sc-PLA/2[bmim][PF <sub>6</sub> ]	57	130	59.3	165	9.2	220	59.3
sc-PLA/5[bmim][PF <sub>6</sub> ]	57	129	58.0	164	4.5	216	55.7
sc-PLA/2[bmim][PF <sub>6</sub> ]/0.04G	—	151	47.0	—	—	220	52.0
sc-PLA/5[bmim][PF <sub>6</sub> ]/0.1G	—	156	64.0	—	—	220	65.7

in the case of our PLA/[bmim][PF<sub>6</sub>] systems, it is possible to hypothesize, as previously reported,<sup>32</sup> the catalytic effect of the acidity of the IL and/or of the compounds resulting from the decomposition of the IL on the degradation of the polymer and the influence of water present in the ionic liquid which can promote the breakage of the ester bonds of the PLA.

These findings clearly demonstrate that it is not possible to draw a general rule, but that the effect of the IL depends on both the type of ionic liquid and on the chemical structure of the polymer matrix.

When PLLA is blended with PDLA, the formation of the stereocomplex form (whose crystallization rate is much higher than that of the two single polymers<sup>41</sup>) enables the system to crystallize directly on cooling from the melt. However, on subsequent heating, two endothermic peaks appear, a low-temperature one (at about 170 °C, ascribable to the melting of homo-crystallites), together with the high-temperature one relative to the melting of the stereocomplex (at about 220 °C).<sup>41</sup>

As in the case of the PLLA-based systems, the IL causes an enhancement of the crystallization rate, the crystallization peak being shifted towards higher temperatures and the enthalpy of crystallization increasing considerably. Moreover, the IL seems to favor the formation of a stereocomplex over that of the homo-crystals, a phenomenon which might be related to the effect of IL on the molecular weight of the system – the viscosity measurements were not carried out for the scarce solubility of sc-PLA – as well as on the nucleation of the system.

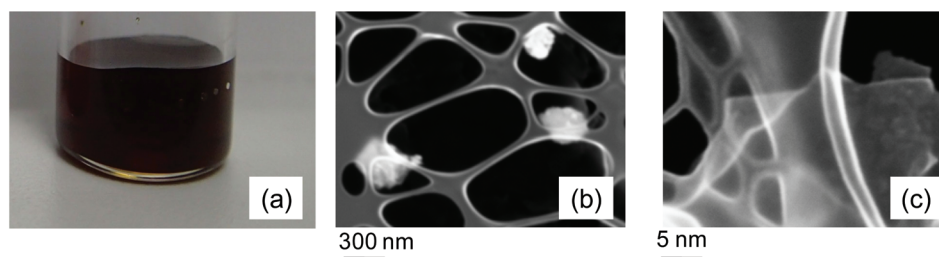
#### Preparation and characterization of PLLA/[bmim][PF<sub>6</sub>]/HSAG and sc-PLA/[bmim][PF<sub>6</sub>]/HSAG systems

The preparation of the systems based on the HSAG consisted of a preliminary dispersion of the nanofiller in [bmim][PF<sub>6</sub>],

through a sonication treatment. As already mentioned, the ILs, and in particular [bmim][PF<sub>6</sub>], were found to be capable of promoting the dispersion/exfoliation of graphite.<sup>35</sup> Thus, in our work, we did not focus only on the specific effect of the IL on the properties of the PLA-based materials, but also investigated its potential as a dispersing agent for the HSAG. As shown in Fig. 2, the sonication of [bmim][PF<sub>6</sub>], containing 2% by mass of the HSAG allowed obtaining a stable dispersion (Fig. 2a), characterized by aggregates with an average dimension of 300 nm (Fig. 2b) and composed of a few layers (Fig. 2c).

The addition of the [bmim][PF<sub>6</sub>]/HSAG system into the polymer matrix, by melt-blending, did not produce any modification of the morphology of the fractured polymer surface, thus highlighting the sub-micrometric dispersion of the nanofiller. In contrast, when the HSAG was directly added to the polymer without performing the pre-dispersion in the ionic liquid, aggregates of 10–20 μm size were formed (results not shown). These findings demonstrate the efficacy of the ionic liquid as dispersing agent for the nano-graphite.

The influence of the HSAG on the thermal properties of PLLA and sc-PLA was evaluated by means of DSC. The DSC results of the samples based on PLLA, shown in Table 2, demonstrate that the incorporation of the [bmim][PF<sub>6</sub>]/HSAG dispersion has no discernible effect on the  $T_g$ ,  $T_c$  and  $T_m$  of the polymer systems as compared to those containing only the IL. However,  $\Delta H_{cc}$  and  $\Delta H_m$  significantly increase in the samples containing the nano-graphite. Indeed,  $W_c$  is ca. 2% and 3% for PLLA/2[bmim][PF<sub>6</sub>] and PLLA/5[bmim][PF<sub>6</sub>], increasing to 10% and 20% for PLLA/2[bmim][PF<sub>6</sub>]/0.04G and PLLA/5[bmim][PF<sub>6</sub>]/0.1HSAG, respectively. It is worth underlining that the increase of  $W_c$  seems to be related not only to the amount of the HSAG, but also to its dispersion in the polymer matrix. Indeed, the sample based on the direct addition of the



**Fig. 2** (a) Photo of the [bmim][PF<sub>6</sub>]/HSAG dispersion, (b) and (c) FE-SEM micrographs of the nano-graphite dispersed by sonication in [bmim][PF<sub>6</sub>].



nanofiller, PLLA/0.1G, has a lower  $\Delta H_m$  than the system in which the nano-graphite was introduced by means of the IL.

In order to elucidate the peculiar behaviour of the HSAG-based systems, “visual” measurements were carried out by means of a hot stage coupled to a polarized optical microscope. By comparing the micrographs, taken during isothermal crystallization at 125 °C, of PLLA/5[bmim][PF<sub>6</sub>] with those of PLLA/5[bmim][PF<sub>6</sub>]/0.1HSAG, it can be seen clearly that the nucleation density (*i.e.* the number of spherulites per unit volume) is much higher in the sample containing the HSAG, which evidence the nucleating action of the nano-graphite (Fig. 3).

As already mentioned, the nucleating effect of graphene and, in particular, of GO, on the crystallization of PLA has been reported in the literature,<sup>16–18</sup> where the carbon nanofiller was used in concentration from 0.5 to 2 wt%. In the present study, the effect of the nano-graphite on the polymer nucleation was observed to be significant already at a concentration of 0.04 wt%. This difference can be ascribed to both the different degrees of dispersion of the nanofiller and the concomitant action of the IL.

Furthermore, the spherulitic growth rate (defined as the slope of the spherulite radii as a function of crystallization time) triplicates in the case of the sample containing the IL/HSAG. Indeed, the synergic action of the nano-graphite and the IL thus produces a strong enhancement of the polymer crystallizability, enabling the crystallization of our composite systems to be complete in a much shorter time than for the neat polymer.

Once again, our approach turns out to be an appealing, economical and environmentally friendly alternative to the above mentioned methods generally applied to prepare graphite-based materials, since neither co-solvents nor the oxidation of graphite were exploited in the preparation of our systems. Indeed, in the case of PLA, some specific high added value applications of the IL/HSAG-based materials can be envisaged in areas where the high cost of ILs is justified, such as in the biomedical field or for the development of sensors.

As far as the thermal properties of the samples based on sc-PLA are concerned, DSC traces of both sc-PLA/2[bmim][PF<sub>6</sub>]/0.04HSAG and sc-PLA/5[bmim][PF<sub>6</sub>]/0.1HSAG systems show, together with a strong enhancement of the crystallization kine-

tics on cooling (to be imputed once again to the nucleating action of the nano-graphite), the exclusive presence of the endothermic peak characteristic of stereocomplex-PLA on heating, the melting peak corresponding to homo-crystals being completely absent. This peculiar effect of the HSAG, which is highly appealing from a factual point of view, has already been reported for systems charged with hydrotalcite,<sup>38</sup> where the enhanced crystallization of the stereocomplex promoted by the presence of the additive was found to suppress the detrimental formation of the homo-crystals.

## Conclusions

In this work, the specific effect of imidazolium type-ionic liquids (ILs) on the properties of both poly(L-lactide) (PLLA) and an equimolar mixture of PLLA and PDLA (sc-PLA), and their function as dispersing agents for a high surface area nano-graphite (HSAG) in the preparation of PLA/HSAG systems was assessed. Indeed, among the tested ILs, 1-butyl-3-methylimidazoliumhexa-fluorophosphate ([bmim][PF<sub>6</sub>]) showed the highest solubility, the lowest tendency to decompose the polymer matrix during the melt-blending process and a slightly plasticizing effect on PLLA. Moreover, [bmim][PF<sub>6</sub>] was characterized by a high capability of dispersing/exfoliating the nano-graphite, thus allowing obtaining a system containing 2 wt% of the nanofiller, characterized by aggregates with an average dimension of 300 nm and composed of a few layers. Conversely to the direct insertion of the HSAG into the polymer matrices, which produced micrometer-sized aggregates, in the case of the use of a [bmim][PF<sub>6</sub>]/HSAG system, a sub-micrometric dispersion was obtained. Thus, the applied approach turned out to be not only easy and highly advantageous time-wise, but also had a low environmental impact, involving neither the use of co-solvents nor the preliminary oxidation of the fillers, steps generally used in the classical methods for the preparation of graphite/graphene polymer systems. Finally, the presence of the finely dispersed nanofiller was found to behave as a nucleating agent for PLLA crystallization and, in the case of the sc-PLA-based systems, to promote the exclusive formation of stereocomplex crystals over homo-crystals.

## Acknowledgements

We are grateful to the Italian Ministry of Education and University through the 2010–2011 PRIN project (Grant No. 2010XLLNM3\_005).

## References

- 1 L.-T. Lim, R. Auras and M. Rubino, *Prog. Polym. Sci.*, 2008, **33**, 820.

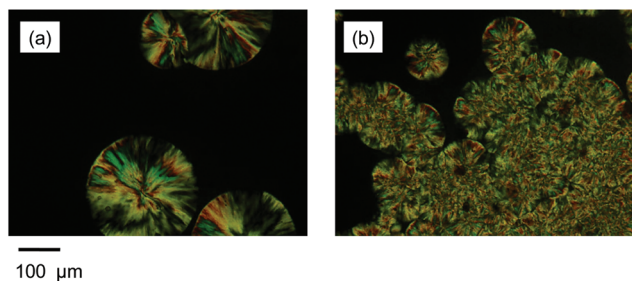


Fig. 3 Micrographs taken at 125 °C during isothermal crystallization of: (a) PLLA/5[bmim][PF<sub>6</sub>] and (b) PLLA/5[bmim][PF<sub>6</sub>]/0.1HSAG.

- 2 O. Monticelli, D. Cavallo, S. Bocchini, A. Frache, F. Carniato and A. Tonelotto, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 4794.
- 3 A. Södergård and M. Stolt, *Prog. Polym. Sci.*, 2002, **27**, 1123.
- 4 T. Mekonnen, P. Mussone, H. Khalilb and D. Bressler, *J. Mater. Chem. A*, 2013, **1**, 13379.
- 5 V. Peinado, L. García, Á. Fernández and P. Castell, *Compos. Sci. Technol.*, 2014, **101**, 17.
- 6 O. Monticelli, M. Calabrese, L. Gardella, A. Fina and E. Gioffredi, *Eur. Polym. J.*, 2014, **58**, 69–78.
- 7 S. Yang, S. A. Madbouly, J. A. Schrader, G. Srinivasan, D. Grewell, K. G. McCabe, M. R. Kessler and W. R. Graves, *Green Chem.*, 2015, **17**, 380.
- 8 T.-W. Lee and Y. G. Jeong, *Compos. Sci. Technol.*, 2014, **103**, 78.
- 9 C. M. Thurber, Y. Xu, J. C. Myers, T. P. Lodge and C. W. Macosko, *ACS Macro Lett.*, 2015, **4**, 30.
- 10 L. Gardella, M. Calabrese and O. Monticelli, *Colloid Polym. Sci.*, 2014, **292**, 2391.
- 11 L. Gardella, D. Cavallo, S. Colonna, A. Fina and O. Monticelli, *J. Polym. Sci., Part A: Polym. Chem.*, 2014, **52**, 3269.
- 12 O. Monticelli, M. Putti, L. Gardella, D. Cavallo, M. Prato and S. Nitti, *Macromolecules*, 2014, **47**, 4718.
- 13 O. Monticelli, S. Bocchini, L. Gardella, D. Cavallo, P. Cebe and G. Germelli, *Eur. Polym. J.*, 2013, **49**, 2572.
- 14 N. Najafi, M. C. Heuzey and P. J. Carreau, *Compos. Sci. Technol.*, 2012, **72**, 608.
- 15 M. Sabzi, L. Jiang, F. Liu, I. Ghasemi and M. Ataib, *J. Mater. Chem. A*, 2013, **1**, 8253.
- 16 D. Wu, Y. Cheng, S. Feng, Z. Yao and M. Zhang, *Ind. Eng. Chem. Res.*, 2013, **52**, 6731.
- 17 H. S. Wang and Z. B. Qiu, *Thermochim. Acta*, 2011, **526**, 229.
- 18 H. S. Wang and Z. B. Qiu, *Thermochim. Acta*, 2012, **527**, 40.
- 19 A. M. Pinto, J. Cabral, D. A. Pacheco Tanaka, A. M. Mendes and F. D. Magalhães, *Polym. Int.*, 2013, **62**, 33.
- 20 W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
- 21 P. Pollet, E. A. Davey, E. E. Ureña-Benavides, C. A. Eckert and C. L. Liotta, *Green Chem.*, 2014, **16**, 1034.
- 22 J. S. Wilkes, *Green Chem.*, 2002, **4**, 73.
- 23 P. Kubisa, *Prog. Polym. Sci.*, 2004, **29**, 3.
- 24 A. Mariani, D. Nuvoli, V. Alzari and M. Pini, *Macromolecules*, 2008, **41**, 5191.
- 25 S. Ding, M. Radosz and Y. Shen, *Macromolecules*, 2005, **38**, 5921.
- 26 M. P. Scott, C. S. Brazel, M. G. Benton, J. W. Mays, J. D. Holbrey and R. D. Rogers, *Chem. Commun.*, 2002, 1370.
- 27 M. P. Scott, M. Rahman and C. S. Brazel, *Eur. Polym. J.*, 2003, **39**, 1947.
- 28 C. Xing, M. Zhao, L. Zhao, J. You, X. Cao and Y. Li, *Polym. Chem.*, 2013, **4**, 5726.
- 29 M. Rahman and C. S. Brazel, *Polym. Degrad. Stab.*, 2006, **91**, 3371.
- 30 S. K. Chaurasia, R. K. Singh and S. Chandra, *CrystEngComm*, 2013, **15**, 6022.
- 31 K. Park, J. U. Ha and M. Xanthos, *Polym. Eng. Sci.*, 2010, **50**, 1105.
- 32 K. I. Park and M. Xanthos, *Polym. Degrad. Stab.*, 2009, **94**, 834.
- 33 P. Xu, H.-G. Gui and Y.-S. Ding, *Ionics*, 2013, **19**, 1579.
- 34 T. Fukushima, A. Kosaka, Y. Ishimura, T. Yamamoto, T. Takigawa, N. Ishii and T. Aida, *Science*, 2003, **300**, 2072.
- 35 Y. Shim and H. J. Kim, *ACS Nano*, 2009, **3**, 1693.
- 36 X. Zhou, T. Wu, K. Ding, B. Hu, M. Hou and B. Han, *Chem. Commun.*, 2010, **46**, 386.
- 37 X. Zhou, T. Wu, K. Ding, B. Hu, M. Hou and B. Han, *Chem. Commun.*, 2010, **46**, 3663.
- 38 I. Ahmad, U. Khanb and Y. K. Gun'ko, *J. Mater. Chem.*, 2011, **21**, 16990.
- 39 Y. Zhao and Z. Hu, *J. Phys. Chem. B*, 2013, **117**, 10540.
- 40 M. Mauro, V. Cipolletti, M. Galimberti, P. Longo and G. Guerra, *J. Phys. Chem. C*, 2012, **116**, 24809.
- 41 H. Urayama, T. Kanamori, K. Fukushima and Y. Kimura, *Polymer*, 2003, **44**, 5635.