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Journal:	<i>Green Chemistry</i>
Manuscript ID:	GC-COM-05-2014-000969.R1
Article Type:	Communication
Date Submitted by the Author:	17-Jun-2014
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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Structuration of ionic liquids in a poly(butylene-adipate-co-terephthalate) matrix: Influence on the water vapour permeability and mechanical properties

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

The use of new building blocks based on phosphonium ionic liquids to develop polymeric materials combining a structuration at nanoscale with the dramatic water vapour permeability and mechanical properties has been successfully investigated for the first time in a biopolymer matrix.

In materials chemistry, the ability to create and design new polymeric materials with unprecedented improvements in their final properties such as thermal, physical, mechanical and barrier properties is an extremely important challenge [1-2]. Currently, different routes are studied to lead to nanostructured polymers composed from block copolymer and/or nanoparticles [3-4]. Recently, one innovative pathway is the introduction of ionic liquids (ILs) within polymer matrix [5]. In fact, these organic salts have unique physical-chemical properties such as their inflammability, their low vapour pressure, their excellent thermal and chemical stability and their endless number of cation/anion combinations which make them suitable ideal additives for advanced materials [6-8]. Thus, ILs have a large variety of applications such as surfactant of layered silicates [9-12], compatibilizer of biopolymer and thermoplastic blends [13-14], efficient solvent for cellulose, lignine or polysaccharide based materials [15-16] and as plasticizer of biomedical polymers [17-18]. For these reasons, the combination of the excellent intrinsic properties of phosphonium ionic liquids to biodegradable aliphatic-aromatic copolyesters synthesized from 1,4-butanediol, adipic acid and terephthalic acid, denoted poly(butylene-adipate-co-terephthalate) (PBAT) have been investigated. Finally, this work report for the first time a nanoscale structuration tuned by the chemical nature of the counter anion (phosphinate, chloride, dicyanamide, TFSI) as well as their impact on the mechanical and water vapour properties into a biopolymer matrix which could open many applications in food packaging and/or in the production of compostable films.

In this paper, a simple and scalable process for the preparation of PBAT-IL materials using twin screw extrusion has been used. Indeed, to prepare PBAT films, various functional ionic liquids based on trihexyl(tetradecyl)phosphonium cation and combined with bis-2,4,4-(trimethylpentyl)phosphinate (IL-TMP), bistriflimide (IL-TFSI) and chloride (IL-Cl) counter anions have been introduced in very low amounts (2 wt%) in PBAT. Then, PBAT-IL blends were sheared for about 3 min with a 100 rpm

speed at 160 °C and injected in a 10 cm³ mould at 60 °C to obtain dumbbell-shaped specimens. In all the cases, the good chemical affinity between PBAT and ILs combined to the chemical nature of the anion induce different morphologies. Based on the ionomer literature in non polar medium, the morphologies due to phase separation is controlled by dipole-dipole interactions which induces the formation of ionic agglomerates [19-21]. Firstly, the effect of the the chemical nature of the counter anion on the structuration of the PBAT matrix was investigated. To reveal the presence of ionic domains in polymer matrix, transmission electronic microscopy (TEM) and small angle neutron scattering (SANS) were used. TEM micrographs and SANS spectra are presented in Figure 1 and 2.

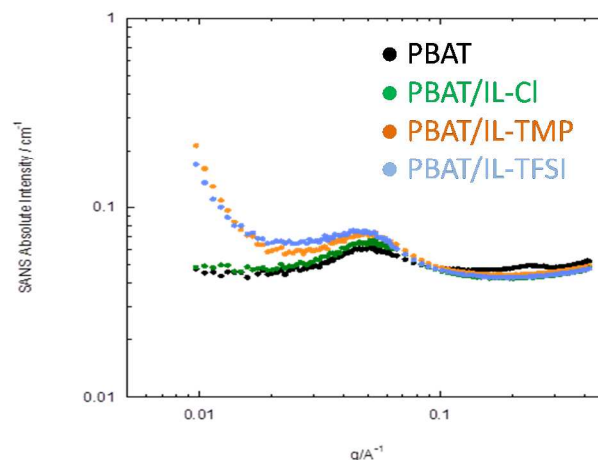


Figure 1. SANS profiles of the virgin PBAT and PBAT-IL blends

SANS profiles highlights that for PBAT filled with 2 wt% of phosphonium ionic liquids denoted IL-TFSI and IL-TMP, a q^{-4} power at lower angles is observed which corresponds to a well-defined interface between matrix and ionic liquids as the possible formation of ionic aggregates. In the opposite, the absence of q^{-4} power at small angles clearly indicates a better affinity of the ionic liquid (IL-Cl) with the polymer matrix. However, these measurement cannot give more additional information on the structure of the ionic liquid into poly(butylene-adipate-terephthalate).

The SANS analysis are confirmed by the TEM micrographs where two different types of morphologies are observed. In fact, phosphonium ionic liquids denoted IL-TMP and IL-TFSI lead to the formation of ionic aggregates coupled with a co-continuous morphology while IL-Cl induces a fine structuration at nanoscale. These different morphologies clearly highlight the better affinity of the IL combined with chloride anion with the biodegradable polymer matrix which shows the consistency of SANS results. In conclusion, the chemical nature of the counter anion plays a key role on the morphologies of PBAT-IL films and should have a significant effect on the mechanical and water vapour permeability properties.

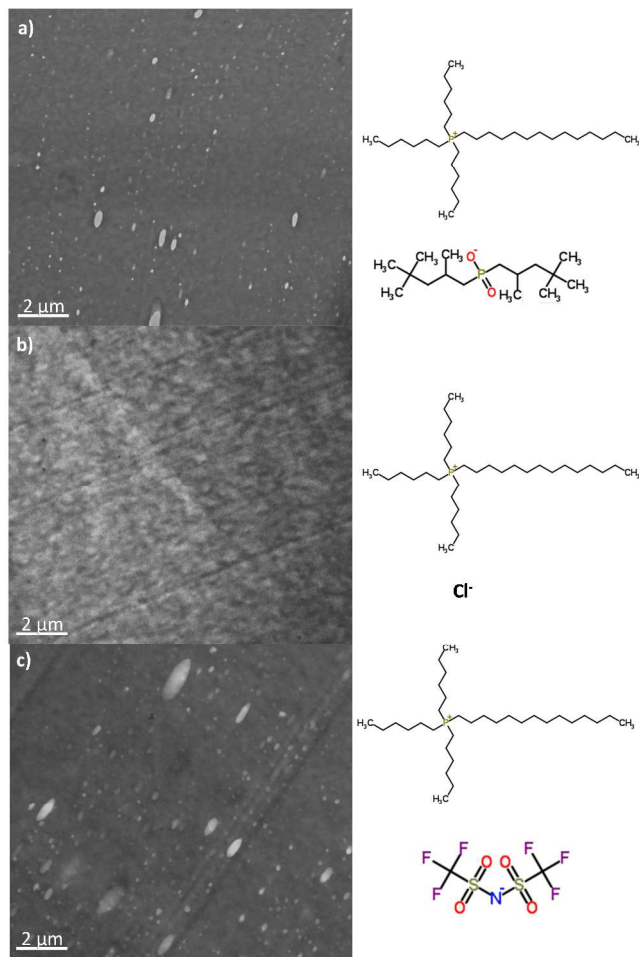


Figure 2. TEM micrographs of (a) PBAT/IL-TMP, (b) PBAT/IL-Cl and (c) PBAT/IL-TFSI

Secondly, neat PBAT, PBAT/IL-Cl, PBAT/IL-TMP and PBAT/IL-TFSI have been analyzed by differential scanning calorimetry (DSC) to highlight the influence of phosphonium ionic liquid on the thermal properties of PBAT matrix. Melting temperature (T_m), glass transition temperature (T_g), melting enthalpy (ΔH_m) and degree of crystallinity are summarized in Table 1.

Sample	T_g (°C)	T_m (°C)	ΔH_m (J/g)	Crystallinity (%)
PBAT	-33±0.2	124±0.3	13.5±0.5	12
PBAT/IL-TMP	-34±1.2	126±0.4	11.9±0.4	10
PBAT/IL-TFSI	-32±0.2	124±0.3	12.3±0.3	11
PBAT/IL-Cl	-36±1.4	124±0.3	11.4±0.3	10

Table 1. The corresponding crystallization and melting parameters for virgin PBAT and PBAT/ILs

The T_g of virgin PBAT was observed at around -33°C whereas the PBAT filled with 2 wt % of IL-TMP, IL-TFSI and IL-Cl show a glass transition temperatures of -34 °C, -32 °C and -36°C, respectively. These results allow to suggest no interfacial adhesion or interaction between biodegradable polymer and ionic liquids since no shift of the T_g is obtained. In addition, based on the values of the ΔH_m of 100 % crystalline of PBAT calculated by Herrera et al [22] from the contribution of the ester, methylene and p-phenylene groups, the degree of crystallinity of the PBAT and PBAT-IL films was determined. Thus, the introduction of only 2 wt % of the phosphonium salts in PBAT causes a slight decrease in crystallinity in the range of 1.5-2 %. Indeed, IL-TMP, IL-TFSI and IL-Cl have percentage of crystallinity of 10, 11 and 10 % compared to 12% for the virgin PBAT. According to the literature, the use of an amount of ionic liquid greater than 3 wt% hinders the formation of a crystalline region which leads to a less effective crystalline network [23-24]. Thus, Li et al have shown that the use of only 3 wt% induces a reduction of 10 % of the crystallinity in polyethylene matrix. Again, a distinction is possible between the various counter anions of the ILs. IL-TMP and IL-TFSI leading to the formation of ionic aggregates due to the poor miscibility between the ionic liquids and the polymer medium induces a greater decrease in the crystallinity compared to IL-Cl having a better distribution in PBAT matrix. The influence of the ILs on the mechanical behavior of the PBAT films was investigated. The mechanical properties of the PBAT and PBAT-ILs with 2 wt % of phosphonium ionic liquids are summarized in Table 2.

IL-TMP and IL-TFSI leads to an increase of the elongation at break of + 30 % and + 10 %, respectively without reducing the Young Modulus of the virgin PBAT (47 Mpa). In the opposite, IL-Cl generates a significant increase in strain at break of 60 % coupled with a slight decrease of the Young Modulus (-11 %). The results are consistent with the morphology as well as the crystallinity. Indeed, the decrease in crystallinity caused by IL-TMP and IL-TFSI explains the slight increase in the strain at break whereas the presence of ionic aggregates in PBAT matrix allows the conservation of material stiffness. These results are comparable to the use of nanoparticles or block copolymers in the preparation of nanocomposites [25-26]. Regarding IL-Cl where a decrease in glass transition temperature was observed, the mechanical behavior of the PBAT-IL film highlights the role of ionic liquid as plasticizer agent [27-28]. In summary, the physical properties and the morphologies of PBAT/IL films can be tuned by the chemical nature of the phosphonium ionic liquids.

Sample	Young Modulus (MPa)	Stress (MPa)	Strain at break (%)
PBAT	47±1	24±1	510±17
PBAT/IL-TMP	46±1	23±1	680±26
PBAT/IL-TFSI	47±2	23±1	560±22
PBAT/IL-Cl	40±2	24±2	810±80

Table 2. Mechanical data from tensile tests performed on neat PBAT and PBAT-IL blends with 2 wt% of ionic liquids

Transport properties were performed using a conventional McBain spring balance system. The temperature was controlled to 30 °C by a constant temperature water bath. Then, sorption measurements were carried out on three different samples. Finally, diffusion coefficients and equilibrium mass uptake were extracted from these kinetic sorption data.

In a first time, the increase in weight with time was measured for all samples exposed to the vapour at a given partial pressure in order to obtain the equilibrium value of sorbed vapour, C_{eq} ($g_{\text{solvent}}/100g$ polymer). In addition, in the case of Fickian behaviour and to use the equation described by Viet and Amini [29]: $C_t/C_{eq} = 4/d * (Dt/\pi)^{0.5}$ where C_t is the penetrant concentration at the time t , C_{eq} is the equilibrium value, d (in cm) is the thickness of the sample and D (cm^2/s) the average diffusion coefficient. Then, when the sorption can be assumed ideal and following the Henry's law, we derived a sorption parameter (S): $S = dC_{eq}/dp$ where p is the partial pressure of the water vapour. In a second time, diffusion depends on concentration for many polymer-solvent systems, and generally this dependence can be expressed by the following empirical law: $D = D_0 \exp(\gamma C_{eq})$ where D_0 is the thermodynamic zero-concentration diffusion coefficient, related to the free volume fraction and to the microstructure of the polymer; γ is the concentration coefficient, which depends on the free volume fraction and on the plasticizing effectiveness of the penetrant. Thus, the permeability of the samples to the vapour is given by the product of diffusion and sorption such as $P = S * D$.

In all the cases, compared to the virgin PBAT, a significant decrease of the water sorption calculated as C_{eq} ($g_{\text{solvent}}/100g$ polymer). In fact, the introduction of phosphonium ionic liquid denoted IL-TMP, IL-TFSI and IL-Cl leads to a decrease of -70 %, -80 % and -40 %, respectively (Table 3).

Sample	Water sorption C_{eq} ($g/100g$)	Water diffusion D (cm^2/sec)	Water permeability ($cc(STP)/cm^3 * atm * cm^2/sec$)*
PBAT	2.37	$2.26 * 10^{-8}$	$3.32 * 10^{-8}$
PBAT/IL-TMP	0.84	$2.50 * 10^{-8}$	$1.30 * 10^{-8}$
PBAT/IL-TFSI	0.47	$3.80 * 10^{-8}$	$1.10 * 10^{-8}$
PBAT/IL-Cl	1.45	$2.10 * 10^{-8}$	$1.90 * 10^{-8}$

Table 3. Water sorption, water diffusion and water permeability for neat PBAT and PBAT-IL blends

These results are due to the hydrophobic nature of the three ionic liquids which have surface energies included between 30.4-30.7 mN/m compared to neat PBAT one of 48 mJ/m (Refs). In fact, the presence of long alkyl chains (C_6 and C_{14}) on the phosphonium cation explain the hydrophobic character of the ILs. These values are consistent with the literature where, for example, Coutinho et al have also determined similar values of surface energies for IL-TMP and IL-TFSI [30-31].

In the opposite, the more hydrophobic ionic liquids promote easier the diffusion of water molecules through the polymer matrix. Indeed, IL-TMP and IL-TFSI leads to an increase of 10 % and 70 % of the diffusion compared to a slight decrease of -6-7% for IL-Cl (Table 3). This phenomenon is clearly explained by the distribution of the ionic liquid in PBAT matrix. Thus, phosphonium ionic liquids combined with TFSI and TMP counter anions promoting the formation of ionic aggregates create a free volume inside the polymer structure allowing an easier diffusion of water vapour molecules in PBAT [32].

Finally, Table 3 reports the permeability data to water vapour pressure at the value of activity (0.53) for the virgin PBAT and PBAT-IL blends. For all samples, the introduction of a small content of ILs increases the barrier properties by creating a "tortuous path" which delays the progress of the water molecules through the biodegradable polymer, in particular thanks to the hydrophobic nature of the ionic liquids reducing the affinity of PBAT with water. In fact, significant reductions in water permeability coefficients in the range of -40 % to -70 % are observed for the first time with IL-Cl, IL-TFSI and IL-TMP.

Compared to the literature, the results of water permeability are very promising and highlight the potential of ionic liquids as new alternative to nanoparticles, commonly used on the development of polymer nanocomposites with enhanced barrier properties [25-26, 33-37]. In fact, great efforts have focused on the incorporation of different nanoparticles such as layered silicates, layered double hydroxide, cellulose, lignin into the polymer with mixed results. Thus, Chen et al also demonstrated that the addition of 10 wt% of modified MMT led to a decrease of water vapor permeation (VWP) (-40 %) compared to the use of unmodified MMT [38]. More recently, Mondal et al highlighted that the use of 8 wt % of ammonium-modified montmorillonites led to a decrease of -17% of the water barrier properties of PBAT matrix [35]. Then, other ways have been explored such as the incorporation of plasticizers, surfactants and biopolymers. For example, Brandelero et al have investigated the effect of surfactant denoted Tween 80 combined with starch of cassava on the VWP of PBAT matrix. They demonstrated that the use of surfactant did not reduce the VWP of the green composites [39]. While other authors highlighted that the combination of PBAT/glycerol/adipic acid/starch or PBAT/glycerol/starch composites induced only a slight decrease of the vapor water properties (7-15 %) depending of the blend composition [37]. Furthermore, another advantage of the use of ionic liquids instead of nanoparticles is their ease of incorporation in the polymer besides ILs do not cause the viscosity increase during polymer

processing unlike the addition of nanoparticles. Indeed, a small concentration (2 wt%) of IL-Cl, IL-TMP and IL-TFSI leads to a decrease of the viscosity[†].

In conclusion, this first study on the use of ionic liquids as structuring agents in a biodegradable matrix opens a new route for the development of high performance polymeric materials for food packaging and compostable film applications. For example, PBAT is often used as protective and compostable film on agricultural lands. However, its low resistance to water permeability causes a rapid degradation of the polymer while the addition of nanoparticles leads to an adverse effect on production of the films such as i) an increase in viscosity, ii) the problem of dispersion of the fillers and iii) a decrease in strain at break.

Thus, this work highlights a new way simple and effective in enhancing the water barrier properties of biodegradable matrix by using a small amount of phosphonium ionic liquids (2 wt %) without reducing the mechanical behavior.

Acknowledgements

The authors acknowledge Dr Annie Rivoire and Dr Christelle Boule for their help in microscopy experiments. The authors thank also Alain Lapp and François Boué as local contacts on the PAXY (LLB) spectrometer. In addition, the authors thank Dr Manuel Marechal for the good advices.

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[†]Electronic Supplementary Information (ESI) available: DSC spectra of neat PBAT and PBAT-IL mixtures, Complex viscosity curves

[‡] Transmission Electron Microscopy (TEM) was performed at the Center of Microstructures (Université de Lyon) using a Philips CM 120 field emission scanning electron microscope with an accelerating voltage of 80 kV. The samples were prepared at room temperature and were set on copper grids for observation.

[§] Differential scanning calorimetry (DSC) analyses were performed on a Q20 (TA instruments) between -70°C to 200°C for virgin PBAT and PBAT/ILs. The samples were heated or cooled at a rate of 10 K.min⁻¹ under nitrogen flow.

Uniaxial tensile tests were carried out on a MTS 2/M electromechanical testing system at 22±1 °C and 50 ±5 % relative humidity at crosshead speed of 50 mm.min⁻¹. Young's modulus measurements were taken by means of an extensometer. A minimum of five tensile specimens were tested for each reported value.

Transport properties experiments were performed using a conventional McBain spring balance system, which consists of a glass water-jacketed chamber serviced by a high vacuum line for sample degassing and permeant removal. Inside the chamber samples were suspended from a helical quartz spring supplied by Ruska Industries, Inc. (Houston, TX) and had a spring constant of 1.52544 cm/mg. The temperature was controlled to 30 ± 0.1°C by a constant temperature water bath. Before beginning the sorption experiments, the sample was exposed to vacuum for at least 24 h in order to remove previously sorbed air gas and water vapour from the polymer. Permeant used was water vapour. Sorption was measured as a function of the relative pressure, $a=P/P_0$, where P is the actual pressure (in mmHg) of the experiment, and P₀ the saturation

pressure at 30°C for water (32 mmHg). The samples were exposed to the penetrant at fixed pressures ($a=0.53$), and the spring position was recorded as a function of time using a cathetometer. The spring position data were converted to mass uptake data using the spring constant and the process was followed to a constant value of sorption for at least 24 h. Data averaged on three samples. Diffusion coefficients and equilibrium mass uptake were extracted from these kinetic sorption data.

The Poly(butylene adipate-co-terephthalate) used in this work, named PBAT, was supplied by BASF (Germany) under the trade name of Ecoflex. The ionic liquid denoted IL-TMP, IL-TFSI and IL-Cl based on tributyltetradecylphosphonium cation associated with *bis*-2,4,4-(trimethylpentyl)phosphinate, bistriflimide and chloride counter anions were provided by Cytec Industries Inc (Canada).

Small-Angle Neutron Scattering (SANS) experiments were carried on the small angle spectrometer PAXY spectrometer of Léon Brillouin Laboratory (Saclay, France). Three sample-to-detector distances (SDD) and neutron wavelengths (λ) were used to cover magnitudes of the scattering vector modulus q from 0.03 to 4.2 nm⁻¹ ($\lambda=1.2$ nm, SDD = 6.75 m, $\lambda=1.2$ nm, SDD = 3 m, and $\lambda=0.5$ nm, SDD = 1 m). The resulting level of the scattering intensity at the high q values is of the order of magnitude of the experimental background, notably the incoherent contributions of the polymer phase and ionic liquids are subtracted.

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