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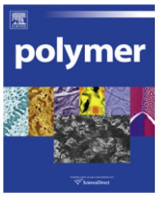

Nanostructuration of ionic liquids in fluorinated matrix: Influence on the mechanical properties

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ABSTRACT

In this work, a new method to prepare fluorinated coatings with mechanical properties enhanced has been developed. Pyridinium, imidazolium, and phosphonium ionic liquids have been synthesized and used as new synthetic building blocks in a polytetrafluoroethylene matrix. The strategy demonstrated using long alkyl chain cations provides an opportunity to prepare nanomaterials with a nanoscale structuration. The design of these new ionic and nanostructured materials is very dependent on the cation–anion combination of ILs. The morphology analyzed by transmission electronic microscopy (TEM) shows that it is clearly tuned by the chemical nature of ILs. The finest structuration leads to a dramatic compromise between stiffness and deformation of material. The small-angle X-Ray scattering (SAXS) shows the evolution of the ionic networks during the mechanical sollicitation.

1. Introduction

In the world of nanotechnology, the goal is to create new materials with significantly improved physical properties from designing matter structuration at nanoscale. For many years, several approaches have been described for designing new structures from organic molecules, polymers, or organic–inorganic hybrids. One of the well-known approach consists in the design of nanostructured thermosets obtained by the use of block copolymers with amphiphilic block [1–3]. Another way for the development of nanostructured polymers is the introduction of inorganic nano-objects having nanometre-scale dimensions such as silica [4], layered silicates [5–10], or carbon nanotubes [11–13]. The problem with these different methods mentioned above is that they require several preparation steps before achieving improved materials. In fact, in the field of the polymer nanocomposites, it is often necessary to modify the surface of the inorganic nanoparticles in order to improve the dispersion as well as the final properties of materials. In the case of thermosets, the synthesis of block copolymers can be long and difficult. Moreover, it is necessary to use large amounts of copolymers to improve properties of the material. To overcome these obstacles, our research has been directed towards organic compounds with intrinsic and unique properties: Ionic Liquids (ILs) especially known for their excellent thermal stability, non-flammability, low saturated vapour pressure, good electrical, and thermal conductivity and commonly used as green solvents in inorganic synthesis [14] and synthesis of nanoparticles [15], homogeneous and heterogeneous catalysis [16], in polymer science as plasticizers [17], or lubricants [18].

They are also commonly used as surfactants in the lamellar silicate nanocomposites. The most frequently used are ammonium salts [19–21]. In recent years, pyridinium, imidazolium, and phosphonium ionic liquids known for their excellent thermal stability are increasingly used [22,23]. And recently, a new approach of ILs has been studied by Wathier and Grinstaff [24] who have suggested that ionic liquids may play an important role in the formation of ionic networks based on coordinating ion pairs. They have demonstrated that Coulomb interactions are governed by pairwise interactions between cation and anion and the extended structure of the ionic liquid may lead to a supramolecular ionic network. Thus, a combination of the mechanical properties linked to ionomers with the homogeneity and the high charge densities typical of ionic liquids could lead to a new range of optimized materials. However, from our knowledge, no paper described the use of ionic liquids within a polymer matrix to design nanostructured phase. In this paper the synthesis of ionic liquids based on various cation: pyridinium, imidazolium and phosphonium but also on the different anions (hexafluorophosphate, iodide and bromide) has been described.

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Then, their influences in a fluorinated matrix, chosen for coating applications as well as the consequences of this structuration at nanoscale on the material physical behaviour such as mechanical properties have been studied.

2. Experimental

2.1. Materials

All chemicals used for to the synthesis of ionic liquids, *i.e.* triphenylphosphine (95%), imidazole (99.5%), pyridine (99%), iodooctadecyl (95%) and all the solvents (toluene, sodium methanoate, pentane and acetonitrile) were supplied from Aldrich and used as received. The polytetrafluoroethylene used in this study, denoted as PTFE, is an aqueous dispersion of PTFE from Solvay. The composition is as follows: PTFE (60 wt %), water (32–33 wt %), octylphenol polyethoxylates Triton® (7 wt %) and ammonium perfluorooctanoate (0,1 wt %). The pH of aqueous dispersion is 10 and the PTFE particle average size is about 220 nm.

2.2. Synthesis of pyridinium, imidazolium, and phosphonium ionic liquids

The synthesis of *1-octadecyl-3-octadecylimidazolium* and *octadecyltriphenylphosphonium* iodide was obtained from a route similar to that described by Livi et al. [25]. Octadecyltriphenylphosphonium hexafluorophosphate and octadecylpyridinium iodide are not commercially available.

2.2.1. Synthesis of octadecylpyridinium iodide ($C_{18}Py\ I^-$)

These compounds are not commercially available and their synthesis was not reported before. In a 100 mL flask was placed under a nitrogen pressure, 10 mmol of octadecyl iodide ($C_{18}H_{37}I$) and distilled pyridine (1.5 equiv.). The stirred suspension was allowed to react for 24 h at room temperature. A yellow precipitate was formed. The reaction mixture was then filtered, and washed repeatedly with pentane. Most of the solvent was removed under vacuum. A white solid was obtained. After drying, alkyl phosphonium salt was fully characterized by spectroscopy ^{13}C NMR and thermogravimetric analysis (TGA).

^{13}C NMR ($CDCl_3$) δ: 14.04 ($\mathbf{C}H_3$); 22.58; 25.91; 28.99; 29.25–29.60; 31.81–31.84 ($\mathbf{C}H_2$); 62.02 ($\mathbf{C}H_2N$]); 128.57 (C]C); 144.82; 145.50 (]$\mathbf{C}N$). Yield = 90%, melting temperature (°C): 102 °C. The degradation temperature of the $C_{18}Py\ I^-$ determined for a weight loss of 50 wt % is 270 °C.

2.2.2. Synthesis of 1-octadecyl-3-octadecylimidazolium iodide ($C_{18}C_{18}Im\ I^-$)

A solution of sodium methoxide was prepared from sodium (1 equiv.) in dry freshly distilled methyl alcohol (10 mL) in a sealed septum, 100 mL round-bottomed, three necked flask equipped with a condenser, under nitrogen atmosphere and magnetic stirring. Imidazole (1 equiv.) diluted in acetonitrile (10 mL) was then added into the stirred mixture of sodium methoxide previously cooled at room temperature. After 15 min, a white precipitate was formed. The suspension was then concentrated under reduced pressure for 1 h. The dried white powder was dissolved in acetonitrile and a powder of alkyl iodide (1 equiv.) diluted in acetonitrile (10 mL) was then added under an inert atmosphere of nitrogen at room temperature. The mixture was stirred for 1 h, then heated under reflux at 85 °C for about 24 h. A powder of alkyl iodide (1 equiv.) diluted in acetonitrile (10 mL) was added to the mixture at room temperature. The stirred suspension was heated under reflux at 85 °C for about 24 h leaving a brownish viscous oil in each case. After cooling to room temperature, the solvent was removed by evaporation under vacuum, the beige coloured powder was filtered, washed repeatedly with pentane and dried. Purification of the resulting imidazolium salts was accomplished by crystallization from ethyl acetate/acetonitrile: 75/25 mixture. After drying, alkyl imidazolium salt was fully characterized by spectroscopy and thermogravimetric analysis (TGA). The assignment of ^{13}C NMR spectroscopy resonance peaks is an evidence of the success of the ionic liquid synthesis.

2.2.2.1. 1-Octadecyl-3-octadecylimidazolium iodide. ^{13}C NMR ($CDCl_3$): δ 14.10 ($2CH_3$); 22.67 ($2CH_2Me$); 26.23; 28.97; 29.35–29.69; 30.24; 31.91 (CH_2); 50.10; (CH_2N]); 50.32 (CH_2N–); 121.69; 122.48 (]CN); 136.88 (N–C]N). Yield = 94%, melting temperature (°C): 67 °C. The degradation temperature of the $C_{18}C_{18}Im\ I^-$ determined for a weight loss of 50 wt % is 310 °C.

2.2.3. Synthesis of octadecyltriphenylphosphonium iodide, bromide ($C_{18}P\ I^-$, $C_{18}P\ Br^-$)

In a 100 mL flask were placed under a positive nitrogen pressure, triphenylphosphine and octadecyl iodide or octadecyl bromide. The stirred suspensions were allowed to react for 24 h at 120 °C in toluene (20 mL), a yellow precipitate was formed. The reaction mixture was then filtered, washed repeatedly with pentane. Most of the solvent was removed under vacuum and the product was dried to a constant weight to give a white solid. These salts were characterized by ^{13}C NMR spectroscopy and thermogravimetric analysis (TGA).

2.2.3.1. Octadecyltriphenylphosphonium iodide. ^{13}C NMR ($CDCl_3$): δ 14.00 (CH_3); 22.67 (CH_2Me); 23.2; 29.37–29.66; 30.24; 31.85 (PCH_2); 118.45; 130.43; 133.70; 135.15 (P-Carom.). Yield = 97%, melting temperature (°C): 86 °C.

2.2.3.2. Octadecyltriphenylphosphonium bromide. ^{13}C NMR ($CDCl_3$): δ 14.00 (CH_3); 22.52 (CH_2Me); 23.0; 28.90–29.66; 30.20; 32.00 (PCH_2); 118.85; 130.80; 133.50; 135.45 (P-Carom.). Yield = 88%, melting temperature (°C): 86 °C. The degradation temperature of the $C_{18}P\ I^-$ and $C_{18}P\ Br^-$ determined for a weight loss of 50 wt % is 320 °C.

2.2.4. Synthesis of octadecyltriphenylphosphonium hexafluorophosphate ($C_{18}P\ PF_6^-$)

In a 100 mL flask, octadecyl iodide ($C_{18}H_{37}I$) (5.0 g, 1 equiv.) was dissolved into dichloromethane (25 mL). The mixture was stirred for 30 min at room temperature. A solution of hydrogen hexafluorophosphate (HPF_6) (3.8 g, 2 equiv.) diluted in water (25 mL) was stirred for 30 min and added to the octadecyl iodide solution. The stirred suspension was allowed to react for 24 h at room temperature. The reaction mixture was then introduced in a separatory funnel and the organic layer was washed repeatedly with distilled water (4 × 25 mL). The mixture was dried over anhydrous magnesium sulphate and concentrated under reduced pressure. The solvent was removed by evaporation under vacuum and the product was dried to a constant weight to give a white solid. The salt was characterized by ^{13}C NMR spectroscopy and thermogravimetric analysis (TGA).

2.2.4.1. Octadecyltriphenylphosphonium hexafluorophosphate. ^{13}C NMR ($CDCl_3$): δ 14.00 (CH_3); 22.35 (CH_2Me); 23.5; 29.12–29.74; 30.35; 31.75 (PCH_2); 118.75; 130.22; 133.50; 135.05 (P-Carom.). Yield = 80%, melting temperature (°C): 80 °C. The degradation temperature of the $C_{18}P\ PF_6^-$ determined for a weight loss of 50 wt % is 450 °C.

In this work, different combinations cation/anion are proposed and are summarized in Fig. 1.