Unique Combination of Mechanical Strength, Thermal Stability, and High Ion Conduction in PMMA−Silica Nanocomposites Containing High Loadings of Ionic Liquid

Florence Gayet,[†] Lydie Viau,[†] Fabrice Leroux,[‡]
Frédéric Mabille,[§] Sophie Monge,[†] Jean-Jacques Robin,[†]
and André Vioux*,[†]

[†]*Institut Charles Gerhardt de Montpellier,
UM2−CNRS−ENSCM − UM1, University Montpellier 2,
Montpellier F34095, France,* [‡]*Laboratoire des Matériaux
Inorganiques, UBP−CNRS−ENSCCF, University Blaise
Pascal, Aubière F63177, France, and* [§]*UMR 1208 IATE,
AgroM, CIRAD, INRA, Université Montpellier 2,
Montpellier F34000, France*

The current strong interest in ionic liquids (ILs) is motivated by their unique combination of properties, such as negligible vapor pressure, thermal stability, non-flammability, high ionic conductivity, and wide electrochemical stability window. There is currently a marked interest in using ionic liquids in materials science, especially in electrochemical devices, such as actuators, lithium batteries, electric double-layer capacitors, dye-sensitized solar cells and fuel cells.[1,2] The immobilization of ionic liquids within polymer membranes makes it possible to take advantage of their unique properties in solid state.[3,4] The superiority of these electrolyte membranes, over the classical water-swollen membranes, lies ion the nonvolatility of ionic liquids and their thermal stability.[5] Different routes to polymer electrolyte membranes have been reported, as polymerization of monomers in ionic liquids, solvent casting, or wetting or swelling of polymers.[3,4,6] However, even though free-standing polymer electrolyte membranes have been reported,[7] the use of these "supported liquid" membranes remains limited by the loss of tensile resistance on increasing the ionic liquid loading.[8] The polymerization of ionic liquid monomers,[9] which results in one-phase systems, offers an interesting alternative, but it does not

Scheme 1. Synthesis of Hybrid Ionogels
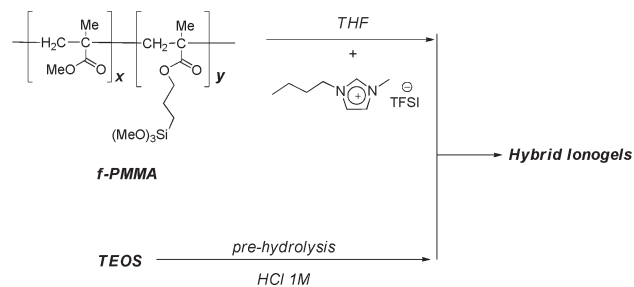
remove the intrinsic limitation related to the weak thermal stability of pure organic matrices. Temperature-resistant electrolyte membranes arising from the immobilization of ionic liquids in silica matrices by sol−gel processing have been achieved;[10,11] however, these inorganic membranes are brittle by nature. Thus, whatever based on organic or inorganic matrices, ionogel binary systems offer limited performances. To the best of our knowledge, this is the first report on ionogel ternary systems based on a covalently bonded polymer−silica hybrid matrix and an ionic liquid.

The basic purpose is to achieve tractable and ion conducting polymer nanocomposites, by incorporating silica nanofillers covalently bonded to the polymer chains to improve mechanical strength, and an ionic liquid loading to provide flexibility, thermal stability, and ion transport. The existence of covalent bonding between the polymer chains and the silica filler domains has been shown to be necessary to get composites homogeneous to the nanometer scale and transparent.[12] The miscibility of ionic liquids with polymers has been yet investigated,[13] and the ability of ionic liquids to act as plasticizers has been highlighted in some cases, especially in poly(methyl methacrylate) (PMMA).[14] Actually, the outstanding compatibility of imidazolium salts with methyl methacrylate and its polymers has been reported.[7] In that case, the specific interaction of PMMA with the bis-(trifluoromethanesulfonyl)imide ([NTf$_2$]) anion was disclosed, which resulted in the restriction of ion pairing or clustering and therefore in the relative increase in the cation mobility. In this work, we implemented a sol−gel synthesis involving modified PMMA, silicon tetraethyloxide (TEOS), and 1-butyl-3-methyl imidazolium bis(trifluoromethane sulfonyl)imide ([BMIm][NTf$_2$]) (Scheme 1). The modified PMMA contained about 5 mol % units bearing pendant hydrolyzable silicon groups arising from methacryloxypropyltrimethoxysilane (MPTMS) monomer.

*Corresponding author. E-mail: vioux@univ-montp2.fr.
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Table 1. Composition, Mechanical and Ionic Conduction Properties of Hybrid Ionogels

								σ (S cm^{-1})	
sample	feed mass ratio (f-PMMA)/ TEOS	molar ratio n = IL/Si	wt (%) IL/ material	wt (%) SiO$_2$/ material [a]	wt (%) SiO$_2$/f-PMMA [b]	Young Modulus E (Pa)	Strain ε	298 K	343 K
HI1	60/40	1	55	5.31	19.47	[c]	[c]	0.05×10^{-3}	0.57×10^{-3}
HI2	60/40	2	72	2.25	22.28	3.37E5	0.35	0.53×10^{-3}	3.00×10^{-3}
HI3	60/40	2.5	76	0.77	15.61	3.07E5	0.20	0.89×10^{-3}	4.70×10^{-3}
HI4	80/20	2	49	2.22	6.50	1.44E7	[d]	0.02×10^{-3}	0.26×10^{-3}
HI5	70/30	2	62	2.19	13.85	9.07E5	0.52	0.15×10^{-3}	1.15×10^{-3}
HI2	60/40	2	72	2.25	22.28	3.37E5	0.35	0.53×10^{-3}	3.00×10^{-3}
HI6	50/50	2	76	1.82	23.87	3.28E5	0.17	1.01×10^{-3}	4.60×10^{-3}
	Neat IL							3.50×10^{-3}	14.7×10^{-3}

[a] Determined by TGA measurements on the hybrid ionogels. [b] Calculated by TGA measurements on the washed hybrid ionogels. [c] Not determined. [d] Hybrid ionogel 80/20 n = 2 (**HI4**) exhibits an elastic behavior with ε_{elast} = 0.15 and a plastic one without rupture until a deformation of 200%.

A series of hybrid ionogels loaded with various amounts of [BMIm][NTf$_2$] were prepared according to general Scheme 1. The functionalized polymer PMMA-*stat*-PMPTMS (f-PMMA) was first synthesized according to a procedure described by Sanchez et al. by free radical polymerization between MMA and MPTMS, using a feed molar ratio [MMA]/[MPTMS] = 20 and 1 wt % of AIBN initiator in respect to monomer.[15] After 24 h refluxing in THF, the polymer (f-PMMA) was recovered by precipitation in cold methanol and analyzed by size exclusion chromatography (M_n = 24300 g mol^{-1}, DPI = 2.5). On the basis of ^{1}H NMR spectroscopy, the ratio of the CH$_2$ protons next to the carboxylate groups in MPTMS moieties (protons d) over the CH$_3$ protons of COOCH$_3$ groups in MMA moieties (protons g) indicated a MPTMS content in the copolymer close to 4.7 molar % (see Figure S1 in the Supporting Information).

The second step consisted of a classical sol−gel process. TEOS was first prehydrolyzed in ethanol solution under acidic conditions (pH 1) overnight. At the same time, the organic polymer (f-PMMA) was dissolved in tetrahydrofuran (THF) at room temperature; then [BMIm][NTf$_2$] was added. The prehydrolyzed TEOS solution was added to the mixture of f-PMMA and [BMIm][NTf$_2$], resulting in colorless transparent crack-free hybrid ionogels within 1 h , which could be cast as rods, films, and pellets. A 12-days aging treatment in an open vial was performed at room temperature and then 48 h at 313 K to complete cross-linking and release all volatiles.

A first set of samples was achieved by varying the IL to silica molar ratio (n), while keeping the feed mass ratio of f-PMMA over TEOS constant to 60/40 (samples **HI1** to **HI3** Table 1). In a second set of samples (**HI4** to **HI6**), n was kept constant to 2, whereas the composition of f-PMMA and TEOS varied (Table 1).

Ionic liquid contents were determined by weighting and further checked by thermogravimetric analyses (TGA). The ionic liquid could be easily washed out by soaking in several THF fractions at room temperature. After extracting the IL, the degree of condensation was valued around 77% by means of MAS ^{29}Si NMR spectroscopy (even though only Q units were considered, given the low rate of

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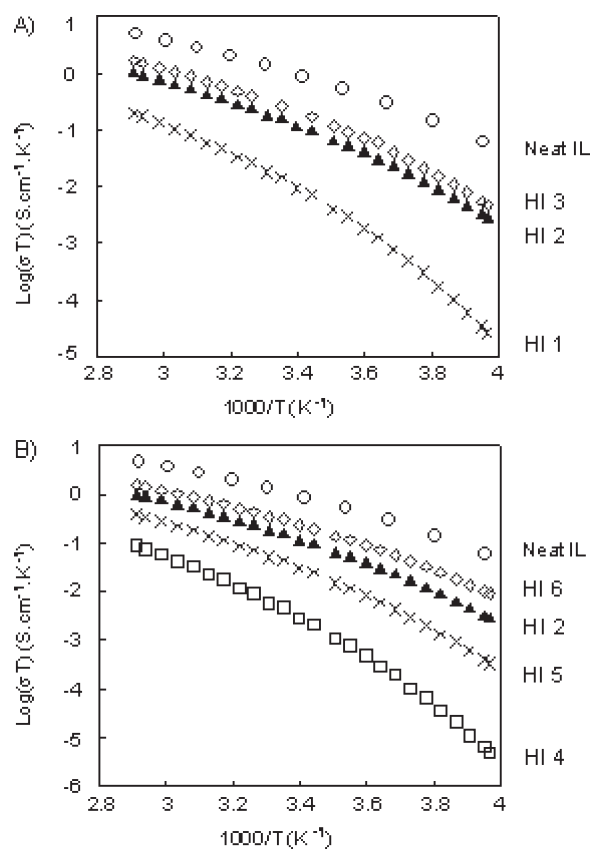
Figure 1. Conductivity plots for hybrid ionogels (A) f-PMMA/TEOS 60/40 with various n (**HI 1−3**), (B) n = 2, various proportions of f-PMMA/TEOS (**HI 2, 4−6**).

T units; Figure S2 in the Supporting Information). Figure 1 shows the Arrhenius plots of the temperature dependency of the ionic conductivity (σ) for the different hybrid ionogels. These plots exhibited convex upward curved profiles and fitted the Vogel−Tamman−Fulcher equation (eq 1 and Table S1 in the Supporting Information).

$$\sigma = \sigma_0 \exp[-B/(T - T_0)] \qquad (1)$$

An increase in ionic conductivity σ was observed when increasing the ionic liquid content, as expected. Typically, with 76% IL the conductivity was found to be about only 1 order of magnitude lower than neat IL. Typical values of σ at room temperature and 343 K are set out in Table 1.
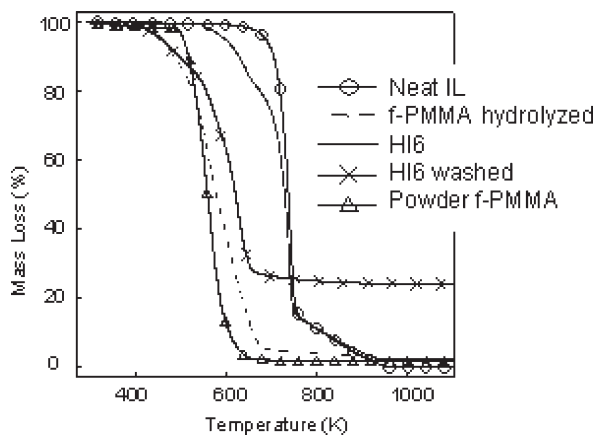
Figure 2. TGA curves of the ionic liquid, monolith f-PMMA hydrolyzed, powder of f-PMMA, hybrid ionogel 50/50 $n = 2$ (**HI6**), and **HI6** washed.

Comparing **HI3** and **HI6**, which have different feed mass ratios f-PMMA/TEOS but similar IL content (76%), similar conductivities were observed, confirming the predominant effect of IL content. It is also worth noticing the different behaviors of neat IL and hybrid ionogels.

Whereas the conductivity of neat [BMIm][NTf$_2$] increased rapidly at low temperature, the conductivities of hybrid ionogels were found to be almost stable before increasing above 270 K, highlighting the temperature dependence of the transport of migrating species in hybrid ionogels (see Figure S3 in the Supporting Information). Additionally, the temperature dependence is more important for high contents of ionic species (see Figure S4 in the Supporting Information).

Hybrid ionogels exhibited high thermal stabilities around 530 K (see Figure 2). The thermal decomposition under air can be divided into two successive losses. The first one, related to the thermal decomposition of the polymer network, occurred between 530 and 690 K, as expected at much higher temperatures than the pure polymer.[7,16] The second weight loss corresponded to the decomposition of [BMIm][NTf$_2$], around 700 K. This allowed a direct measurement of the IL content in ionogels (see Table 1), checking the values obtained by simple weight.

Note that after extraction of the IL, the thermal behavior of the pure polymer was recovered (as expected, the relative SiO$_2$ residue was found to be higher in that case, as in the sample prepared without IL; see Figure S5 in the Supporting Information).
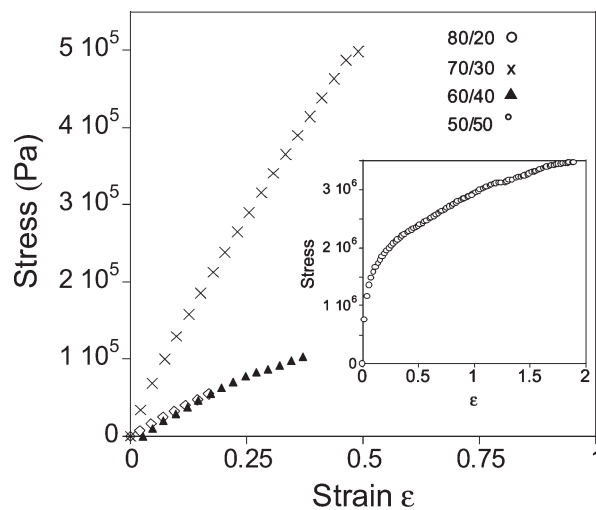
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Figure 3. Mechanical properties of the hybrid ionogels $n = 2$ (**HI2**, **4**, **5**, **6**).

Mechanical properties were determined by uniaxial stress−strain tests (Figure 3 and Table 1). **HI4** with a feed mass ratio f-PMMA/TEOS equal to 80/20 was typical of ductile materials with a short elastic zone and an uniform extension showing no fracture even after a 200% strain. The behavior of others samples was found to be different, with only a short elastic area and a fracture occurring at low strain. When increasing the IL content, a decrease in Young modulus (E) was observed as a result of the plasticizing effect.[14] These results indicate that the mechanical properties of hybrid ionogels can be modulated by varying both f-PMMA/TEOS and IL/Si ratios.

In conclusion, in these ternary systems each component endows the whole material with its specific properties without weakening the other performances: the ionic liquid provides thermal stability, plasticity, and ionic conduction, whereas the silica nanofillers covalently bonded to the polymer chains permit us to considerably improve the mechanical strength without hampering the ion transport. The extension of this new approach to other polymer nanocomposite systems should permit us to play on infinite combinations of components and compositions to modulate the properties of electrolyte membranes.

Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.