Experimental report

25/01/2024

Proposal: **9-11-2120** **Council:** 4/2023

Title: IMPACT OF THE IONIC LIQUIDS ON THEBEHAVIOUR OF FLUORINATED POLYMER COMPOSITES

Research area: Soft condensed matter

This proposal is a new proposal

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Samples:
poly(vinylidene fluoride) (PVDF)
1-butyl-3-methylimidazolium tetrachloroferrate ([Bmim][FeCl4])
1-methyl-1- propylpiperidinium bis(trifluoromethylsulfonyl) imide ([Pmpip] [TFSI])

Instrument	Requested days	Allocated days	From	To
IN5	1	1	27/11/2023	28/11/2023
IN16B Si 111 BATS	2	0		
WASP	1	1	28/11/2023	29/11/2023

Abstract:

Smart materials, defined as materials with the ability to change their properties through the application of external physical stimuli and with high functionality in simplified structures, are gaining increasing interest to act as sensors and actuators. In this context, smart materials based on electroactive polymers have emerged as particularly attractive candidates and research in the area has been essentially focused on the development of actuators based on ionic electroactive polymer composites, allowing much larger deformations at a lower voltage than piezoelectric actuators. In particular, on the development of ionic liquid-based ionic electroactive polymers, obtained through the inclusion of ionic liquids (ILs) into the polymer matrix. ILs are salts, usually composed by an organic cation and an organic / inorganic anion. The idea here is to establish a correlation between the macroscopic properties of technological interest and the molecular mobility of ILs in these hybrid materials. We plan to follow the self-H-dynamics of the cations in two hybrid materials with different structure by the combination of IN16B (BATS) and IN5 instruments.

IMPACT OF THE IONIC LIQUIDS ON THE BEHAVIOUR OF FLUORINATED POLYMER COMPOSITES

The aim of the performed experiment was to investigate the dynamics of ionic liquid (IL) in PVDF/IL composites, and compare it with dynamics in bulk IL. ILs are salts, typically composed of an organic cation and an organic/ inorganic anion, remaining in a liquid state at room temperature. For this investigation, the [Bmim][FeCl$_4$] ionic liquid was employed, featuring an organic cation containing protons and an inorganic anion. This IL was embedded in the matrix of poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE) copolymer. Composite films were produced as follows: initially, solutions of PVDF-TrFE and IL in DMF were prepared. Subsequently, they were cast onto a Petri dish, and the thickness was evened out using a doctor blade. Finally, the solvent was evaporated for 24 h at elevated temperature (453 K).

We investigated a composite sample containing PVDF-TrFE (with 30 mol% of TrFE units) and 40 wt% of IL, as well as the neat polymer matrix and the bulk IL. The samples were placed in cylindrical aluminum sample holders, and the thicknesses were calculated to achieve a transmission of 90%.

Neutron spin-echo (NSE) experiments were conducted using the WASP spectrometer. For these experiments, an incident wavelength of 6 Å was employed, covering a Q-range between 0.1 and 1.6 Å^{-1}. Five different temperatures were studied. Figure 1 displays representative examples of the measured polarization decay curves at different compositions and temperatures.

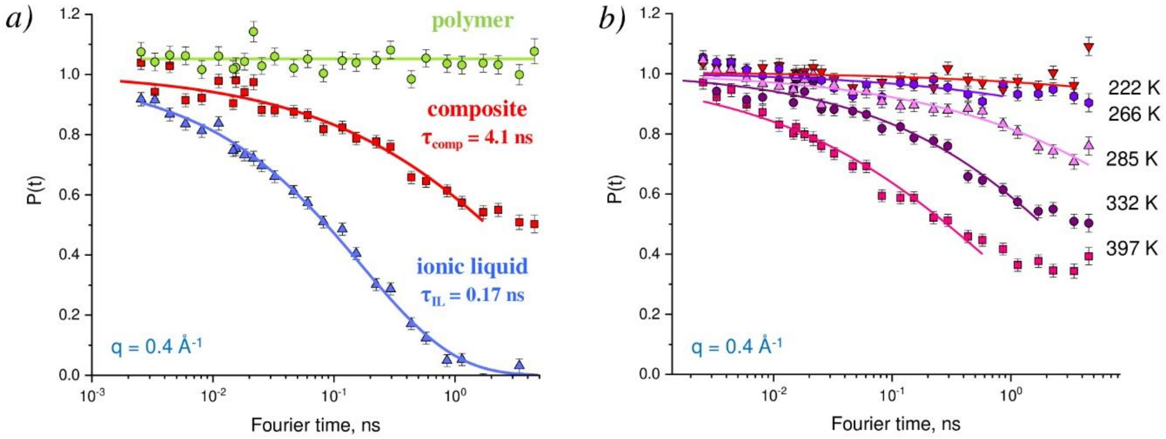

Figure 1. a) WASP profiles for the composite containing PVDF-TrFE (with 30 mol% of TrFE units) and 40 wt% of [Bmim][FeCl4] IL, as well as for the neat polymer and bulk IL; q = 0.4 Å^{-1}, temperature 332 K; b) WASP profiles for the same composite at different temperatures.

Polarization analysis with WASP revealed predominance of the incoherent contribution to the NSE signal in a q-range of 0.1-1 Å^{-1}; therefore, data form this q-range were used for further analysis. The WASP results at 332 K (Fig. 1a) indicate that the neat polymer signal is elastic, while a clear relaxation is observed for the composite, which is attributed to the motion of IL, with an associated characteristic time much larger than for the neat IL. This suggests that the dynamics of IL is slowed down due to the presence of polymer at this temperature and to the interaction between IL molecules and the polymer. Simultaneously, an increase in temperature induces a faster IL dynamics in the composite, as expected (Figure 1b).

The same samples were investigated through quasielastic neutron scattering (QENS) experiments using the IN5 spectrometer, enabling the study of pico-second dynamics in the samples. For these experiments, an incident wavelength of 6 Å was employed. Figure 2 displays representative examples of the measured dynamic structure, normalized to its value at $\hbar\omega = 0$.

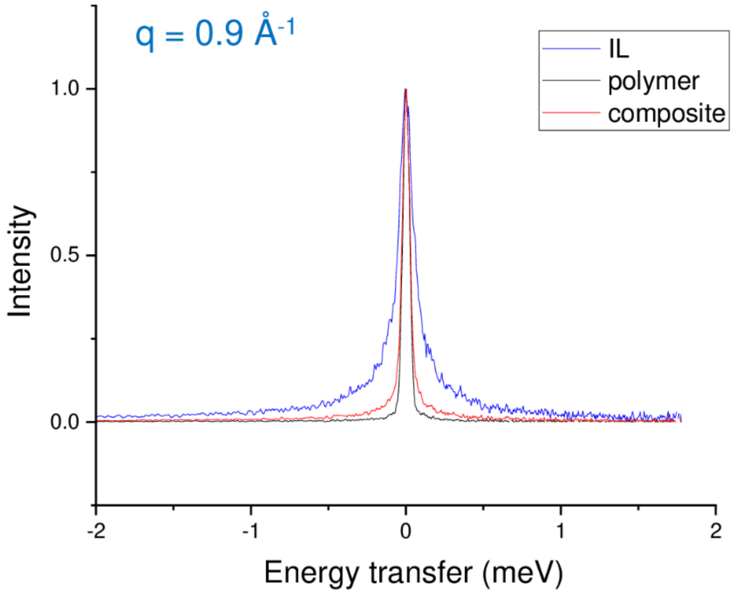

Figure 2. Normalized IN5 spectra obtained at Q = 0.9 $Å^{-1}$ for the composite containing PVDF-TrFE (with 30 mol% of TrFE units) and 40 wt% of [Bmim][FeCl4] IL, as well as for the neat polymer and bulk IL.

At 332 K, the spectrum of bulk IL is much broader than in the composite, indicating that the IL is characterized by much faster dynamics. The spectrum of the composite is broader than that of the neat polymer but narrower than that of the IL. These observations align with the WASP results for nanosecond dynamics presented above. Quantitative analysis of the results is in progress.

Thus, WASP and IN5 experiments revealed that the dynamics of IL molecules inside PVDF-TrFE/IL composites is slower than in the bulk IL, both in the nanosecond and picosecond ranges. This deceleration is likely attributed to the confinement of IL in the polymer matrix and the interactions between the components.