Experimental report

16/04/2026

Proposal: 9-11-2228 **Council:** 10/2024

Title: DYNAMICS AND STRUCTURE OF THE COMPOSITE FILMS OF FLUORINATED POLYMERSAND IONIC LIQUIDS

Research area: Materials

This proposal is a new proposal

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Samples: PVDF-TrFE with ILs

Instrument	Requested days	Allocated days	From	To
WASP	5	5	28/05/2025	02/06/2025
D22	1	1	26/05/2025	27/05/2025

Abstract:

¿Smart¿ electroactive composite polymeric materials attract wide attention due to their ability to respond to external stimuli in a controllable manner. A novel nanoparticle-free approach consists of using ionic liquids (ILs) instead of common fillers (nanoparticles, carbon-based materials, etc.) A practically important relation of the macroscopic properties of these new polymer/IL composites to the mobility and structural organisation of the ILs is not understood. The aim of the experiment is to investigate the dynamics and nanostructure of two ILs in matrices of an electroactive copolymer - poly(vinylidenefluoride-co-trifluoroethylene). We plan to follow the self-H-dynamics of the IL cations in composite materials with different structure by WASP. We will vary the interaction between IL and polymer by using two ILs and polymer matrices differing in polarity and crystalline structure. We will correlate the observed dynamics with nanostructure by employing SANS at D22 spectrometer. Our preliminary WASP experiments show that the dynamics of IL is different in confinement (within the composite) and in the bulk, which is due to specific interactions between the components.

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Aim. The aim of the performed experiment was to investigate the dynamics and structure in composites of an electroactive polymer poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE) with several ionic liquids (ILs), in order to elucidate how the nanostructuration in these composites affects the movements of the IL molecules, and the practically important macroscopic properties (e.g. conductivity, electromechanical response, etc.)

Samples. Composite films of PVDF-TRFE with various concentrations (10-40 wt%) of the ionic liquids and thickness in the range 50-90 microns were produced by solvent casting method. The study was performed with several ionic liquids – iron-based (Fe-IL), cobalt-based (Co-IL) and fully organic. For the neutron spin echo (NSE) measurements, the films were put in coaxical cylindrical aluminium cells, and the total thickness was adjusted to obtain a transmission of ca. 90%. Small angle neutron scattering (SANS) was performed on the free-standing films.

Measurements. The mobility of protons in the composites was investigated at different q values (in the range 0.1 – 1.6 $Å^{-1}$) by following the NSE signal at WASP spectrometer. The temperature range was 220-367 K. The structure of the composites was elucidated by small-angle neutron scattering (SANS) at D22 in the q-range of 0.0015 – 0.3 A^{-1}.

Results. First, polarization analysis of the NSE signal showed that incoherent scattering is predominant in the q range 0.2 - 1 $Å^{-1}$. Above 1 $Å^{-1}$, coherent fraction increases due to the presence of the structural peak in this q range, attributed to the nearest neighbour correlations. Therefore, self-dynamics of protons was mainly deduced from the q range where incoherent scattering is predominant.

Then, the dynamics was investigated for the composites containing a small concentration (10 wt%) of various ILs. At 367 K, the neat polymer matrix without any ILs already shows some relaxation (Figure 1a), which is attributed to the segmental motions. Indeed, the glass transition temperature (*Tg*) of PVDF-TrFE is ca. 240 K [1]; therefore, at 367 K segmental mobility is "de-frozen" and falls into the energy window of WASP. Interestingly, at low concentration of the Fe-IL or the organic IL, composites show almost the same dynamics as the neat polymer matrix (Figure 1a). This is attributed to strong electrostatic interactions between the IL cations and the highly polar polymer, resulting in the "cooperative" motion of both species (IL cation and the polymer segment) with a similar relaxation time. By contrast, a slightly faster relaxation is seen for the Co-IL composite. This is explained by the fact that its morphology is different from the other composites, as it contains some fraction of the "bulk-like" IL exhibiting a faster relaxation.

The dynamics was also compared for the different concentrations of the ILs. All the ILs showed a similar tendency, which is illustrated in Figure 1b for the organic IL. With increasing concentration, the amplitude of the NSE signal relaxation increases, meaning that the elastic fraction becomes smaller. This fact supports the hypothesis that

incorporation of more IL imparts more mobility to the composites. Also, at higher concentrations the relaxation becomes faster and closer to the bulk IL. This is explained by the fact that bulk-like IL domains appear at higher IL content, which is supported by the structural data obtained by SANS.

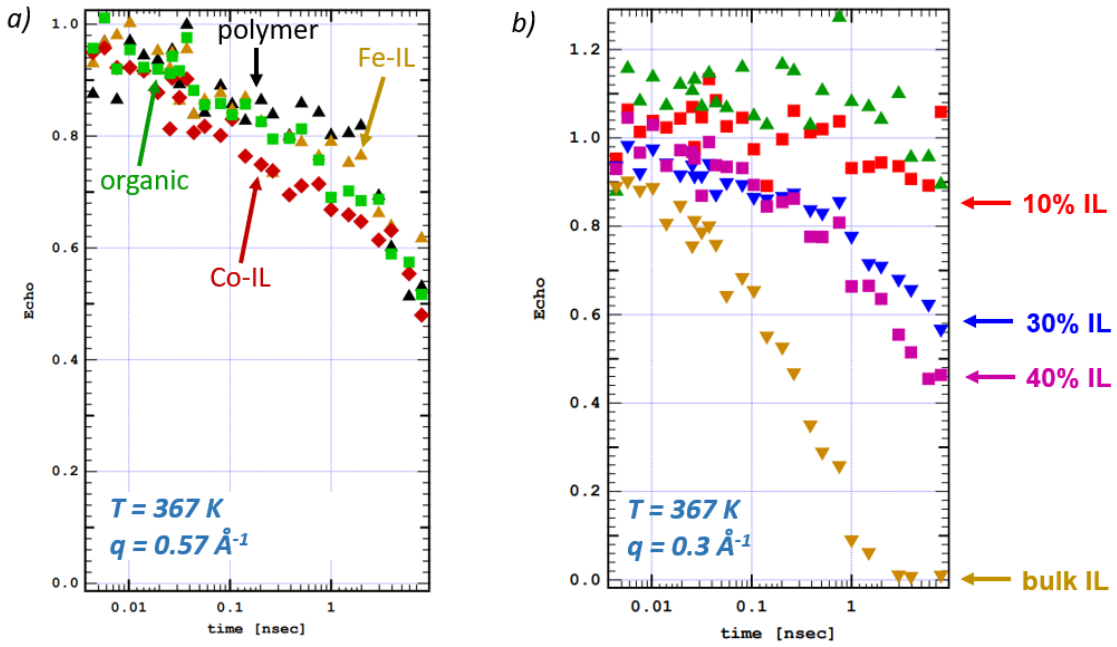

Figure 1. NSE profiles for the composites containing: a) no IL or 10 wt% of various ILs; b) various concentrations of the organic IL.

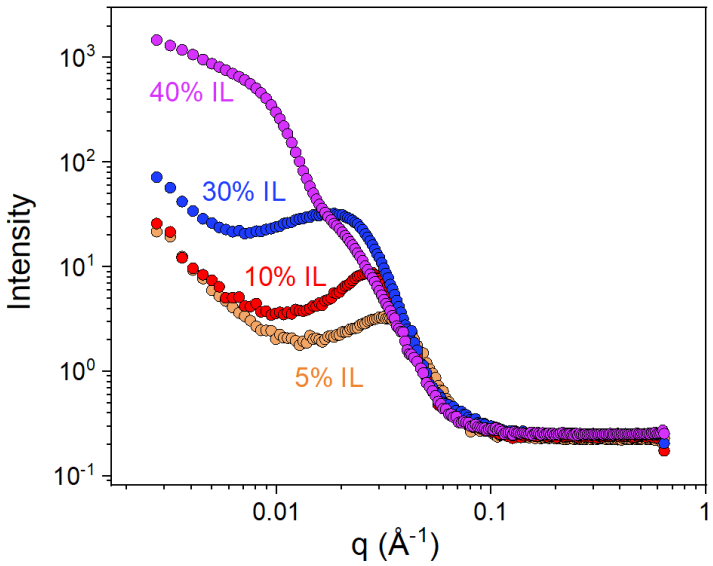

Figure 2. SANS curves for PVDF'TrFE composites with various concentrations of the organic IL

SANS scattered intensities I(q) for P(VDF-TrFE) composites with various amounts of organic IL are shown in Figure 2, indicating the development of a nanostructure with IL increasing content.

The scattering curves at low IL concentrations exhibit a profile characteristic of PVDF and other semi-crystalline polymers, showing a power-law decay at low q, which is a result of Porod scattering from the surface of big microstructures (e.g., assemblies of crystalline lamellae). A structure peak at intermediate q corresponds to the parallel stacking of the crystalline lamellae, interspersed with the confined amorphous phase layers. With increasing IL content, the structure peak shifts to lower q values, indicating an increase of the long period of the lamellar organization. At higher IL concentrations (30 and 40 wt%), there is an additional contribution to scattering arising from the formation of IL nanostructures. Most probably, these nanostructures are formed within the amorphous polymer phase$ according to the SANS data, their size is in the range of 10-12 nm. Finally, at 40 wt% IL, a strong increase of the low-q intensity is seen, which is due to the formation of larger bulklike IL accumulations.

Conclusions. Dynamics and nanostructure of PVDF-TrFE composites with various ILs were followed by combined NSE experiments at WASP spectrometer and SANS studies at D22. The results show that dynamics in the composites is altered in the composites as compared to the neat matrix, which is due to the interaction of the IL with the matrix, as well as its nanostructuration.

References

[1] K. Kumbhakar, T. D. Pham, K. K. Lee, K. Kwak, and M. Cho, Electrochimica Acta 462 (2023): 142759