



Université Claude Bernard



# DIPLÔME NATIONAL DE DOCTORAT

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## Résumé

The general context of this PhD thesis is the development of highly filled polymer-silica model nanocomposites by solvent route, based on copolymers of vinylidene fluoride and hexafluoropropylene, denoted as P(VDF-co-HFP). Due to their unique combination of mechanical, dielectric, piezoelectric and pyroelectric properties, PVDF and VDF-copolymers combined with silica are good candidates for new advanced applications like actuation or energy harvesting.

In this context, the primary objective was to understand how the filler surface chemistry and formulation parameters (nature of the solvent, concentrations of filler and copolymer), as well as the solvent casting process, affect the final structure and properties of the materials.

To elaborate P(VDF-co-HFP) nanocomposites with silica by solvent casting, a first step was to prepare solutions of silica and the polymer in a common solvent which will be subsequently dried. Aliphatic ketone solvents of various chain length, namely methyl ethyl ketone (MEK) and 2-heptanone, were used. For this purpose I have developed a generic approach to transfer silica nanoparticles from water to organic solvent through a transfer agent.

VDF-based copolymer solutions (filled or not with nanoparticles) exhibit thermoreversible gelation in ketone solvents, which may subsequently impact the processing of materials by solvent casting. Studying the phenomenology of PVDF gelation is thus of major concern for controlling the processing of those nanocomposites. No general consensus on the gelation mechanisms is found in the literature. In this context, the gelation of a semi-crystalline P(VDF-co-HFP) in MEK or 2-heptanone was studied (chapter 3). The gelation kinetics was investigated by tube-tilting and linear rheology. A combination of  $^{19}\text{F}$  Nuclear Magnetic Resonance (NMR), Differential Scanning Calorimetry (DSC), Small-Angle X-ray Scattering (SAXS), Wide-Angle X-ray

Scattering (WAXS) and nonlinear rheology was used to probe the structure of these systems and the gelation mechanisms.  $^{19}\text{F}$  NMR shows the occurrence of a polymer network-like structure with rigid zones which may act as cross-links. Such a behavior is only observed in the gel state: no polymer network or rigid zones are present when the polymer solution is in the liquid state. The nature and volume fraction of the rigid zones present in the gel state were investigated with DSC and X-ray diffraction. A small crystalline fraction, which may correspond to the rigid zones, is observed in gels.

In a third step (chapter 4), the impact of adding silica nanoparticles on the gelation kinetics of P(VDF-co-HFP) was studied. To do so, copolymer – silica gels were formulated in MEK and 2-heptanone using two sources of organic silica solutions, the one prepared previously by phase transfer and a commercial one from Nissan. We found that the presence of silica nanoparticles hardly disturbs the gelation of P(VDF-co-HFP). Conversely, the process, and more particularly the presence of residual water within the material, has a strong impact on the structure of the gels and gelation kinetics.

The nonlinear rheological properties of the P(VDF-co-HFP) physical gels filled or not with silica nanoparticles were investigated in 2-heptanone only (as MEK is too volatile), using Large Amplitude Oscillatory Shear (LAOS) experiments (Chapter 5). The behavior of all materials changes from elastic at small strain to viscous at high strain amplitudes. Before abruptly changing from elastic to viscous behavior, unfilled gels exhibit strong strain-hardening. Incorporating silica nanoparticles is found to inhibit strain-hardening.

In a last step (chapter 6), P(VDF-co-HFP) – silica solid films were obtained by solvent casting the previously prepared systems. Homogeneous materials filled up to 40 wt% of silica nanoparticles were obtained, with different and finely controlled dispersion states of nanoparticles, related to the structure of the initial gels or solutions. The impact of the concentration and dispersion state of the fillers on the mechanical performances (particularly the mechanical toughness) was investigated.