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Influence of POSS as a Nanofiller on the Structure, Dielectric, Piezoelectric and Ferroelectric Properties of PVDF

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In this paper, different amounts of fluoropropyl polyhedral oligomeric silsesquioxanes (FP-POSS) were incorporated into the poly(vinylidene fluoride) (PVDF) matrix by the solvent evaporation method. The scanning probe microscope (SPM) and Fourier transform infrared spectroscopy (FTIR) results indicated that FP-POSS nanofiller exhibited good miscibility with PVDF matrix, and morphology of the poled composites showed a smooth region influenced by the polarization. As for the dielectric properties, the dielectric contents reduced with increasing amount of POSS under the same frequency. The dielectric loss reduced when a small amount of filler was added, but with the addition of FP-POSS over 5%, the dielectric loss of composites increased. With respect to the piezoelectric and ferroelectric behavior, although the corresponding contents reduced as the wt% of FP-POSS increased, the composites still have good piezoelectric properties and typical ferroelectric behavior.

Keywords: Nanocomposite; Morphology; Dielectric property; Piezoelectricity; Ferroelectric polymer

1. INTRODUCTION

Poly(vinylidene fluoride) (PVDF) is widely investigated and used in applications including actuators, transducers, and smart sensors due to its outstanding piezoelectric and pyroelectric properties. PVDF is semicrystalline and exists α, β, γ, and δ crystalline phases at least[1, 2]. The former two phases are more widely used and studied. The α phase is the most stable one by cooling from the melt; the β phase of PVDF, has a highly polar arrangement of the positively charged hydrogen and negatively charged fluorine atoms, and presents all trans-TTT zigzag structure, which is responsible for piezoelectric and pyroelectric properties and is strongly dependent on preparation and polarization processing[3, 4]. The unoriented β-phase may be obtained by evaporation and crystallization from dimethylformamide (DMF) solutions at temperatures below 70 °C [5, 6]. The oriented β PVDF is normally obtained by stretching α phase film at temperatures between 70 and 100 °C [6]. When a proper electric potential is applied across the material, the dipoles of β phase change from a randomly to an order array and a net positive charge is produced. However, pure PVDF cannot meet the mechanical, thermal, and electrical property requirements of a space environment [7, 8]. Hence, it is necessary to choose proper nanofillers to improve the overall properties of PVDF to adapt to the new condition.

Polyhedral oligomeric silsesquioxane (POSS) based on organic–inorganic hybrid nanomaterial have been studied widely. Due to the core structure of groups containing Si-O bonds and R group, superior properties of the matrix such as mechanical strength[9], thermal stability[10], oxygen permeability[11] can be improved by POSS nanofiller. Consequently, POSS nanocomposites are being implemented in space-survivable coatings[7] and fire-resistant materials[12]. Fluorinated POSS are a new kind of POSS compounds with high molecular weight and density [13, 14]. Most importantly, fluoropropyl POSS (FP-POSS) has a 3:4 F/H ratio similar with PVDF, indicating the compatibility between PVDF and POSS, and this compatibility is of a huge factor in keeping inherent properties of the matrix.

The ferroelectric, piezoelectric and dielectric behaviors of pure PVDF and its copolymer with trifluoroethylene (TrFE), have been studied widely in several works [15-19]. Fukada [20] reported that crystalline phase and the mechanical softness affect the coupling of residual polarization with electrostriction and dimensional change. Bharti et al. [21] reported that the different ferroelectric properties can be produced due to the crystallite size and dipole alignment obtained by the different processing and poling conditions. Jiang et al. [22] compared the influence of the polarizing conditions including thermal poling and corona charging on the structure and characteristics of PVDF. R. Gregorio et al. [23] discussed the dielectric behavior of the composites formed by PVDF and lead zirconium titanate (PZT) and also barium titanate with 0–3 connectivity. PVDF need to be reinforced by some nanofiller to meet the overall properties containing the mechanical, thermal and electric properties in some special field. However, there are no reports about electric properties of PVDF matrix filled by non-copolymer or nanofiller.

In previous works [24, 25], the elastic properties and miscibility of mixtures of PVDF and four kinds of fluorinated POSS compounds, have been studied using molecular dynamics simulations. The mixture of PVDF and fluorinated POSS is found to be fully miscible at any temperature. Meanwhile, PVDF and FP-POSS nanocomposites were also prepared by the solvent evaporation method and studied the miscibility, crystalline phase, thermal properties and mechanical properties of the nanocomposites: Low addition of FP-POSS led to remarkable improvement in mechanical properties, including hardness[26]. In the present research, with the aim of studying the electrical properties of the PVDF and FP-POSS nanocomposites as advanced piezoelectric materials, different amounts of FP-POSS were incorporated into the PVDF matrix by the solvent evaporation method.

2. EXPERIMENTAL

2.1. Materials and sample preparation

PVDF (Mw = 534000; 99.99% purity) and N, N-dimethyl formamide (DMF; 99%) were purchased from Aldrich Chemical Co., and (3, 3, 3-Trifluoropropyl)$_8$Si$_8$O$_{12}$ (FP-POSS; cod. FL0578) (Fig. 1) was purchased from Hybrid Plastics (USA) as crystalline powders.

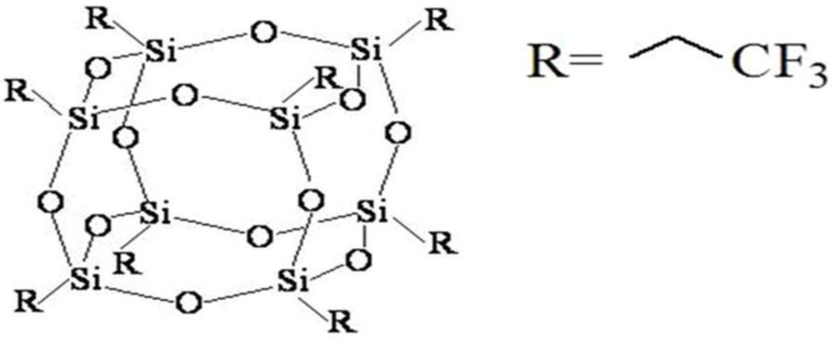

Figure 1. The molecule structure of FP-POSS compound

Firstly, PVDF and FP-POSS were spread in DMF solution, and the solution was stirred at room temperature under vacuum to remove entrapped air and subsequently ensure complete dissolution of PVDF and FP-POSS. The solution containing PVDF and FP-POSS became homogeneously transparent. Then total evaporation was performed at 70 °C to remove the solvent, and finally composite films with thickness of approximately 70 μm each were obtained. The whole process of the preparation was performed in a vacuum. The mass ratios of FP-POSS added to the PVDF matrix were 0, 3, 5, and 8%, and nanocomposites with different FP-POSS contents are denoted as PVDF-nFP (n=3,5 and 8 respectively).

2.2. Characterization

SPM measurements were carried out with a scanning probe microscope (SPM-9500, Shimadzu) equipped with a conductive probe. The current images were measured with a contact mode (a bias of 0.5 V).

Fourier transform infrared spectroscopy (FTIR) analysis was performed using FTIR spectrometer (Avatar360, Nicolet). The scan range was from 4000 cm^{-1} to 500 cm^{-1}, with a resolution of 4 cm^{-1}.

The dielectric properties of samples containing the capacitance and dielectric loss were measured using Agilent impedance analyzers. The Frequencies of Measure were 1k, 10k, 100k and 1 MHz.

The piezoelectric response (d_{33}) of the poled samples was measured with Standard static piezoelectric constant measuring instrument (Institute of Acoustic, Chinese Academy of Sciences). A constant electric voltage (6kV) was applied to the samples for 10 minutes at 80 °C, and the samples were cooled to room temperature while the electric field unchanged.

The ferroelectric hysteresis loops of samples were analysed using Radiant Ferroelectric Premier Equipments, containing Radiant Precision High Voltage Interface and Precision Premier II.

3. RESULTS AND DISCUSSION

3.1. Morphologic analysis

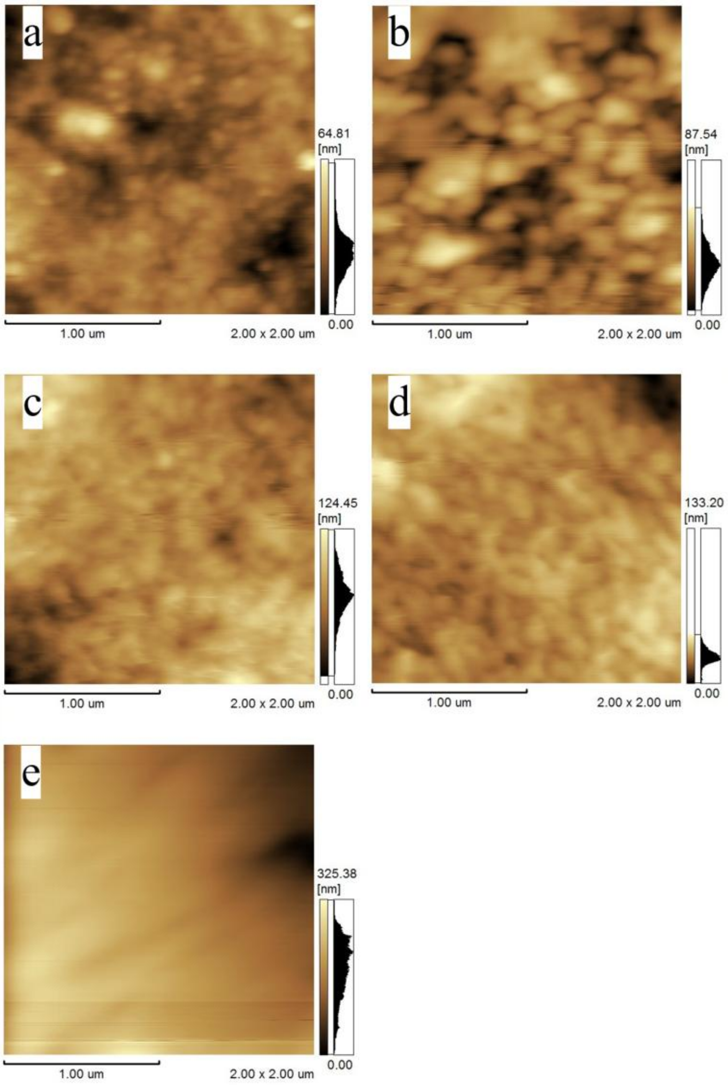

Figure 2. The SPM microscopy of the structure of PVDF/FP-POSS composites (a) PVDF (b) PVDF-3FP (c) PVDF-5FP (d) PVDF-8FP (e) PVDF-3FP after poling

Morphological analyses were performed by means of SPM measurements.

The morphologies of the free surface of the films, i.e., the surface opposite to the one in contact with the glass substrate, were analyzed. The surface SPM images of composites are at the finer sizescale level. The morphology of the composites at scan ranges of 2.0 um× 2.0 um containing 0, 3, 5, and 8% FP-POSS are shown in Fig. 2a-d, respectively. It can be observed clearly that FP-POSS had a good compatibility with the matrix at the nano-scale level. The morphology features of all composites were similar, showing regular and uniform dispersion. Compared to size of neat PVDF (80nm) (Fig. 2a), the sizes of PVDF and POSS composites were larger, between 120 nm and 220 nm. When the addition of FP-POSS was over 5%, further addition made the particles longer and wider, and the molecules formed the net-like morphology. Meanwhile, large FP-POSS domains were also uniformly dispersed all around the matrix rather than agglomerated together forming a bulk. No any POSS aggregates could be observed in all composites at the nano-scale level. It seemed that the influence of FP-POSS was just to form bigger PVDF particles and very similar to the nucleating agents in some PVDF mixtures[27, 28]. Due to the similarities in the chemical structures and the specific polar interactions of the matrix and nanofiller, the same polar C-F bonds on PVDF and FP-POSS molecules tend to make more PVDF molecules be nucleated around FP-POSS particle.

More interestingly, the polarization also has very positive effect on the morphology of the composites. Poling is achieved by applying an electric field of 80 MV/m between parallel plates. For example in the poled PVDF-3FP composite, the morphology of the poled composites (Fig. 2e) showed a smooth region, which was different from the aforementioned unpoled ones (Fig. 2b). No globular or net-like particles can be observed in the poled composites. It seemed that the polarized elements in the whole area, such as molecules and the chain, respond uniformly to electric field. The high voltage induced the molecular chain to remove and rotate with the movement of polar molecules. The roughness of morphology was related to the movement of dipoles under an electric field within the crystalline and interfacial regions[3]. Meanwhile, the smooth regions due to the orientation of dipole cannot be influenced by the addition of FP-POSS, due to the unique structure of organic-inorganic cage, i.e., when the electric field is applied, the Si-O cage of FP-POSS did not hinder the movement of the molecular chain in the poled composites.

3.2 Phase content analysis

The β phase of PVDF, which is responsible for piezoelectric and pyroelectric properties, is strongly dependent on preparation and polarization processing. The FTIR spectra of the non-poled PVDF/FP-POSS composites and poled PVDF-3FP composite are shown in Fig. 3. In the FTIR spectra, the bands at 764 cm^{-1}, 840 cm^{-1} and 1120 cm^{-1} are attributed to the characteristic absorption bands of the crystalline α- and β phase and the stretching vibration of Si-O-Si in POSS. No remarkable variations for pure PVDF and PVDF/FP-POSS composites can be observed. Peak intensity (1120) slightly increased upon the addition of FP-POSS. The characteristic peak intensity (840) of β phase is stronger than the one (764) of α phase, indicating that the unoriented β phase may be obtained by evaporation and crystallization from dimethylformamide (DMF) solutions at temperatures below 70 °C. Meanwhile, after the poling process, no new characteristic peaks appeared or suppressed in PVDF-3FP-Poled composite, but the peak of α phase was almost nonexistent.

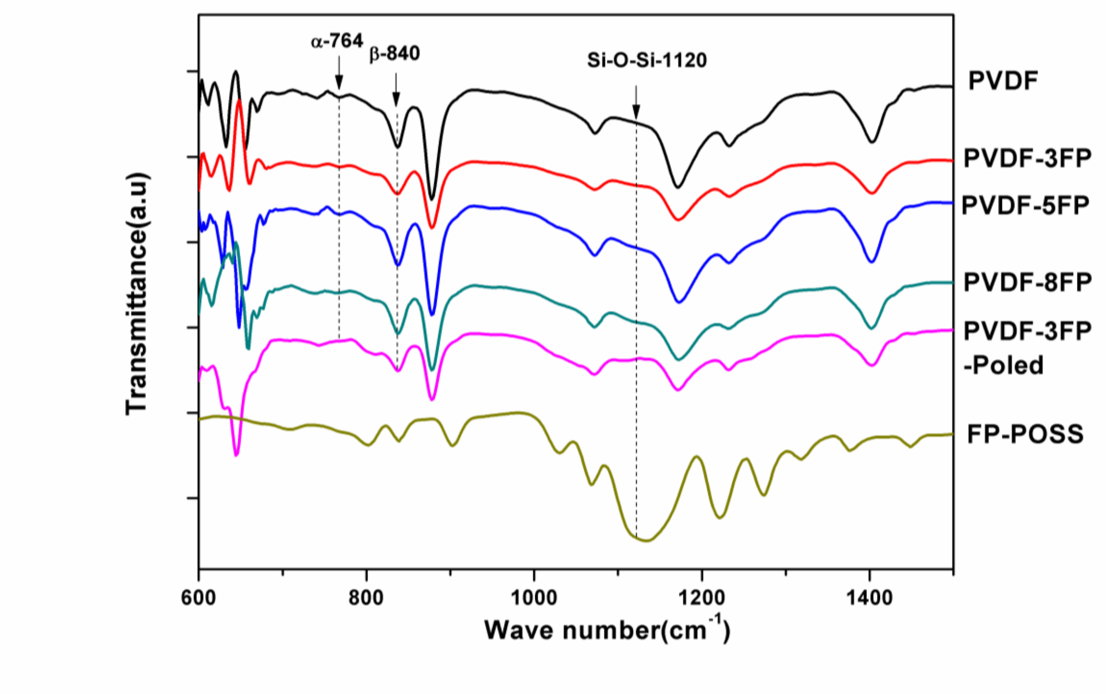

Figure 3. FTIR spectra of PVDF/ FP-POSS and PVDF-3FP after poling

3.3 Dielectric behavior

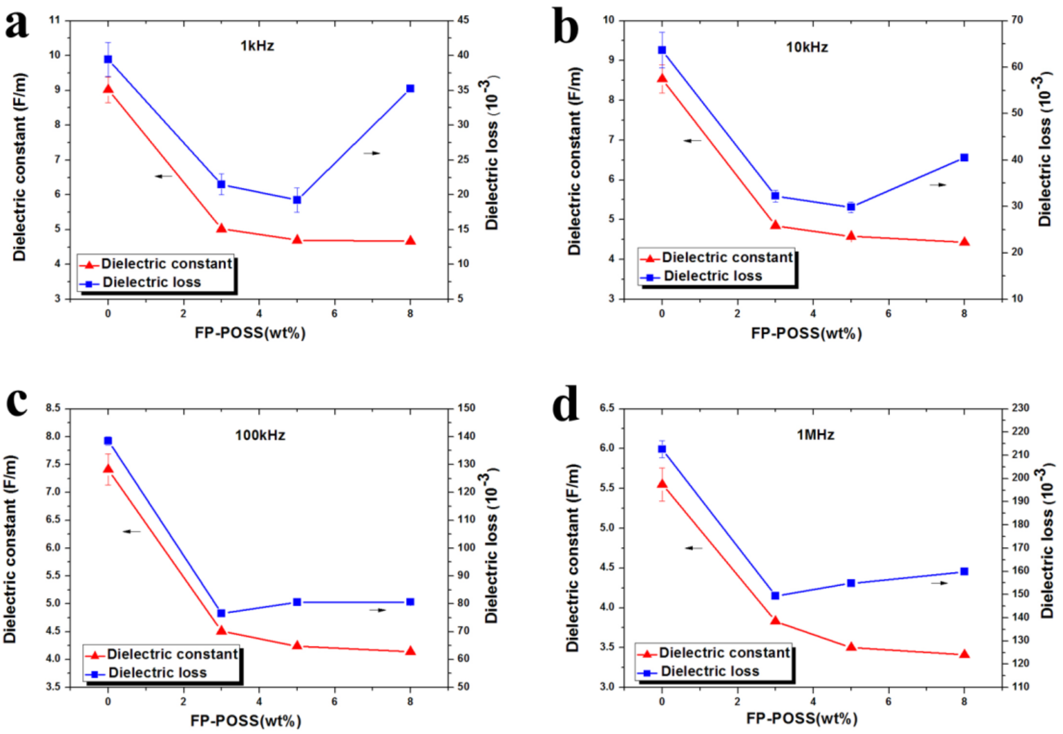

Figure 4. The dielectric properties of PVDF/ FP-POSS under different frequency

Figure 4 shows the dielectric content and dielectric loss for samples with different compositions at different frequency. It was shown that under the same frequency, the dielectric contents reduced with the increasing wt% of FP-POSS, while the variations of dielectric loss were not monotonous. It is well known that the electrical properties are significantly influenced by the structure of molecules. As a lot of dipoles were obtained due to the special polarization structure (H-F) of PVDF under the poling process, polymer molecular showed strong polarity, which contributed to large value of dielectric content and dielectric loss of the composites. However, FP-POSS had a low dielectric content due to its symmetric structure of the Si-O nanocage, and as a nucleating agent, FP-POSS attracted more molecules and restricted the dipolar alignment within each polymer chain. Additionally, in our previous work, the degree of crystallinity slightly increased with the increasing addition of FP-POSS. Polymer with higher crystallinity is prone to exhibit lower tendency of dielectric relaxation due to the constraint imposed on the phase dipoles [29]. The orientation of the dipole moment in chain segment can be restrained due to crystal under polarization, so the dielectric loss of polymer reduced with the increase of crystallinity. These resulted in reduction of the dielectric content and the dielectric loss.

With the addition of FP-POSS over 5%, the dielectric loss of composites increased, which was possibly associated with the role of FP-POSS as a plasticizer. Addition of plasticizer can enhance the mobility of charge and result in increase of the dielectric loss due to both dipolar and free charge contributions [30]. In previous work, it had been found out that the inorganic cage-like cores with Si-O atoms acting as a reinforcing agent were able to provide enough stiffness at a low content while the organic R branches acted as a plasticizer at a high content to form the net-like morphology, especially in the case of similar polar C-F bonds. When the addition of POSS exceeded 5%, POSS acting as a plasticizer, reduced the adhesion and increased the activity of polymer chains, resulting in rising of the dielectric loss.

3.4 Piezoelectric behavior and ferroelectric hysteresis

The piezoelectricity of PVDF is derived from the dipole moments of molecule, which can exhibit an electric potential in response to applied stress or strain. In this work, piezoelectricity of composites was characterized by piezoelectric coefficient d_{33}. The piezoelectric coefficient measured at room temperature was 18 Pc/N, which was lower than the one (23-28 Pc/N) given by Jiang [22]. With the increasing addition of POSS, the piezoelectric coefficient reduced. The piezoelectric coefficients were 14 Pc/N, 12 Pc/N and 11 Pc/N at 3 wt%, 5 wt% and 8 wt% respectively. It is well known that the existing dipole and large polar group are key factors to polymer electric. The addition of Si-O nanocages of POSS decreased the relative concentration of dipole moment in samples and the ability of reorientation of the dipoles along the field direction, which resulted in reduction of the polarization effect. However, the FTIR result indicated that the PVDF/POSS composites were mainly composed of a β phase crystalline phase, i.e., FP-POSS did not change the crystalline phase of PVDF matrix and exhibited a good compatibility with PVDF due to similar substituent group and the specific polar interactions between them, which ensured that the dipolar moments could be orderly oriented after poling and the good piezoelectric property of the materials.

The ferroelectric hysteresis loops for PVDF/FP-POSS composites with different FP-POSS contents at room temperature under 120 MV/m at 1Hz were showed in Figure 5.

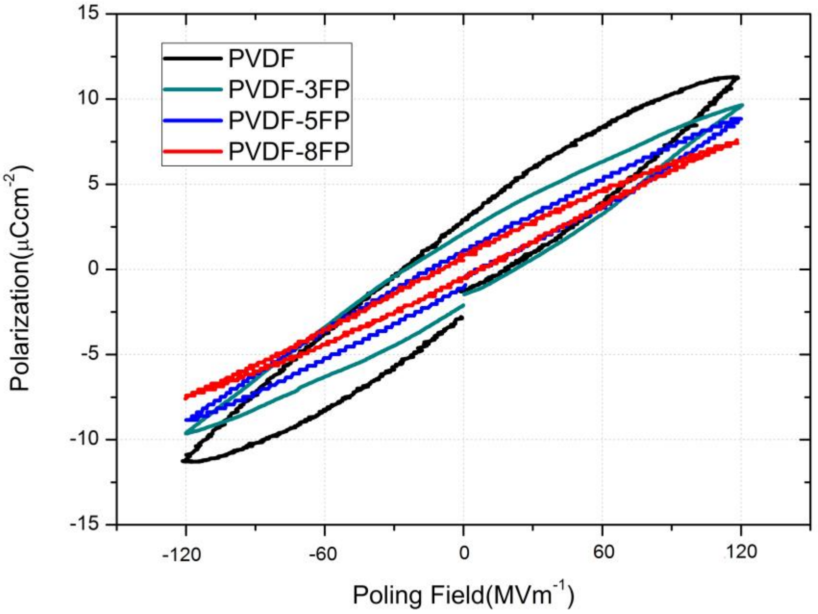

Figure 5. The ferroelectric behavior of PVDF/ FP-POSS

Similar shape of loop for PVDF was obtained by Jiang[22]. With the addition of POSS, the shape of hysteresis loops changed a little. The polarization hysteresis reduced after the POSS was incorporated into the polymer matrix. The remanent polarization (P_r) and maximum polarization decreased gradually as the content of POSS increased. It seemed that the composites were more difficult to be polarized than pure polymer, i.e., in the same field strength, the polarization effect for pure PVDF was more fully than the one for composites with the filler of POSS. Most fillers in the form of comonomers, like HFP [18], broke large polar domains into smaller ones and resulted in a decrease in the remnant polarization (Pr) and maximum polarization. However, POSS, as an inorganic-organic filler, partly restricted the dipolar alignment and reorientation, as well as reduced polarization level and energy barrier. Meanwhile, the dipole moments of FP-POSS were less than that of pure PVDF after poling. These resulted in reducing the corresponding contents as the wt% of POSS increased. Even so, FP-POSS exhibited a good compatibility with PVDF and did not thoroughly restrict the reorientation of the dipoles. These advantages ensured that the composites still had good piezoelectric properties and typical ferroelectric behavior.

4. CONCLUSION

Nanocomposites composed of a poly(vinylidene fluoride) (PVDF) matrix and 0% to 8% fluoropropyl polyhedral oligomeric silsesquioxane (FP-POSS) were obtained by the solvent evaporation method.

The SPM and FTIR results indicated that FP-POSS nanofiller exhibited good miscibility with PVDF matrix. The high voltage induced the molecular chain to remove and rotate with the movement of polar molecules, showing a smooth region.

The dielectric contents reduced with increasing wt% of FP-POSS, and the dielectric loss reduced when a small amount of filler was added, but with the addition of FP-POSS over 5%, the dielectric loss of composites increased. The corresponding contents of piezoelectricity and ferroelectricity reduced with the weight of FP-POSS increasing. The Si-O nanocages of FP-POSS decreased the relative concentration of dipole moment but not thoroughly restricted the reorientation of the dipoles. That ensured the composites still had good piezoelectric properties and typical ferroelectric behavior.

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