Phase Transformation Mechanisms and Piezoelectric Properties of Poly(vinylidene fluoride)/Montmorillonite Composite

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ABSTRACT: Poly(vinylidene fluoride) (PVDF)/montmorillonite (MMT) composite with different MMT contents were prepared by solutions-casting method. The effects of MMT on crystalline structure, morphology, dielectric property, piezoelectric property and phase transformation mechanism were studied. The results showed that acted as effective nucleation agents, the orientation of MMT were almost parallel to the surface of the film. The beta phase in the PVDF matrix was increased and the alpha phase was decreased. Relative dielectric constant and loss of the composite were increased with the increasing of MMT. The d_{33} was also increased with MMT, which reached a maximum (5.8pC/N) with 2.0 wt % MMT. The mechanisms of changes in phase transformation and piezoelectric property were proposed based on experiment results. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2595–2600, 2012

Key words: composites; films; phase transformation; dielectric properties; piezoelectric properties

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) have gained extensive attention in the past decade due to its outstanding piezoelectric, pyroelectric and ferroelectric properties.[1,2] PVDF is a semicrystalline polymer. It can crystallize in five different forms: the nonpolar TGTG' α and δ phase, the polar TTTT β phase, and TTTGTTTG' γ and ε phase, in which T and G are the Trans and gauche chain conformations found in PVDF crystal.[3] The β phase is the most attractive one due to its piezoelectric and pyroelectric property.

Though the β phase has great technological utility, α phase is thermodynamically more stable in PVDF than β phase. It is difficult to obtain a β phase dominant PVDF film. There have been numerous attempts to stabilize this phase. For example, the β phase of PVDF has been obtained by crystallization from certain solution,[4] by drawing films containing α phase,[5,6] by crystallization from solution under special conditions,[7] or by induced by special substrate.[8] Incorporation of halide[9,10] and carbon tubes[11–13] can also resulted in beta phase, thermal and electrical variation of PVDF. Yu et al.[14] and Yu and Cebe[15] also have observed that the addition of montmorillonite (MMT) led to beta phase of PVDF. They assumed that the possible mechanism for the stabilization of the β phase might due to the matching of the crystal lattice of the MMT with that of PVDF's β phase. Although some research efforts have been devoted to the crystal structure and crystallization behavior of PVDF/MMT composite, only a few works studied the crystallization kinetics of composite. More importantly, no attention has been paid to the origin of piezoelectric properties.

In this work, we investigated the influence of different MMT contents on crystalline structure, morphology, dielectric property, piezoelectric property, and phase transformation mechanism of PVDF/MMT composite. A new mechanism was proposed for beta phase formation and piezoelectric properties in the PVDF/MMT composite.
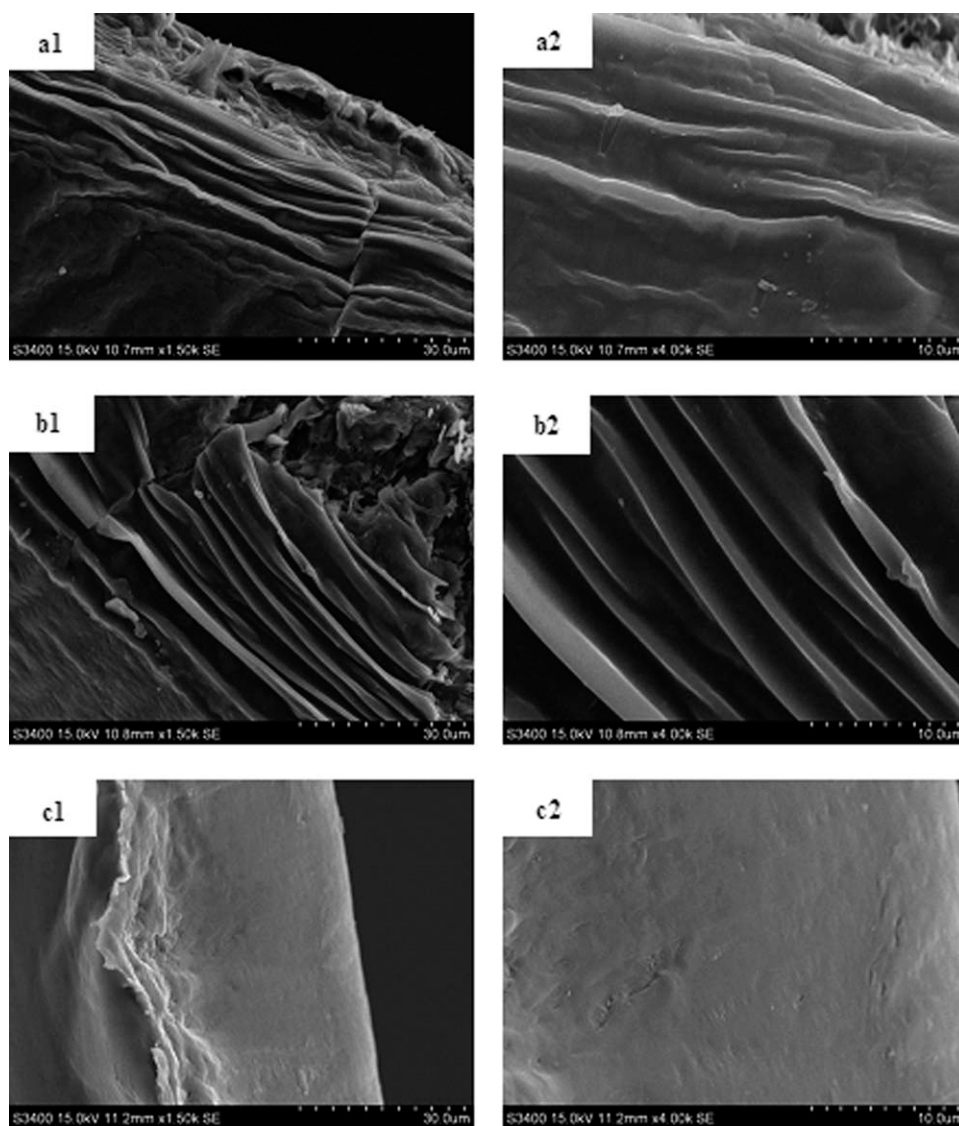
EXPERIMENTAL PROCEDURES

Raw materials

PVDF powder used in this study was a product of Academic of Sichuan Chenguang Chemical Center, Sichuan, China. MMT, which was provided by Zhe-Jiang Feng-hong MMT, Zhejiang, China. The MMT was an organically modified layered silicate. These MMT have a two-dimensional platelet like geometry and are composed of 1-nm thick layers.

Figure 1 SEM cross-section micrographs of PVDF doped with different fraction of MMT: (a1)(a2)0.4%; (b1)(b2)2%; and (c1)(c2)2.5%.

Sample preparation

PVDF was dissolved in *N,N*-dimethylformamide (DMF), and the MMTs were dispersed in DMF by sonication for 1.5 h to form a stable suspension. The PVDF solution was then mixed with the MMT solution. The PVDF/MMT mixture solution was mechanically stirred at room temperature for 1 h and then sonicated for 1 h before poured into uncovered glass dishes, which were heated at 100°C for 1 day to ensure the removal of the solvent traces. The films had a thickness in the range of 0.08–0.09 mm. The films were prepared with mass fractions of MMTs of 0.0, 0.4, 0.8, 1.2, 1.6, 2.0, and 2.5%, respectively. The low-temperature silver-slurry was daubed onto the composite samples and then solidified at 100°C for half-an-hour as electrodes. Then the samples were poled in silica oil at 30 kV/mm for half-an-hour (at 130°C).

The cross-section morphology was examined by using a scanning electron microscope (SEM, FEI, Holand). The crystalline structure analysis was performed at room temperature by Fourier transform infrared (FTIR) spectroscopy (VERTEX 70, BRUKER, Germany). The differential scanning calorimetry (DSC) tests were carried out by WCR-2C, using a heating rate of 5°C min^{-1}.The dielectric properties of material in the frequency ranging from 40 Hz to 10 MHz were measured by Agilent 4294A. The piezoelectric coefficient was tested using the ZJ-3A.

RESULTS AND DISCUSSION

The SEM images of the cross-section of PVDF doped with different fraction of MMT were shown in Figure 1. Figure 1(a1) and Figure 1(b1) all showed
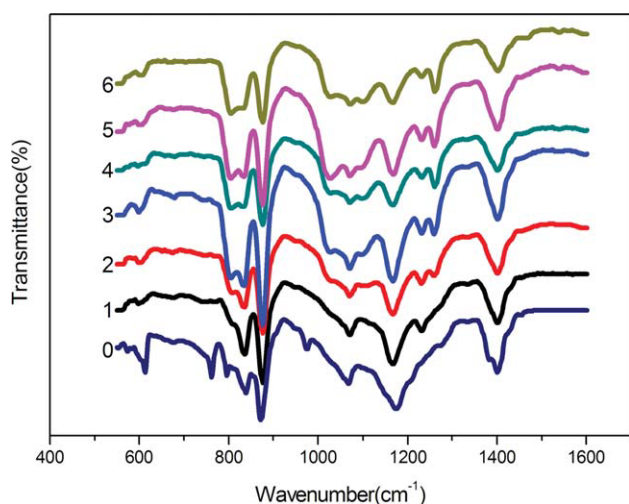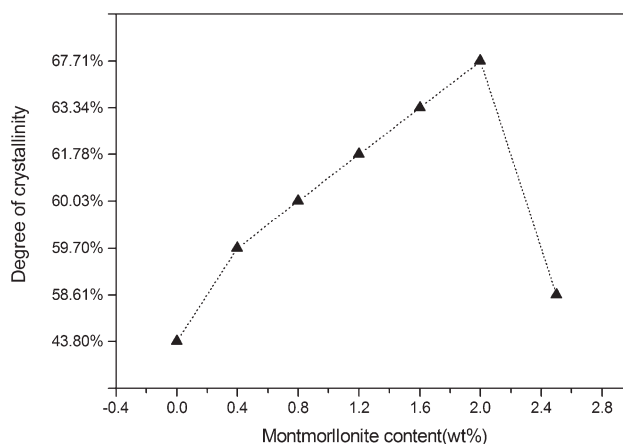
Figure 2 FTIR spectra of PVDF and PVDF/MMT composite. 0: PVDF-MMT(0.4%); 1: PVDFMMT(0.4%); 2: PVDF-MMT(0.8%); 3: PVDF-MMT(1.2%); 4: PVDF-MMT(1.6%); 5: PVDFMMT(2.0%); and 6: PVDF-MMT(2.5%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that the MMT were parallel to the surface of PVDF film. In Figure 1(a2), some area had no MMT. With the increasing of MMT content, the MMT were uniformly dispersed in the composite, which could be seen from Figure 1(b2). When MMT was up to 2.5%, the cross-section of PVDF seen from Figure 1(c2) was smooth. As a great number of MMT were added in a limited space, the MMT could not be parallel to each other. The PVDF which generated from the nucleation agent simultaneously grew and led to the formation of small size crystal.[16] The small
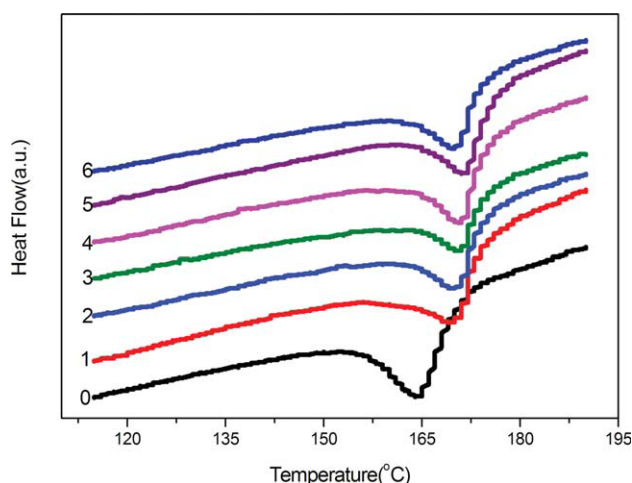
Figure 3 DSC scans of PVDF and PVDF/MMT composite. 0: PVDF-MMT(0.4%); 1: PVDFMMT(0.4%); 2: PVDF-MMT(0.8%); 3: PVDF-MMT(1.2%); 4: PVDF-MMT(1.6%); 5: PVDFMMT(2.0%); and 6:PVDF-MMT(2.5%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
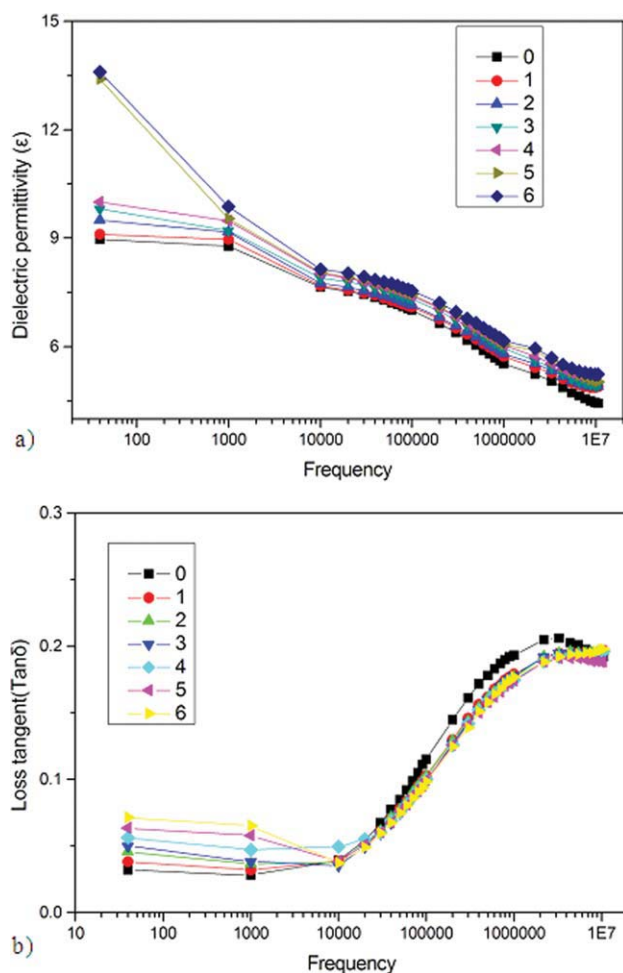

Figure 4 Degree of crystallinity of PVDF and PVDF/MMT composite.0:PVDF-MMT(0.4%); 1: PVDFMMT(0.4%); 2: PVDF-MMT(0.8%); 3: PVDF-MMT(1.2%); 4: PVDF-MMT (1.6%); 5: PVDFMMT(2.0%); and 6: PVDF-MMT(2.5%).

crystal was attached closed to the MMT and had no obvious interface. So the cross-section of PVDF was smooth.

The FTIR studies of PVDF and PVDF/MMT composite with different MMT contents were carried out to ascertain the presence of the beta phase in PVDF matrix, as seen in Figure 2.The bands at 615, 765, 795, 1182, and 1400 cm^{-1} were referred to alpha phase, and the bands at 600, 840, and 1270 cm^{-1} were belong to the beta phase, whereas the 795 and 1233 cm^{-1} were corresponded to the γ phase. As the MMT content was added, the bands 615, 765, 795 cm^{-1}, which refer to alpha phase vanished, the bands 600, 840, 1270 cm^{-1} which refer to beta phase increased relatively, while the bands belonging to γ phase also increased relatively. Our FTIR results suggested that the MMT could induce the beta phase and reduce alpha phase in the PVDF matrix. Some possible mechanisms are proposed: The silicate layers of MMT are acted as nucleation agents in the PVDF matrix during crystallizing of the composite owing to strong interaction between MMT and PVDF. Such an interaction may be based on ion-dipole interaction as proposed by Ramasundaram et al.[17]

DSC was performed in the PVDF and PVDF/MMT composite in order to determine the melting temperature and the degree of crystallinity of the samples. Figure 3 shows the results obtained from samples with different MMT concentrations. The incorporation of MMT in the composites has a direct influence on the melting temperature of PVDF. With the increasing of MMT content, the melting temperature of the composites increased. It can be attributed to more beta phase contained in the composites while increasing the MMT, which is consistent with results of FTIR.
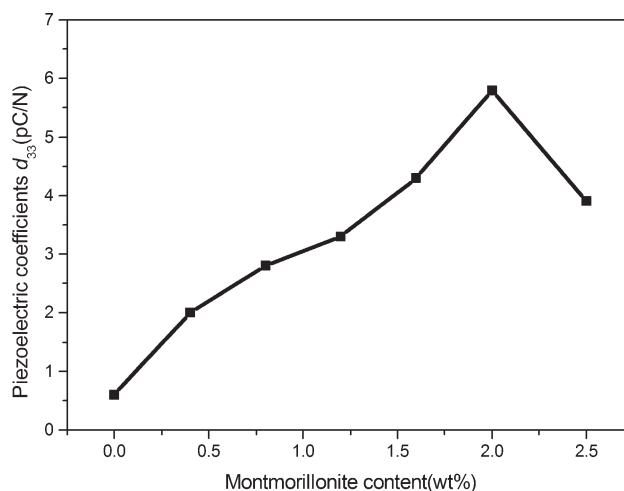
Figure 5 Dielectric properties of PVDF and PVDF/MMT composite as a function of frequency. 0: PVDF-MMT(0.4%); 1: PVDF-MMT(0.4%); 2: PVDF-MMT(0.8%); 3: PVDFMMT(1.2%); 4: PVDF-MMT(1.6%); 5: PVDF-MMT(2.0%); 6: PVDF-MMT(2.5%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The degree of crystallinity of PVDF films can be obtained as follows:

$$\Delta X_c = \frac{\Delta H_m}{\Delta H_{100\%,crystalline}} \tag{1}$$

where ΔH_m is the melting enthalpy of the samples and $\Delta H_{100\%,crystalline}$ is the melting enthalpy for a 100% crystallinity sample of pure PVDF, which is reported to be 104.6 J/g.[18]

Figure 4 shows the degree of crystallinity of PVDF films with the filling content. Obviously, an increase of the degree of crystallinity of the composite was observed when compared with pure samples of PVDF. It indicates that the MMT acts as a nucleation agent in the composites increases the degree of crystallinity. When 2.0 wt % MMT is added, the degree of crystallinity reaches maximum. This is because excessive MMT confines the movements of polymer

Figure 6 Piezoelectric constant of the PVDF films doped with different contents of MMT.

chains, which results in the decrease of the degree of crystallinity.

Figure 5 shows the dielectric properties of PVDF and PVDF/MMT composite as a function of frequency at 25°C. It was found that the more the MMT introduced, the larger the dielectric and dielectric loss of the composite had at 1 kHz. The enhancement in dielectric value and loss could be attributed to the high dielectric constant and electric conductivity of MMT. In Figure 5(a), it can be found that dielectric permittivity measured at lower frequency is always greater than higher frequency. In Figure 5(b), the dielectric loss curve shows a relaxation at $4 \times 10^{+06}$Hz, which is related to the glass transition relaxation of PVDF and is denoted as α_a relaxation. The peak is related to the micro-Brownian cooperative motions of the main chain backbone
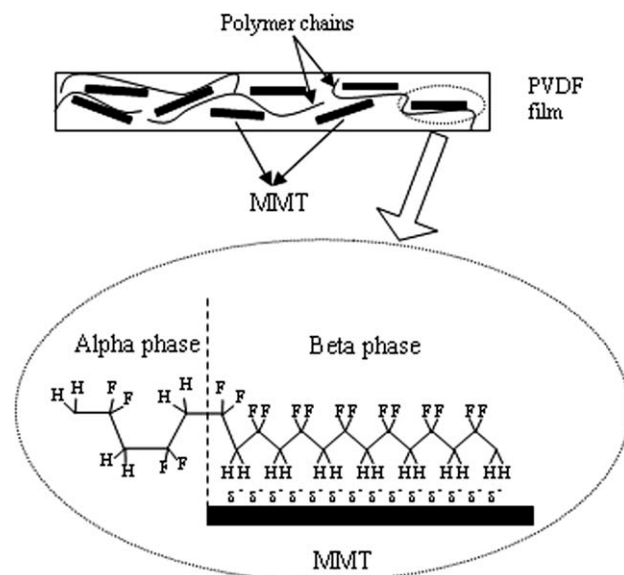
Figure 7 Schematic showing the proposed mechanism about beta phases formation.
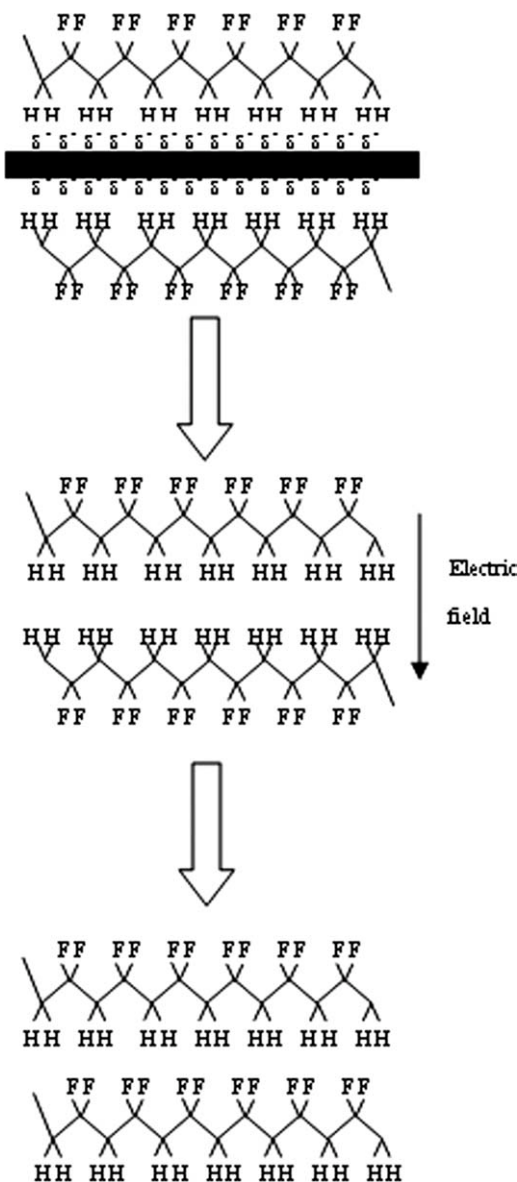
Figure 8 Schematic showing the proposed mechanism about piezoelectric formation.

and is dielectric manifestation of the glass transition temperature of PVDF.[19]

Figure 6 showed the d_{33} value of piezoelectric constant for PVDF films with different contents of MMT. The d_{33} was increased with an increase of MMT content, and reached a maximum (5.8pC/N) with 2.0 wt % MMT. The highest d_{33} value of the composite was eight times more than that of pure PVDF. This could be because that when MMT is added, the MMT acted as substrates of PVDF nucleation. The TTTT conformation chains would be tethered on the surface of silicate layers and form beta phases. The mechanism was shown in Figure 7, which will be discussed next. When the MMT was introducing more, the piezoelectric activity was decreased. There were two reasons: one was that the

high dielectric loss at this stage make it difficult to apply the voltage required for poling PVDF beta phase because the electric energy was dissipated by large leakage currents; the other reason was that the MMT and TTTT long chains cannot be parallel to surface of composite, So the applied voltage cannot induce the hydrogen atoms and fluorine atoms to reversal to form electrical dipoles, thus the piezoelectric activity was decreased.

We can give an overall picture about beta phase formation and the origin of piezoelectric properties from Figures 7 and 8. PVDF's beta phase consists of TTTT conformation chains, whereas alpha phase consists of TGTG' conformation chains. When MMT was added, the MMT was parallel to the surface of PVDF film and provided the substrates of PVDF nucleation. So the TTTT conformation chains will be tethered on the surface of silicate layers and form beta phases. Such stabilized long chains conformation was favorable for the formation of polar, because the PVDF molecular chains were consisted of carbon atoms, hydrogen atoms and fluorine atoms, the electrical dipoles were generated between fluorine and hydrogen atoms in individual molecular chains. When MMT was added, the long chains were parallel to the surface of PVDF film, whereas hydrogen atoms and fluorine atoms were perpendicular to the surface of composite. When more MMT were added, the MMT were stacked with each other, so the long chains were not parallel to the surface. When the electric field was applied to the film, the direction of electric filed was parallel to hydrogen atoms and fluorine atoms. The hydrogen atoms and
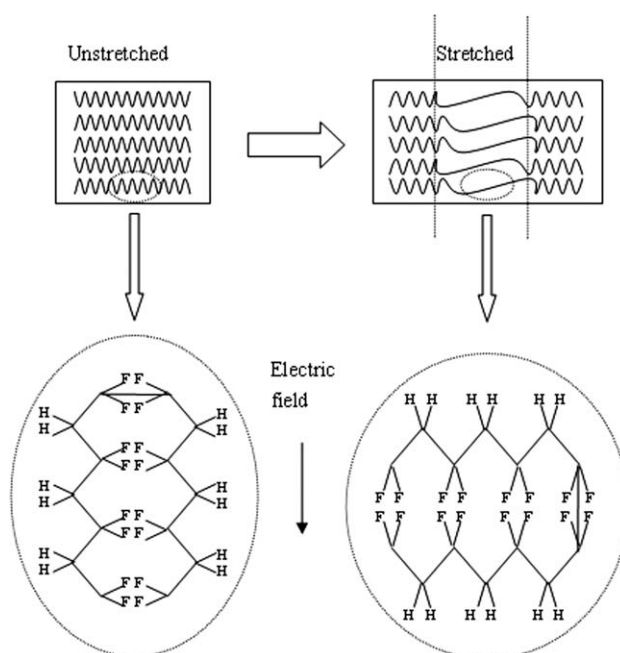

Figure 9 Schematic showing the proposed mechanism about orientation of stretched film.

fluorine atoms can easily inverted by electric field and then the electrical dipoles formed. Because the long chains were not parallel to the surface, although they were β phase, the piezoelectric activity decreased as the hydrogen atoms and fluorine atoms cannot invert by electric field. The mechanism was similar to the film by stretched as proposed by Salimi, A.[7] Figure 9 was the schematic of the proposed mechanism about orientation of stretched film. Unstretched and stretched films all contain the same fraction of β phase, but the piezoelectric constant have a great difference. The phenomenon was attributed to that the chains belong to stretched film were parallel to the strain direction, hence provided the net dipole moments to be aligned under the applied electric field.

CONCLUSIONS

PVDF/MMT composite with different concentrations of MMT were prepared using solutions-casting method. The MMT are parallel to the surface of PVDF film from the SEM results. FTIR result showed that addition of MMT could stabilize the TTTT long chains and induced the beta phase content. The d_{33} was increased with the increasing of MMT content and reached a maximum 5.8pC/N with 2.0 wt % MMT. Owing to a strong interaction between MMT and PVDF, addition of MMT induced beta phase, and disturbed alpha crystal. The working mechanism could be due to the silicate layers of MMT providing the substrates of PVDF nucleation. The TTTT conformation chains were tethered on the surface of silicate layer. The long chains were parallel to the surface of film. When the electric field applied to the composite, hydrogen atoms and fluo-

rine atoms were easily rotated, then the electrical dipoles (piezoelectric) formed.

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