A facile method to enhance ferroelectric properties in PVDF nanocomposites

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Abstract

Poly(vinylidene fluoride) (PVDF)/nanoclay composites were prepared using melt compounding. The effect of acrylic rubber (ACM) as a compatibilizer on different polymorph formation and on the ferroelectric properties of nanocomposites were investigated. The intercalation and morphological structure of the samples were studied using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The infrared spectroscopy and X-ray analysis revealed the coexistence of beta and gamma crystalline forms in PVDF-clay nanocomposite, while in partially miscible PVDF/ACM/clay hybrids, three polymorphs of alpha, beta and g coexisted. The coefficients of electric field-polarization (E-P) Taylor expansion were calculated based on the Lorentz theory. Using a genetic algorithm, complex dielectric susceptibilities as well as the dielectric constants for each sample were calculated and optimized. The predicted dielectric constants were found to be in good agreement with the experimental results. A dielectric constant of 16 (10 Hz) was obtained for PVDF/ACM/clay (90/10/5), which was 40% higher than that of the PVDF-clay (100/5) nanocomposite without ACM. The improved dielectric performance of the nanocomposites can be attributed to the compatibilizing effect of ACM, which facilitated the growth of b polymorph in the sample.

Keywords

method, enhance, ferroelectric, properties, facile, pvdf, nanocomposites

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PVDF/Clay Nanocomposites: Effect of ACM Compatibilizer on Polymorphs Formation and Ferroelectric Properties

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Abstract

Poly(vinylidene fluoride) (PVDF)/nanoclay composites were prepared using melt compounding. Effect of acrylic rubber(ACM) as a compatibilizer on different polymorph formation and ferroelectric properties of nanocomposites were investigated. Intercalation and morphological structure of the samples were studied using X-ray diffraction (XRD) and transition electron microscopy (TEM). Infrared spectroscopy and X-ray analysis revealed the coexistence of β and γ crystalline forms in PVDF/Clay nanocomposite while in partially miscible PVDF/ACM/Clay hybrids three polymorphs of α, β and γ coexisted. Inclusion of ACM found to improve the ferroelectric properties of PVDF/Clay nanocomposites which is mainly due to the growth of β polymorph in the sample. Coefficients of Electric field-Polarization (E-P) Taylor expansion were calculated based on free energy function according to Landau-Devonshire theory. Using genetic algorithm, complex dielectric susceptibilities as well as dielectric constant for each sample were calculated and optimized. Predicted electric displacement was found to be in quite good agreement with experimental results.

Keywords: nanocomposite, polymorph, D-E hysteresis loop, dielectric constant, E-P Taylor expansion, free energy

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1. Introduction

In last decade, ferroelectric materials have received numerous attentions due to their industrial applications, such as nonvolatile memory and transducers in sensors and actuators, electrostriction, electric energy storage, electrocaloric cooling, fuel injectors for high efficiency-low emission diesel engines, and ultrasonic rotary inchworm motors with high power and torque densities [1-5].

Ferroelectric materials are mainly divided into two groups: ceramics and polymer ferroelectrics. Ceramic ferroelectrics properties are highly desirable; however, they are brittle and quite heavy. On the other hand, the ferroelectric polymers are light, flexible, easy to process and low cost, nevertheless, their polar properties are an order of magnitude weaker[1,6]. Among polymers, PVDF and its copolymers are the most well-known and widely used family of polymer ferroelectrics with significant ferroelectric properties mainly due to its β polymorph.

PVDF as a polymorphous crystallizable polymer has at least five crystal polymorphs, i.e., α, β, γ, ε and δ. However, only the β and γ crystalline phases with trans conformation have dipole moment in crystalline phase. So, the β and γ crystalline phases are the most important and attractive phases among others with outstanding electric properties [7-10] . Nevertheless, in study of polarizability, β polymorph plays a more significant role therefore much efforts have been made to induce formation of this polymorph type to take the full advantage of ferroelectric properties that PVDF has to offer.

Various methods have been proposed and implemented [11-14] to increase the β phase content of PVDF films; however high temperature mechanical stretching and high voltage poling using are proved to be efficient and practical [15-17].

Nanoparticles have been long used in polymer matrices to improve mechanical, thermal and electrical properties. Lately, it has been reported that addition of clay platelets into PVDF polymer matrix induces polar crystalline phase [12,18-24]. Priya and Jog [18-20] reported the effectiveness of organically modified montmorillonite for the induction of β polymorph formation in PVDF films.

Peng et al [25] reported the nucleation of β polymorph with the addition of 1-2wt% clay, however, the nanocomposite containing 5wt% nanoclay exhibited reduced crystallinity. Shukla et al [26] have shown changes in dielectric constant as a result of frequency changes at room temperature for pure PVDF and PVDF nanocomposite containing 10wt% clay. At low frequency, dielectric constant of PVDF-clay nanocomposite were lower than pure PVDF, however, at 100 Hz this trend was reverse . Carbon-based nanoparticles have shown to enhance the ferroelectric properties of polymers. Kim et al [17] have used multiwalled carbon nanotubes (MWCNTs) to improve piezo- and ferroelectric properties of PVDF matrix. Ma et al. [27] have studied the crystalline structure of polymer blends and found that PMMA can increase β phase content of PVDF, while Li et al [28] have further investigated PVDF/PMMA ferroelectric properties and reported 4 $\mu C/m^2$ of P_r for blend of PVDF with 20wt% PMMA.

The performance of polymer based nanocomposites depends on distribution and dispersion of nanoparticles within the matrix and how strong is the interfacial bonding between nanoparticles and polymer matrix. It has been shown that employing block or graft copolymers as compatibilizing agents in nanocomposites can improve the interaction between polymer matrix and inorganic nano particles [28]. Moussaif et al. [29] reported that a small amount of PMMA can act as a compatibilizer and enhances the affinity of PVDF to organoscilicate particles . However, in this study, no results are provided for the effect of PMMA on the crystalline structure of PVDF matrix.

In the present study we have used an inorganic nanofiller (clay) and a rubbery polymer (ACM) as a compatibilizer to prepare ferroelectric PVDF thick films. We have shown that the ferroelectric property can be obtained in a simple fashion and with no further post treatments such as high temperature stretching. A correlation was found between the improved ferroelectric properties and growth of β phase content in PVDF nanocomposites containing ACM compatibilizer.

To the best of our knowledge it is the first time that the effect of intercalation of layered inorganic nano-fillers on ferroelectric properties of PVDF is studied.

To investigate the ferroelectric properties of PVDF/clay nanocomposites first the P-E hysteresis loops of nanocomposites which are indicative of polarizability were compared. The coefficients in Taylor expansion between E and P were then formulated using free energy function. Finally, using the new

generated equation, linear susceptibility or dielectric constant as well as nonlinear optical values were calculated.

2. Theory of ferroelectricity

There are two main theories to study the ferroelectric property of materials i.e. Landau-Devonshire theory [30] and Landau-Khalatnikov theory [31]. Landau-Khalatnikov theory is a dynamical version of Landau-Devonshire by which P-E hysteresis loop could be regenerated. .

According to Landau-Devonshire theory, Free energy, G, could be determined based on a few variables including temperature (T), electric field (E), polarization (P), stress (s), strain (e) and so forth.

In the absence of mechanical stress, free energy would be described as:

$$G = f(P_x, P_y, P_z, E, T)$$ Equation 1

where P_x, P_y, P_z are the components of the polarization, T is the temperature and E is the external electric field.

Assuming that for an uniaxial ferroelectric the free energy of unpolarized crystals is equal to zero [32-34], the free energy, G, of polarized crystals could be written as:

$$G = \frac{1}{2} \alpha P^2 + \frac{1}{4} \gamma P^4 + \frac{1}{6} \delta P^6 + \cdots - EP$$ Equation 2

For all known ferroelectrics, the coefficient α is a function of temperature; note that at below Curie temperature this coefficient is negative. The δ parameter is positive while γ depends on the type of transition (it is negative for first-order transitions and positive for second-order transitions).

In equilibrium thermodynamic condition at constant temperature, when $\left(\frac{\partial G}{\partial P}\right)_T = 0$, equation 2 can be rewritten as:

$$E = \alpha P + \gamma P^3 + \delta P^5 + \cdots$$ Equation 3

Furthermore for uniaxial ferroelectric, general relation between polarization, P, and applied electric field, E, has been given as a Taylor expansion [35-38], namely:

$$P = a_1 E + a_2 E^2 + a_3 E^3 + \cdots \qquad\qquad\qquad \text{Equation 4}$$

where a_1, a_2 & a_3 are the first, second, and third derivatives of Taylor expansion. In equation 4, $a_1 = \varepsilon_0 \chi$, where χ or $\chi^{(1)}$ is the linear susceptibility and dimensionless physical property; $a_2 = \varepsilon_0 \chi^{(2)}$ and $a_3 = \varepsilon_0 \chi^{(3)}$ where $\chi^{(2)}$ & $\chi^{(3)}$ are first and second hyper-susceptibilities (sometimes referred to optical susceptibilities) [36]. In general, the complex dielectric susceptibilities, $\chi^{(n)}$, are related to the microscopic (electronic and nuclear) structure of material [35] and are a function of the frequency of the applied electric field. Linear dielectric susceptibility is generally much larger than nonlinear coefficients $\chi^{(2)}$, $\chi^{(3)}$ and so forth.

3.   Experiments
3.1. Materials and methods

PVDF (Kynar 710) with melting flow rate of 25 g/10 min (2328C/12.5 kg load) from Arkema and acrylic rubber (Grade AR71) from Zeon Advanced Polymix Co.(Thailand) were used in this work. The major component of the acrylic rubber was poly (ethyl acrylate) (PEA), which contains a minor amount (5%w) of chlorine cure-site monomer. Organically modified clay, Cloisite 30B with a cation exchange capacity of 90 meq/100 g was supplied by Southern Clay. All components were dried in a vacuum oven at 80°C for at least 12h before processing. Clay content in composite samples is 5 wt%. From now on in this manuscript we use NPVDF, NACM and NPVDF/ACM nomenclature for PVDF nanocomposite, ACM nanocomposite and PVDF nanocomposite with 10%ACM as compatibilizer, respectively. All samples were prepared using a Brabender internal mixer at a rotation speed of 100rpm at 190°C for 10min. Samples were hot pressed at 200°C to a thin film and allowed to slowly cool down to room temperature.

3.2. Characterization

To investigate the level of clay layers dispersion, Molau test was done by adding 1 gram of PVDF/clay samples in 10 ml N,N-dimethylformamide (DMF). The mixture was shaken vigorously at 50ºC and then left at room temperature for one month to observe the turbidity of the solutions.

Fourier transform infrared spectroscopy (FTIR) was carried out using Bruker 70 equipped with ATR unit. FTIR spectra were acquired (64 scans at 4 cm^{-1} resolution) from500 Cm^{-1} to 1500 Cm^{-1}.

X-ray diffraction measurement was performed on a Panalytical XRD instrument. The data were recorded in the range of 2θ = 5–40° and 2–10°. Samples were scanned continuously with a 0.5° scan step and 1 s scan time.

The composite samples were sectioned using a Leica UC6 ultramicrotome with FC6 cryochamber at -120°C, at a nominal thickness of 70 to 80 nm. Sections were imaged using a Gatan Orius SC1000 digital camera on a JEOL 2100 transmission electron microscope (TEM) operating at an accelerating voltage of 200kV.

Ferroelectric hysteresis loops were measured at ambient temperature with a continuous triangular wave signal electric field at frequency in the range of 5 to 100 Hz and amplitude up to 4000 MV/m. Electric polarization versus electric field was obtained using an Easy Check 300 (aixACCT Systems GmbH, Germany) equipped with Trek 610E high voltage amplier T at room temperature.

4.   Results and discussion
4.1. The interaction between nanoclay, PVDF and ACM

Figure 1. illustrates the results of Molau tests after one month. There is a distinct phase separation in DMF/clay sample. The top part of the solution which is DMF is clear, while the bottom part is nanoclay, indicating that there is no interaction between nanoclay and DMF. Molau test results for DMF/clay/ACM and DMF/clay/PVDF samples reveal that the nanocomposite maintained a stable solution state in DMF. This indicates a strong interaction between silicate layers of clay, PVDF and ACM molecules. Nevertheless, there is some nanoclay precipitated in the bottom of PVDF/Clay solution. This is due to the better interaction of ACM with clay compared to PVDF.

Morphology and Clay dispersion

Figure 2. presents the WAXD patterns of Cloisite 30B, NPVDF, NACM and NPVDF/ACM samples. The Cloisite 30B has a d-spacing of 1.8nm, evidenced by the XRD peak at 2θ~4.8º. In the NPVDF containing 5 wt% clay, this peak is shifted towards the left (lower frequencies), resulting in a diffused peak at 2θ~2.5º, corresponding to d-spacing of 3.4nm. This suggests that the PVDF has penetrated into the gallery region   and formed the intercalated structure

with increase in the clay interlayer space. This type of structure is formed due to the interaction between the modified clay and PVDF or shear induced intercalation. The peak at $2\theta \sim 5.8°$ corresponding to the d-spacing 1.4nm is due to the second order diffraction d(002) [39]. The appearance of this peak could be attributed to a partially collapsed structure resulting from quaternary ammonium degradation. NACM and NPVDF/ACM samples showed different behavior, these samples has two small peaks at $2\theta \sim 2°$ corresponding to d-spacing of 4.2nm and a broad peak at around $2\theta \sim 5°$ which is almost the same as the neat Cloisite 30B peak. However, the relative intensity of the peak reduced significantly which suggests that the clay is exfoliated but a small fraction of the clay layers remain as local aggregates in ACM nanocomposites.

TEM images for NPVDF, NACM and NPVDF/ACM samples are shown in Figure. 3. TEM images of NPVDF shows clearly the clay tactoids which have a thickness of ~150 nm as a result of high interfacial tension between PVDF and Cloisite 30B. From TEM images it can be seen that NPVDF sample failed to form an exfoliated structure. In sharp contrast, NACM and NPVDF/ACM samples showed individual layers as well as stacks containing parallel oriented layers with various degree of intercalation. The compatibilizing effect of ACM chains is enhanced by the strong polar interaction developed between the oxygen groups of the silicate and the oxygen groups of ACM. Therefore ACM acts as a compatibilizer and increases the intercalation of nanoclay in PVDF.

XRD Analysis

In our earlier work, we showed [40-42] that the neat PVDF and PVDF/ACM blends formed α polymorph, while PVDF/Clay nanocomposite induce both β and γ polymorphs. In this paper our aim is to explore the compatibilizing effect of ACM on the ferroelectric polymorph formation of PVDF in the presence of nanoclay. Figure 4. shows the WAXD patterns of neat PVDF, NPVDF and NPVDF/ACM samples. The three α phase peaks of neat PVDF and PVDF/ACM samples in WAXD plot observed at $2\theta \sim 17.7°$, 18.4° and 20.0° correspond to the (100), (020) and (110) planes and d-spacing of 5.08, 4.88 and 4.52 Å, respectively. Nevertheless, according to the literature the only specific peak of α phase is $2\theta \sim 17.7°$ and peaks at $2\theta \sim$ 18.4° and 20.0° overlap with β and γ characteristic peaks [23]. As for the NPVDF sample, a

shoulder in the right hand peak of 20.0º is observable. The peak at 2θ~20.7º corresponds to d-spacing 0.427 nm for β phase. γ phase of PVDF has a very similar d-spacing reflection at 0.431 nm [23]. Therefore, WAXD pattern suggests the formation of β and/or γ phases. However, the characteristic peak of α phase (2θ~17.7º) disappears and is no longer present. This means that nanoclay hindered the formation of α polymorph while β and γ phase peaks have overlapped.

A part from the presence of β and γ polymorphs in PVDF/clay, the addition of ACM, to the PVDF/Clay nanocomposite can cause build-up of 2θ~17.7º and 26.6º peaks which are representing the α polymorph formation in NPVDF/ACM sample(Figure 4). It is worth mentioning that presence of nanoclay hindered the nucleation of α polymorph in PVDF/Clay nanocomposite while addition of ACM again causes the nucleation of α polymorph. As a result of these interactions at molecular level, in NPVDF/ACM sample three polymorphs of α, β and γ coexist.

FTIR analysis

To further clarify the formation of β and/or γ phase in NPVDF sample and its phase transformation to α polymorph in NPVDF/ACM composites, FTIR technique was used to investigate the skeletal and chain conformational changes of PVDF segments. Figure 5 displays the FTIR spectra of neat PVDF, NPVDF and NPVDF/ACM samples. The frequencies and the vibrational assignments for α, β and γ phases are 763, 811 and 839cm^{-1}, respectively [39]. Neat PVDF shows only α phase characteristic peak while NPVDF sample showed both β and γ phase peak. However, for NPVDF/ACM sample all three polymorphs peaks are observable. This observation supports the WAXD study findings and demonstrates that the presence of nanoclay hindered the formation of α polymorph in NPVDF sample while compatibilizing effect of ACM induced α phase formation. Formation of β and γ polymorph in NPVDF composite can be attributed to the similar crystal lattices between clay and these polymorphs [23] and the presence of an ion-dipole interaction between nanoclay layers and PVDF chains in molten state [12].

To further explain the results, the change of α, β and γ phase contents for NPVDF and NPVDF/ACM sample are compared in Table 1. The peak at 1072cm^{-1} is selected as a reference band, because this band is well-known to be proportional only to the sample thickness regardless of the crystalline modification of PVDF [39]. The ratio of FTIR absorbance of 763cm^{-1}(α polymorph), 839cm^{-1}(β polymorph) and 811cm^{-1}(γ

polymorph) with respect to the reference band are used to calculate the percent of α, β and γ polymorph as shown in Table 1. Since the absorption peak at 1234cm^{-1} is solely for γ polymorph, it can be employed for quantitative analysis. However, when this peak is detected as a shoulder, the content of γ polymorph cannot be calculated quantitatively as it is difficult to separate this peak from the overlapped peaks of the two other crystalline polymorphs, i.e. α and β, at 1214 and 1276cm^{-1}, respectively. Therefore, the very small but discernible shoulder at 811cm^{-1} is designated to show the change in the γ polymorph content in the resultant samples. As seen in Table 1. the addition of ACM as a compatibilizer has increased the β phase content from 17% in NPVDF to 30% in NPVDF/ACM sample. High amount of γ phase in NPVDF is related to the molecular chains which have had enough time to form gauche defect at high temperatures, as suggested by Ramasandrum at al. [39]. However, decreasing the γ phase content and increasing the β polymorph by addition of compatibilizer can be related to better dispersion of clay in presence of ACM which can result in enhanced nucleation of β polymorph in NPVDF/ACM compared to NPVDF nanocomposite. In other words, in NPVDF/ACM sample there are more nanoclay layers to be surrounded by PVDF polymer chains and therefore nucleation of β polymorph is facilitated. Meanwhile, nucleation of α phase is related to the nucleus which formed independent of nanoclays due to hindrance effect of ACM. We have recently reported this phenomenon for PVDF/ACM/Clay hybrid with more than 70%wt ACM content [40,43]. Note that in this work all composite samples were hot pressed and slowly cooled down to room temperature when increasing the β phase content was simply achieved by addition of a compatibilizer. Obtaining even larger β phase content is possible by isothermal crystallization and stretching at high temperature which are the subject of our next paper. In the following section we will show that the increase in the electroactive β polymorph leads to improved ferroelectric properties of NPVDF/ACM compared to NPVDF nanocomposites.

Effects of ACM on ferroelectric properties of NPVDF nanocomposite

P-E hysteresis loop

As earlier discussed, a common method to observe ferroelectric polarization characteristic is via the hysteresis loop which can be translated into the existence of β phase crystals in PVDF polymer. Figure 6 and Figure 7 show the sequence of electric displacement for applied electric field up to 4000 MV/m in different frequencies for NPVDF and NPVDF/ACM composites, respectively.

In both samples increase in electric field is followed by increasing in electric displacement or polarization. Higher electric field mean rise in ferroelectric domain or number of dipole moment in crystals which have the ability to participate in polarization. Simultaneously, rise in frequencies is resulted in decreasing electric displacement. This suggests that the increase in time of applied electric field induced more polarized dipole moment.

Comparing NPVDF and NPVDF/ACM composites revealed that ACM has increased the electric displacement up to 900% at the same frequency and electric field. This observation is associated to the crystal structure of PVDF, in which β polymorph nucleation increased in the presence of ACM. Addition of ACM would also affect the number of domains, a region of a ferroelectric material within which the spontaneous polarization is constant.

In NPVDF sample, for frequencies ranging from 100 to 10 Hz and 10 to 5 Hz , the electric displacement increased to 52% and 15% , respectively. These results are independent of electric field which confirms that increase in electric field at constant frequency won't change the polarization mechanism; however it would increase polarizability. Nevertheless, for NPVDF/ACM samples, As frequency decreases from 100 to 10 Hz and from 10 to 5 Hz, the electric displacement is increased to 13.5% and 5.4%, respectively. This is due to the exponential nature of electric displacement or polarization as a function of frequency.

Note that decrease in frequency increased the area under the curve which is associated to the dissipated energy. Therefore, optimization of dielectric constant and dissipated energy has been an interesting subject of research for many years[1,44].

Calculation of dielectric & nonlinear optical constants

To calculate the dielectric constant as well as optical susceptibilies of nanocomposites (represented by equation 4), the Landau-Devonshire theory is used. This was formulated by derivation of equation 3; taking into account the first three terms of each equation. The complex dielectric susceptibilities, $\chi^{(n)}$, are described as:

$$\chi^{(1)} = 1 - \varepsilon_r = (1/\varepsilon_0)[\alpha + 3\gamma P_0^2 + 5\delta P_0^4]^{-1} \qquad \text{Equation 5}$$

$$\chi^{(2)} = -(\varepsilon_0^2)[6\gamma P_0 + 20\delta P_0^3](\chi^{(1)})^3 \qquad \text{Equation 6}$$

$$\chi^{(3)} = (\varepsilon_0^4)[-6\alpha\gamma + 90\gamma^2 P_0^2 + 900\delta^2 P_0^6 + 510\gamma\delta P_0^4 - 60\alpha\delta P_0^2](\chi^{(1)})^5 \qquad \text{Equation 7}$$

where α, γ & δ are coefficients of equation 3, ε_0 is vacuum permittivity, P_0 is defined as $(-\alpha/\delta)$ and ε_r is relative permittivity, which is equal to dielectric constant. Linear susceptibility is related to dielectric constant by $\varepsilon_r = 1 + \chi$.

In the second step, using genetic algorithm and a series of data, equation 4 in combination with equations 5-7 is optimized. Objective function, OF, are defined as:

$$OF = \sum(P - (a_1E + a_2E^2 + a_3E^3))^2 \qquad \text{Equation 8}$$

The results of optimization for NPVDF and NVPVDF/ACM nanocomposites were calculated using D-E hysteresis data and are reported in Table 2. As it can be seen, the addition of ACM as a compatibilizer in nanocomposite has increased the dielectric constant of NPVDF/ACM nanocomposite up to 50% compared to NPVDF. Note that this increase in dielectric constant was obtained simply by addition of ACM into PVDF nanocomposite. However, we believe that further increase in ferroelectric constant can be achieved using optimum amount of clay, isothermal crystallization and high temperature stretching of samples.

As shown above, dependency of electric displacement to frequency varies from 100 to 10 Hz and from 10 to 5 Hz. The ratio of dielectric constants at the range of 100 to 10 Hz is much higher than that of 10 to 5 Hz. This observation may be attributed to the ionic polarization or decrease in dissipation factor which arises in low frequencies i.e. 10 Hz [44]. However, the dependency of electric displacement to frequency for NPVDF and NPVDF/ACM samples can be related to the uniform dispersion of clay platelets as a result of using ACM as a compatibilizer.

Finally, the dielectric susceptibilities obtained using genetic algorithm optimization applied to the equation 4. The equation 4 was rewritten for NPVDF and NPVDF/ACM composites at 10 Hz and results are compared with experimental data (Figure 8).This shows a good agreement between theoretical and experimental data. Using genetic algorithm along with information on D-E hysteresis data, the dielectric constant and free energy of nanocomposites can be predicted in a broad range of electric fields without large experimental effort.

Conclusion

In this study, compatibilizing effect of ACM on various polymorph contents of PVDF was investigated. WAXD and TEM results proved that clay tactoids formed an intercalated structure in PVDF nanocomposite while NPVDF/ACM nanocomposite showed individual layers as well as stacks containing parallel and oriented layers with various degree of intercalation. WAXD study revealed the formation of β and γ polymorphs in NPVDF nanocomposite and α, β and γ polymorphs in NPVDF/ACM sample which was further confirmed by FTIR analysis. Investigation of ferroelectric properties of nanocomposites containing ACM showed nine-fold increase in electric displacement and 50% improvement in dielectric constant, compared to samples without ACM. This is due to the enlargement of β polymorph in the presence of ACM. Theoretical value of electric displacement calculated using optimized coefficient was found to be in good agreement with experimental results. It is expected that employing the mechanical and thermal processes such as isothermal crystallization and high temperature drawing of nanocomposites combined with optimum amount of clay and ACM can notably improve the ferroelectric properties of PVDF. This is the subject of our current research and will be reported in future.

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