Improvement of electrocaloric properties of P(VDF-HFP)/GNPs composites for refrigerator cooling

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Abstract. Electrocaloric effect originally comes from the cross-coupling between temperature and polarization of dielectric materials. Poly (vinylidene fluoride)/P(VDF) and its copolymers exhibit high displacement and dielectric properties among all ferroelectric polymers with additional advantages like lightweight, flexible and low cost compared with other dielectric materials. Moreover, poly (vinylidene fluoride hexafluoropropylene)/P(VDF-HFP) copolymers shows highest breakdown strength. P(VDF-HFP) copolymers was used as the main matrix with graphene nanoplatelets (GNPs) conducting materials as nanofillers. The P/GNPs composites thin films were prepared by solution casting method with the final thickness of 30 +/- 5 µm using N,N-dimethylformamide (DMF) as solvents. The GNPs content was varied of 0, 1, 2, 3, 4 and 5% by weight. The dielectric and electrical properties were measured by LCR meter with various frequency of 1 to 100 kHz. The structure and crystallinity were observed by XRD and DSC. The polarization as a function of external electric field was investigated by P-E loop instrument in 40 MV/m with varying temperature from room temperature to 140 °C. Furthermore, electrocaloric effect was measured by indirect method by calculating adiabatic temperature change (ΔT) with help of Maxwell relation. The experimental results show that dielectric constant of P/GNPs composites was increased by increasing the GNPs content but dielectric loss is kept constant with low loading, far away from the percolation threshold. Moreover, the ΔT of the P/GNPs composites is higher than the pure P(VDF-HFP) copolymers that leads to higher electrocaloric effect. The Increasement of the ΔT of P/GNPs composites will be discussed based on their microstructure, phase transition and crystallinity. As conclusion, adding GNPs nanofillers to P(VDF-HFP) matrix can improve dielectric constant as well as electrocaloric properties which has capability for refrigeration cooling system.

1. Introduction

Compared with another materials that possess pyroelectric, piezoelectric, and ferroelectric, P(VDF) and its copolymers like P(VDF-HFP) are the best one that possess all electroactive properties [1]. P(VDF)-based materials have three molecular conformation modes, TGTG’, TTTT, and T3GT3G’ with five crystalline phase, α, β, γ, δ, and ε. Among them, β-phase possesses the strongest pyroelectricity as well as piezoelectricity that very useful for real application. It is caused by its disimetrics structure that creates highest dipole density compared with another phases [2]. To get higher β-phase of the semicrystailine polymers, graphene nanoplatelets (GNPs) were used as filler. GNPs is carbon-based material that contain positive ions that can facilitate β-phase transformation when interacting with negative ions from fluorine atoms of P(VDF-HFP). Hence, the higher polarization will be obtained. Besides that, (GNPs) particles show a good performance in dispersion since no significant
agglomerates were observed at micron scale [3]. This study focuses on how to enhance the electrical properties as well as electrocaloric effect for refrigerator cooling.

2. Materials and methods

2.1. Materials and film preparation method

P(VDF-HFP) powder, Solef 11010/1001, was purchased from Solvay Solexis, Belgium. Graphene nanoplatelets (GNPs) powder 306633-25G, was purchased from Sigma Aldrich, USA. N,N-dimethylformamide (DMF, ≥99% purity), was purchased from RCI Labscan, Thailand.

Pure poly(vivylidene fluoride-hexafluoropropylene), P(VDF-HFP), and poly(vivylidene fluoride-hexafluoropropylene)/Graphene nanoplatelets, P/GNPs composites thin films were prepared by solution casting method with the final thickness of 30 ± 5 μm. For P/GNPs composites, GNPs were added to the P(VDF-HFP) copolymers at different loadings (1, 2, 3, 4, and 5 wt% based on the weight of copolymers). Firstly, GNPs was dispersed in DMF by using sonicateur for 20 min. Then, P(VDF-HFP) were added into the suspension of GNPs in DMF. The mixtures were stirred by using magnetic stirrer for 16 h and rested for 1 h. Then, the solutions were casted onto the glass plate and dried in the oven for 12 h at 80 °C.

2.2. Characterizations and measurements

The dielectric properties and AC conductivity were measured by LCR meter (IM 3533 HIOKI) at frequency range 1 Hz - 100 kHz at room temperature by applying 1 V AC of voltage. The capacitance (C), conductance (G) and dielectric loss value were obtained.

To determine the crystalline phase, X-ray diffraction (XRD) from Empyrean, PANalytical, Netherlands was operated at 40 kV and 30 mA using wavelength of 0.154 nm (CuKα). Samples were scanned in the Cu tube with the scan range (2θ) of 5 - 90° at a speed of 0.04° sec⁻¹.

Differential scanning calorimetric (DSC) was used to determine melting point and crystallization. The analyses were finished on 1-3 mg samples using DSC7 from Perkin Elmer (USA) from 20 °C to 200 °C at a heating rate of 10 °C min⁻¹ in nitrogen atmosphere. The melting temperature (Tm) is gained from the maximum endothermic peak. Degree of crystallinity (Xc) was calculated from DSC results.

To obtain the polarization-electric field hysteresis loops, high voltage supplier with low current, Trek model 601E was carried out. A 40 MV m⁻¹ electric field with frequency of 10 Hz was applied to the samples. The temperature was varied from 21 °C to 140 °C. The electrocaloric effect was measured by indirect method. The adiabatic temperature change (ΔT) was calculated by using Maxwell relation:

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\Delta T = -\frac{T}{C} \int_{E_1}^{E_2} \left( \frac{\partial P_i}{\partial T} \right)_{X,E} dE_j
\]

where \(T, C, P, E\) are temperature, heat capacity (1600), polarization and electric field [4].

3. Results and discussion

Figure 1 shows frequency dependence of dielectric constant \((\varepsilon_i)\) and dielectric loss \((\varepsilon'')\) for pure P(VDF-HFP) and P/GNPs composites with various GNPs contents at room temperature. \(\varepsilon_i\) at low frequency (1 Hz) increases significantly when GNPs were added. At that condition, GNPs conducting nanoparticles take a role as microcapacitor electrodes that very close each other and arrange serial or parallel but still in isolated system [3]. As frequency increased, the net polarization of the materials drops due to the ceasing of each polarization mechanism. The lack of structural components that can couple to the external electric field in the repeat unit causes the maximum dipole reorientation cannot be reached [5]. Consequently, the dielectric constant drops when the frequency increases. Figure 1 also shows that the dielectric loss \((\varepsilon'')\) of the obtained composites is not significant and still low content below the percolation threshold.
Figure 2 shows the XRD patterns of pure P(VDF-HFP) and P/GNPs composites for different phases. Peaks at 18.5°, 26.5° and 39.0° that correspond to (020), (002) and (211) are the characteristic of α-phase. The peak at 26.5° is identified as GNPs (002) plane. Peaks at 18.5° and 36.2° that correspond to (020) and (200) crystal planes of PVDF are the characteristic of γ-phase [6]. Nevertheless, the γ-crystal planes (020) assigned at peak 18.5° can overlap with (020) α-crystal planes. On the other hands, peaks at 20.2° and 36.6° that correspond to (200) and (101) crystal planes of PVDF are the characteristic of β-phase [3,6-7]. Pure P(VDF-HFP) shows diffraction peaks at 18.5° and 20.2° that refers to γ- and β-phase with intensity of 525 and 653 respectively. The intensity of these peaks drastically increases by the increasing of GNPs content from 1 wt% (P/GNPs1) until 4 wt% (P/GNPs4), and then slightly decreases for 5 wt% (P/GNPs5 composites). It showed by the γ- and β-phase peaks get sharper than that of pure P(VDF-HFP). Hence, P/GNPs4 possesses the highest intensity of 825 and 1146 respectively. Besides that, adding GNP fillers also leads to create new peaks at 36.2° and 36.6° that also refers to γ- and β-phase respectively.

Figure 3 shows the polarization-electric field loop (P-E loop) of pure P(VDF-HFP) and P/GNPs composites with various filler content at room temperature (25 °C). Adding GNPs content effects to the bigger loop as well as higher remnant polarization. P-E loop data then were calculated to get the adiabatic temperature change (delta T). It is well known that high electrocaloric effect refers to high adiabatic temperature change [4]. The adiabatic temperature change results showed by figure 4. The highest delta T belong to P/GNPs composites of -72.34 °C that is much higher than that of pure P(VDF-HFP) of -52.95 °C. Besides high delta T, many studies also focus on lowering Curie temperature (Tc) that leads to reduce the energy barrier that resist the polar β-phase to be released before the polymer chain segments could freely to rotate [8]. The P/GNPs4 composites possess the lowest Tc of 86.28 °C among the others condition. P/GNPs4 generally also shows the best condition for electrocaloric effect. It can be seen from the biggest ratio of delta T/Tc with value of 0.79, much bigger than pure P(VDF-HFP) of 0.45.
DSC results summarize the melting enthalpy (ΔHm), melting temperatures (Tm), and degree of crystallinity (Xc). Tm of the composites shows the enhancement as well. The highest value gained by P/GNPs4 of 162.67 °C. It has been reported that Tm relate to the crystalline phase [9]. The Tm enhancement of P/GNPs composites might be caused by the transformation of α- to dominant γ-phase and small amount of β-phase. It indicates that adding small amount of GNPs filler to the P(VDF-HFP) can induce the transformation of nonpolar to polar phase. Furthermore, the degree of crystallinity (Xc) of P/GNPs composites tend to increase from 26.52 of pure P(VDF-HFP) to the highest 38.34% of P/GNPs2. The role of the fillers in influencing the crystallization process depends on the dispersion state and the quantity of the fillers [10].

4. Conclusions
Adding GNPs nanofillers to P(VDF-HFP) significantly increases the dielectric constant especially in low frequency. As mentioned, GNPs act as a nucleation agent. So, adding small amount of GNPs fillers to the P(VDF-HFP) matrix can induce the transformation of nonpolar α-phase to the polar γ- and β-phase. Besides that, P/GNPs composites possess better electroaloric properties for refrigerator cooling. It showed by the ratio of adiabatic temperature change and Curie temperature. Among all conditions, P/GNPs4 shows the best properties for electroaloric effect.

Acknowledgments
This work was supported by Thailand Center of Excellence in Physics (ThEP-61-PHY-PSU3) and Department of Physics, Faculty of Science, Prince of Songkla University (PSU), Thailand.

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