Science and Innovation
of Advanced Materials

The Materials Research
Society of Thailand

Research Article

Effects of Silane and Graphene Doping on Hysteresis Loop and Curie Temperature of P(VDF-TrFE-CTFE)/P(VDF-HFP) Film Composites

Ponkrit Itsaradamkoeng, Suphita Chaipo, Chatchai Putson*

Materials Physics Laboratory, Division of Physical Science, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand

* Corresponding author e-mail: chatchai.p@psu.ac.th

Received: *September 15th, 2022* | ***Revised:*** *December 15th, 2022* | ***Accepted:*** *December 19th, 2022*

Abstract: The electrocaloric (EC) effect is a pathway to the new cooling technology for refrigeration and air conditioning systems. This EC cooling is a green technology with higher energy conversion efficiency. In this study, ferroelectric copolymer blending poly(vinylidene fluoride hexafluoropropylene) (P(VDF-HFP)) with poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene) (P(VDF-TrFE-CTFE)) were prepared by the solution casting technique. Blended PVDF-based polymers with fillers were widely investigated due to strong dipole interaction polarization. Hysteresis loops were measured at varying electric fields and filler contents. The Curie temperature (T_c) was obtained from the graph between adiabatic temperature change (ΔT) and temperature. From the experimental results, the T_c of the sample was reduced to near room temperature when the P(VDF-TrFE-CTFE) ratio was increased. Furthermore, graphene nanoplatelets (GPNs) were used as fillers to enhance surface energy and interfacial polarization between the phases in the polymer. It was found that the hysteresis loop area was increased while the T_c was reduced with graphene fillers. Moreover, the loss energy density (U_l) of composites filled with graphene was increased due to their conductivity. However, the U_l was decreased when the graphene with silane was used. Consequently, the ferroelectric P(VDF-HFP) combining P(VDF-TrFE-CTFE) with graphene and silane additions can be used as EC materials for refrigeration cooling in the future.

Keywords: Poly(vinylidene fluoride hexafluoropropylene), Poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene), Curie Temperature, Dielectric properties , Electrocaloric effect

1. Introduction

Nowadays, cooling systems come in various forms, including thermoelectric, thermoacoustic, and vapor compression. The typical vapor compression cooling works with chlorofluorocarbons (CFCs), which affects global warming. Researchers have attempted to develop new cooling technologies to replace the vapor compression system. Electrocaloric (EC) cooling is one of the new cooling technologies based on solid-state materials [1,2]. It is a green technology with high energy conversion. The EC effect is achieved via the control of the entropy change within dielectric materials by the electric field. Influential factors in the EC effect are the entropy change (ΔS) and the dipolar change when applied an electric field (ΔE). The temperature change (ΔT) is due to the polar dielectric material changes when an electric field is applied to the material under the adiabatic process. Thus, both ΔS and ΔT are critical factors for EC cooling. Another factor is Curie temperature (T_c), the temperature change phase from ferroelectric to paraelectric. The maximum dielectric constant in ferroelectric materials is observed at this T_c.

In this work, composite films are fabricated by blending poly(vinylidene fluoride hexafluoropropylene) (P(VDF-HFP)) and poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene) (P(VDF-TrFE-CTFE)). The P(VDF-HFP) has a high ferroelectric property and high Curie temperature (T_c). The P(VDF-TrFE-CTFE) can improve EC properties and the T_c following the increased EC properties by filling with graphene nanoplatelet (GPNs). This carbon-based material with positive ions can induce the non-polar phase to the polar phase and improve EC properties [3,4]. Furthermore, dielectric loss (U_l) can be enhanced by filling silane [5,6]. They are then fabricated in a composite thin film to study their hysteresis loop and T_c.

2. Methodology

2.1 Materials and film preparation methods

P(VDF-TrFE-CTFE) 63-033 was obtained from PolyK Technologies State College, and P(VDF-HFP) powder, Solef 11010/1001, purchased from Solvay Solexis, Belgium. P(VDF-TrFE-CTFE) and P(VDF-HFP) were blended in five different ratios (100/0, 70/30, 50/50, 30/70, and 0/100) and dissolved in N, N-dimethylformamide (DMF, ≥ 99% purity), purchased from RCI Labscan, Thailand. After stirring for 6 h at 50 °C, the solutions were cast on a glass plate and annealed at 120 °C for 12 h to evaporate the solvent. Subsequently, the films from the solution casting method were removed from the glass plate with deionized water. Then, 1% graphene nanoplatelets (GNPs) powder 306633-25G, purchased from Sigma Aldrich, USA, were filled in P(VDF-TrFE-CTFE)/P(VDF-HFP) of four different ratios (70/30, 50/50, 30/70, and 0/100). First, GPNs were dissolved in DMF and sonicated. Afterward, P(VDF-TrFE-CTFE) and P(VDF-HFP) were added. Finally, the solution was cast similarly to unfilled samples.

For the sample with the silane coupling agent, 1 g of GPNs were treated with 30% hydrogen peroxide (H_2O_2) to get the OH group on the surface by sonicating for 1 h and drying for 12 h at 100 °C. Afterward, 0.01 g of 3-Aminopropyltriethoxysilane was hydrolyzed by 10 g of DI water and 10 g ethanol for 20 min to initiate the functional group. The solution was stirred with GPNs powder for 24 h. As a result, 1% GPNs/silane was obtained by removing the excessive silane by centrifuging DI water 5 times. The 1% GPNs/silane was completely dried at 100 °C for 12 h. The 1% GPNs/silane powder was then used in fabricating composite thin films by the solution casting method. The thickness of all composite films was 30 ±10 μm.

2.2 Characterization methods

Scanning Electron Microscopy (SEM; FEIQuanta 400, USA) was used to observe the morphology of the sample surface. The P-E loop setup characterized the hysteresis loops of a sample. A 40 MV m^{-1} electric field (high voltage supplier with low current, Trek model 601E) was applied to the samples. The temperature was varied from 24 °C to break down the temperature. The EC effect was measured by indirect method. The adiabatic temperature change (ΔT) was calculated by using the Maxwell relation:

$$\Delta T = -\frac{T}{c_E}\int_{E_1}^{E_2}\left(\frac{\partial D_i}{\partial T}\right)_{X,E} dE_j \qquad (1)$$

where T, C, D, and E are temperature, heat capacity, displacement polarization, and electric field, respectively.

3. Results and discussion

The surface of composite films, shown in Figure 1 is continuous. Pore distribution is higher in terpolymer than copolymer films. The films filled with GPNs show GPNs distribution and grouping (Figure 1(b)). The films with silane coupling agent are similar to membranes around GPNs (Figure 1(c)).

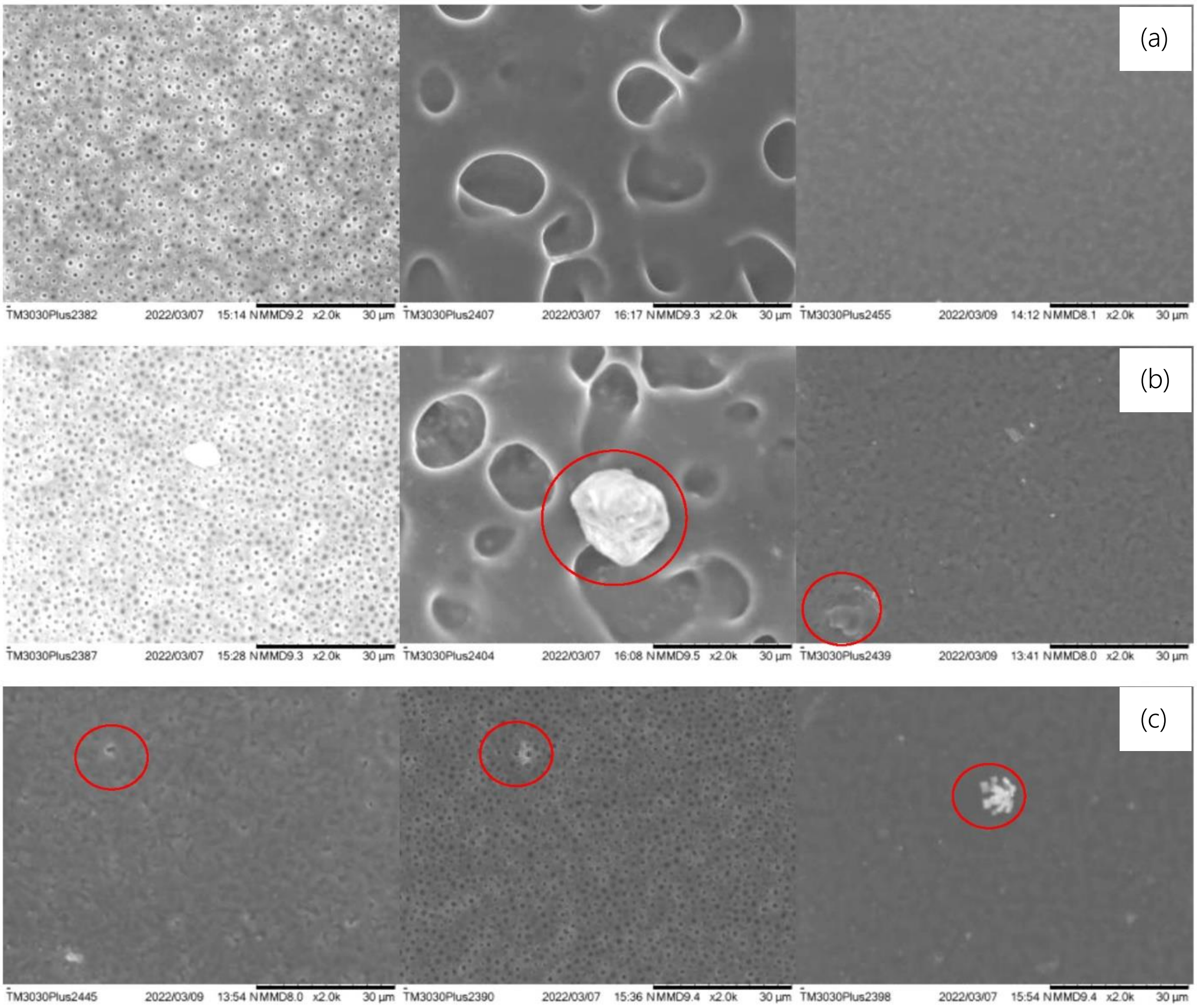

Figure 1 SEM images of (a) terpolymer/copolymer 30/70, 50/50, and 70/30, (b) terpolymer/copolymer + 1% GPNs 30/70, 50/50 and 70/30, and (c) terpolymer/copolymer + 1% GPNs +1% silane 0/100, 30/70 and 70/30.

Figure 2 shows the hysteresis loops of all films at room temperature (25 °C). The remnant polarization (P_r) is increased with the terpolymer ratio, i.e., 0.07087 μC/cm^2 for the ratio of 0/100 to 0.3276 μC/cm^2 for the ratio of 100/0 in Figure 2(a); 0.1737 μC/cm^2 for the 0/100-1% GPN to 0.6588 μC/cm^2 for the 70/30-1% GPN in Figure 2(b); 0.09313 μC/cm^2 for the 0/100-1% GPN/silane to 0.3252 μC/cm^2 for the 70/30-1% GPN/silane in Figure 2(c). These results are attributed to the increase of the polar phase (β-phase) from the grouping of monomers. Adding GPNs enhances the loop and remnant polarization (P_r) because GPNs are electrical conductors that can induce the non-polar phase to the polar phase and increase the surface charge. On the other hand, the silane coupling agent leads to a smaller loop and a lower remnant polarization (P_r) because silane can reduce conductivity and dielectric loss [6].

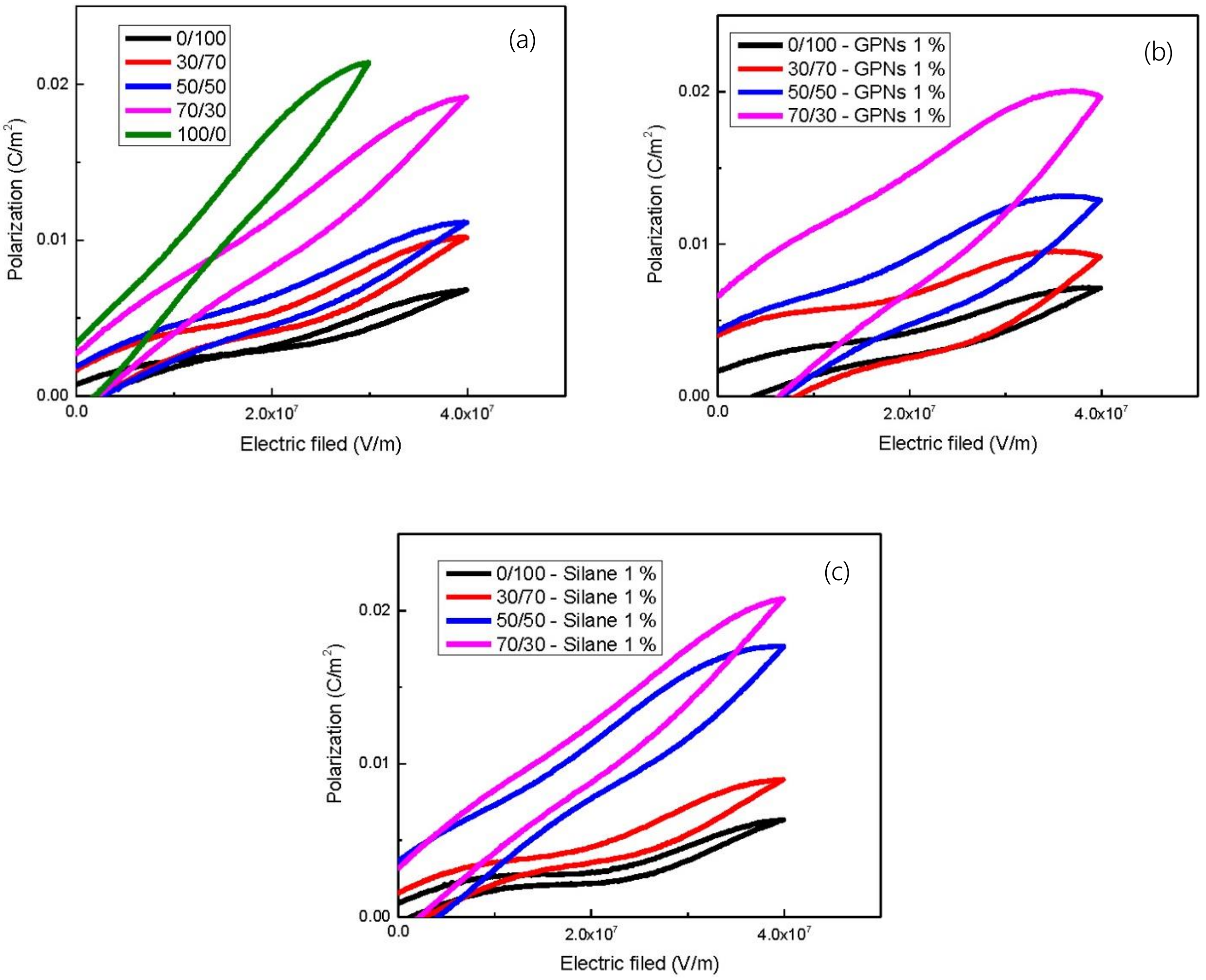

Figure 2 Hysteresis loops of (a) terpolymer/copolymer films, (b) terpolymer/copolymer + 1% GPNs films, and (c) terpolymer/copolymer + 1% GPNs + 1% silane films.

Figure 3 shows the adiabatic temperature change (ΔT) and T_c results of all conditions. The ΔT evaluated from hysteresis data is used to calculate T_c, which is the temperature of changing from the ferroelectric to the paraelectric phase. The T_c is reduced from 160.85 °C to 94.90 °C with increase in terpolymer, i.e. from 0/100 to 100/0, due to the increase of β-phase from the grouping of monomers [7,8]. The values cannot be identified for the ratio 30/70 because of incomplete process in the crystal associated with the breakdown (Figure 3(a)). The T_c of 50/50-1% GPNs is less than 70/30-1% GPNs due to the crystalline structure and amount of β-phase in PVDF-HFP with increasing PVDF-TrFE-CTFE (Figure 3(b)). Moreover, addition of nanoparticles has also imposed a positive effect on the formation of crystalline layers into PVDF-HFP with dispersion of GPNs. The ΔT is also an important parameter because a high electrocaloric effect corresponds to high ΔT. The ΔT is also decreased with the increase in terpolymer with exception of 70/30-1% GPN and 50/50- 1% GPN.

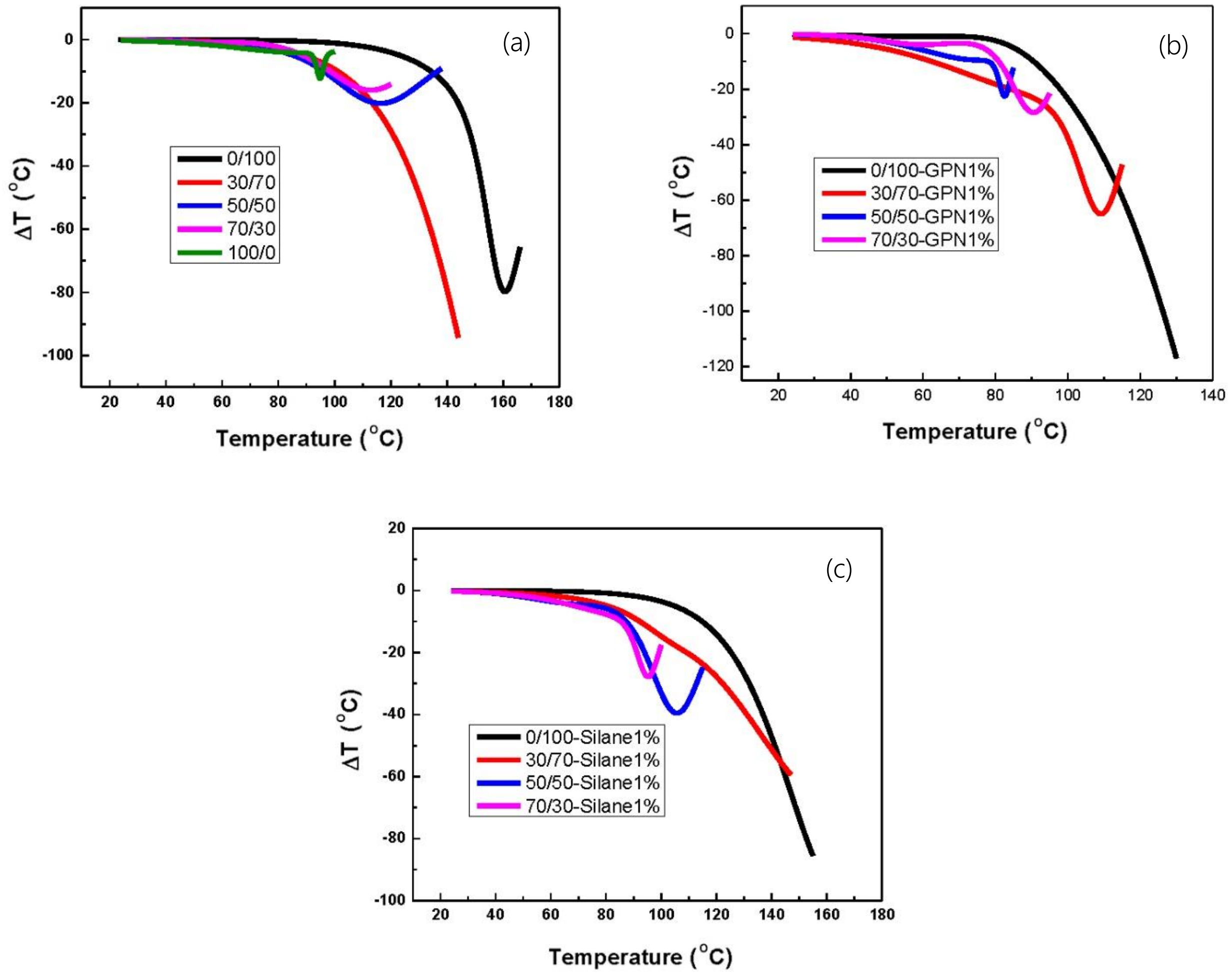

Figure 3 ΔT and T_C of (a) terpolymer/copolymer films, (b) terpolymer/copolymer + 1% GPNs films, and (c) terpolymer/copolymer + 1% GPNs + 1% silane films.

4. Conclusion

The study investigates ΔT and T_c, which are influential in the EC effect. P(VDF-TrFE-CTFE)/P(VDF-HFP) blends exhibit the T_c of 160.85 °C and 94.90 °C for the ratio of 0/100 and 100/0, respectively, due to the increase in the polar phase (β-phase). On the other hand, the ΔT of composite films is reduced with increasing PVDF-TrFE-CTFE terpolymer. Incorporating GPNs reduces the T_c to room temperature, which the lowest T_c being 82.56 °C in 50/50-GPN 1%. Compared to the film without GPNs, the ΔT is increased because the induction of GPNs can enhance the polar γ-phase and β-phase. Adding silane increases the T_c but the value is less than those of terpolymer/copolymer films. The lowest T_c of 95.35 °C in 70/30-1% silane is due to the decrease in induction of GPNs with silane. On the other hand, silane can reduce dielectric loss. Therefore, both fillers should be included in EC materials to enhance the cooling efficiency.

.

Acknowledgment

This work was supported by the Development and Promotion of Science and Technology Talents Project (DPST), Institute for the Promotion of Teaching Science and Technology Thailand (IPST), and Thailand Center of Excellence in Physics (ThEP-61-PIP-PSU3). We also acknowledge the Department of Physics Faculty of Science, Prince of Songkla University (PSU), Thailand.

References

[1] J. F. Scott, Electrocaloric materials, *Annual Rev. Mater. Res.* **41** (2011) 229e240.

[2] F. L. Goupil, A. Berenov, A.-K. Axelsson, M. Valant, N. M. Alford, Direct and indirect electrocaloric measurements on ⟨001⟩-$PbMg_{1/3}Nb_{2/3}O_3$-$30PbTiO_3$ single crystals, *J. Appl. Phys.* **111** (2012) 124109.

[3] A. Salea, S. Chaipo, A. A. Permana, K. Jehlaeh, C. Putson, The microstructure of negative electrocaloric Polyvinylidene fluoride-hexafluoropropylene copolymer on graphene loading for eco-friendly cooling technology, *J. Clean. Prod.* **251** (2020) 119730.

[4] M. Choolaei, V. Goodarzi, H. A. Khonakdar, S. H. Jafari, J. Seyfi, M. R. Saeb, L. Haußler, R. Boldt, Influence of graphene oxide on crystallization behavior and chain folding surface free energy of poly(vinylidenefluoride-cohexafluoropropylene), *Macromol. Chem. Phys.* **218** (2017) 1700103.

[5] Q. Zhang, F. Gao, C. Zhang, L. Wang, M. Wang, M. Qin, G. Hu, J. Kong, Enhanced dielectric tunability of $Ba_{0.6}Sr_{0.4}TiO_3$/Poly(vinylidene fluoride) composites via interface modification by silane coupling agent, *Compos. Sci. Technol.* **129** (2016) 93-100.

[6] A. Salea, R. Saputra, C. Putson, Enhanced interfacial dielectric polarization in PVDF-HFP copolymer with treating PPy by using silane coupling agent, *IOP Conf. Ser.: Mater. Sci. Eng.* **773** (2020) 012020.

[7] D. Eka, S. Arifin, J. J. Ruan, Study on the curie transition of P(VDF-TrFE) copolymer, *IOP Conf. Ser.: Mater. Sci. Eng.* **299** (2018) 012056.

[8] K. Jehleaeh, A. Salea, C. Putson, Electrocaloric properties of ferroelectric P(VDF- HFP)/PU composites, *J. Phys. Conf. Ser.* **1380** (2019) 012033.