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Abnormally enhanced dielectric permittivity in poly(vinylidene fluoride)/nanosized-$La_2NiO_{4-\delta}$ films

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ABSTRACT

The abnormally enhanced dielectric properties of poly(vinylidene fluoride)/nano-sized $La_2NiO_{4-\delta}$ (PVDF/LNO) nanocomposite films were investigated. To study the effects of surface modification of LNO nanoparticles caused by a combustion process on the formation of a percolating network and interfacial polarization, micro-sized LNO was also used as filler. The abrupt changes in the dielectric permittivity (ε') and loss tangent ($\tan\delta$) of PVDF/LNO composites were observed, indicating the formation of percolation network of LNO filler particles. ε' of the nanocomposites was larger than that of the microcomposites. Significantly improved dielectric properties with $\varepsilon' \approx 431.17$ and $\tan\delta \approx 0.43$ were successfully achieved by optimizing loading content of LNO filler to be 25 vol%. Large interfacial polarization intensity due to nano-sized filler particles and modified-surface LNO particles were suggested to be primary causes for improving the dielectric properties of PVDF/LNO nanocomposite films.

1. Introduction

In recent years, flexible-polymeric dielectric materials with large dielectric permittivity (ε') have been intensively investigated due to their potential for many applications, especially for embedded capacitor technology [1–12]. Thus, high ε' value of a dielectric polymer is required for capacitor applications [1,13]. Unfortunately, ε' of polymer is very low compared to those of many dielectric ceramics. Poly(vinylidene fluoride) (PVDF) is often chosen as a polymer matrix because of its high ε' value [2–7,10,14–16]. The excellent mechanical properties of polymer and high-performance electrical properties of ceramics are usually required for fabricating polymer–ceramic composites with good mechanical and electrical properties. An insulating properties of the polymer matrix used was strongly decreased as loading content of filler increased. In this case, the conductivity and dielectric loss tangent ($\tan\delta$) will also be increased, which is undesirable for capacitor applications [10].

Lead–zirconate–titanate [17], $Ba_{0.6}Sr_{0.4}TiO_3$ [4], $CaCu_3Ti_4O_{12}$ [15,18,19] and $BaTiO_3$ [2,7,8,12,14,16,20] are often used as fillers in polymeric composites due to their high ε' values. A ceramic filler with large particle sizes (~1–10 μm) lead to the degradation of dielectric properties due to the existence of pores and poor dispersion in the polymer composites [10], especially when filler loading is close to 50 vol%. For example, filling 52 vol% $CaCu_3Ti_4O_{12}$ with sizes of 0.5–1.5 μm into PVDF matrix resulted in the existence of a large amount of pores [19]. Moreover, micro-sized powder limits the thickness of the polymer composite films used for embedded capacitor applications. Thus, polymer matrix composites filled with ceramic nanoparticles are highly desirable. Dang et al. [3] reported the strong increase in interfacial polarization intensity of $BaTiO_3$/PVDF nanocomposite prepared by a solution processing method increased with decreasing $BaTiO_3$ particle size from 500 to 100 nm. This resulted in an increase in a low-frequency ε' value. It was also found that the dielectric response in $CaCu_3Ti_4O_{12}$/PVDF composites was extensively increased ($\varepsilon' \approx 10^5$ at 1 kHz) by using $CaCu_3Ti_4O_{12}$ nanoparticles with sizes of about 200 nm as a filler material, while the ε' value of the micro-sized $CaCu_3Ti_4O_{12}$ powder/PVDF composite with 52 vol% was ≈40 at 1 kHz [19]. This was resulted from the strongly improved interfacial polarization caused by reduction in filler particles. Unfortunately, $\tan\delta$ of such $CaCu_3Ti_4O_{12}$/PVDF nanocomposites was greatly increased as well.

Usually, greatly enhanced ε' value of many polymer–ceramic composite systems mentioned above can successfully be obtained by filling with large volume fractions of ceramic fillers ($f > 0.4$) [2,14–16,19]. This has a great influence on the mechanical properties of the fabricated polymeric nanocomposites. Furthermore, ε' values of most two-phase polymer–ceramic composite systems

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were found to be lower than 100 at 1 kHz and room temperature (RT) because ε' values of ceramic fillers are not large enough ($\varepsilon' \approx 10^3$–$10^4$). High ε' and low $\tan\delta$ in a polymer–ceramic composite containing low ceramic filler loading are difficult to accomplish. Recently, $La_{2-x}Sr_xNiO_4$ has become one of the most interesting dielectric ceramics due to its extremely large $\varepsilon' \approx 10^5$–$10^6$ [21]. Such a high ε' of $La_{2-x}Sr_xNiO_4$ can be observed in a GHz region. Note that $La_2NiO_{4-\delta}$ can also exhibit large ε' due to the presence of Ni^{2+} and Ni^{3+}. The giant dielectric response was attributed to the adiabatic small polaronic hopping process of Ni^{2+} and Ni^{3+} [22]. Unfortunately, this high-permittivity ceramic has never been used for incorporating in PVDF polymer.

Thus, the aim of this work is to represent a novel high-performance polymeric nanocomposite system. Good dielectric properties were achieved in PVDF/$La_2NiO_{4-\delta}$ nanocomposite films. We found that greatly enhanced dielectric properties with $\varepsilon' \approx 431.17$ and $\tan\delta \approx 0.43$ were successfully achieved in the PVDF/$La_2NiO_{4-\delta}$ nanocomposite film incorporating with 25 vol% $La_2NiO_{4-\delta}$. The effect of filler particle size was also investigated.

2. Experimental details

2.1. Preparation of $La_2NiO_{4-\delta}$ powders

$La_2NiO_{4-\delta}$ (LNO) nanocrystalline powder was prepared by a combustion method using urea as a fuel for reaction initiation. The starting raw materials consisted of $Ni(NO_3)_2 \cdot 6H_2O$ (99.0%, Kanto Chemical), $La(NO_3)_3 \cdot 6H_2O$ (99.99%, Sigma–Aldrich), deionized water, citric acid ($C_6H_8O_7 \cdot H_2O$, 99.7%), and urea (CH_4N_2O, 99.0%). First, stoichiometric amounts of $Ni(NO_3)_2 \cdot 6H_2O$ and $La(NO_3)_3 \cdot 6H_2O$ were dissolved in an aqueous solution of citric acid. Second, urea powder was added into the mixed solution with stirring at 200 °C until a viscous gel appeared. Then, the gel was dried at 300 °C for 0.5 h. Finally, the resulting dried porous precursor was ground and calcined at 1000 °C for 6 h to form pure phase of nano-sized LNO powder. Micro-sized LNO powder was prepared by a solid state reaction method. The mixture of starting powders was ball milled in ethanol for 24 h. The mixed powder was calcined at 1200 °C for 12 h to achieve pure phase of micro-sized LNO powder.

2.2. Preparation of PVDF/LNO nanocomposite films by a solution processing method

In this work, PVDF (Sigma–Aldrich Co., France) polymer was used as a matrix. PVDF/LNO nanocomposite films with different loading LNO volume fractions ($f_{LNO} = 0.05$–0.45). First, an appropriate amount of PVDF was dissolved in *N,N* dimethylformamide (DMF). Second, LNO nanoparticles were added into the above solution under constant stirring for 4 h. The PVDF/LNO mixture solution was further stirred by means of ultrasonic action for 1 h in order to drive the dispersion of LNO nanoparticles. Then, the mixture was kept in an oven at 100 °C for 6 h to completely evaporate the DMF solvent. Finally, the obtained polymer nanocomposite films were cut into a disc-shape with 12 mm in diameter and molded by hot-pressing at a temperature of 200 °C and 10 MPa for 30 min.

2.3. Characterization techniques and electrical measurements

X-ray diffraction (XRD) (PANalytical, EMPYREAN) and scanning electron microscopy (SEM) (SEC, SNE4500M) were used to characterize the phase composition and microstructure of PVDF/LNO nanocomposite films. Transmission electron microscopy (TEM, ZEISS EM902) was used to reveal the LNO micro and nanoparticles. For the dielectric measurements, silver paint was used as electrodes and painted on surfaces of composite samples. The dielectric properties were measured using an Agilent 4294A Precision Impedance Analyzer over the frequency range of 10^2–10^6 Hz at RT with an oscillation voltage of 500 mV. Thermo gravimetric (TG) analyses were performed using the Pyris Diamond TG/DTA (Perkin Elmer Instrument), with alumina as the reference material. The experiments were carried out at a heating rate of 10 °C/min in flowing N_2 atmosphere (flow rate: 100 cm^3/min). To reveal the oxidation states of Ni atoms, X-ray photoelectron spectroscopy (ULVAC-PHI, Japan) analysis and X-ray absorption near edge structure (XANES) spectra were collected at the SUT-NANOTEC-SLRI XAS beamline (BL5.1 and BL5.2) (electron energy of 1.2 GeV; bending magnet; beam current 80–150 mA; 1.1–1.7×10^{11} photon s^{-1}) at the Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand.

3. Results and discussion

Figs. 1(a) and (b) show the SEM images of nano-sized and micro-sized LNO powders, respectively. It is clearly seen that the particle-size distributions of these LNO powders are narrow with average sizes of ≈200 nm and ≈1.0 μm, respectively. The cross-section SEM images of the PVDF/LNO nanocomposite films with $f_{LNO} = 0, 0.1, 0.2, 0.25$, and 0.3 are respectively shown in Fig. 1(c)–(g), revealing the dispersion of LNO particles in the PVDF polymer matrix. As shown in Fig. 1(c), the PVDF polymer matrix forms a continuous phase. The dispersion of LNO nanoparticles is quite well. However, a slight inhomogeneity of the filler distribution in the PVDF matrix is still observed, as indicated in circle areas. Nevertheless, the 0–3 connectivity pattern is clearly to exist in all nanocomposites because LNO nanoparticles are randomly surrounded by the PVDF matrix [23]. The thickness values of PVDF/LNO nanocomposite films are in the range of 90–150 μm [insets of Fig. 1(d)–(g)], while the thickness of pure PVDF film is ≈300 μm. Interestingly, the PVDF/LNO nanocomposites with $f_{LNO} \leq 0.25$ show good flexibility, as demonstrated in Fig. 1(h).

The phase formation of pure PVDF and LNO nanopowder is represented in Fig. 2. It is found that the existence of α-phase of PVDF was confirmed [24]. It is confirmed that the prepared LNO nanopowder is pure in phase without any possible impurity (JCPDS 32-1241). All XRD peaks are perfectly indexed as a tetragonal structure. Fig. 3 illustrates the XRD patterns of PVDF/LNO nanocomposite films with different loading contents of filler. XRD peak of PVDF was observed in the composites with low loading content of filler. The XRD patterns of LNO are unchanged for all compositions. The intensities of α-phase diffraction peaks slightly decrease and become amorphous phase with increasing LNO content in the nanocomposites.

Fig. 4 reveals the thermogravimetric analyses (TGA) of the PVDF/LNO nanocomposite films to study the thermal stability of the polymer and the composites. It is observed that the degradation of pure PVDF polymer occurred at around ≈500 °C. This is similar to that observed in literatures [15,25]. The thermal degradation behavior of the PVDF/LNO composites is similar to that pure PVDF. The residual weight in the composites at 800 °C are 22.1, 30.03, 44.11, 57.04, and 67.45 wt% for pure PVDF and nanocomposite films with $f_{LNO} = 0.1, 0.2, 0.3$, and 0.4, respectively. The composition obtained from the experimental results is slightly lower than that of theoretical calculation results. This may be caused by a slight inhomogeneity of filler distribution in the PVDF matrix [25], as clearly seen in the circle areas of Fig. 1(d)–(g).

The dielectric properties of the PVDF/LNO nanocomposite films are demonstrated in Figs. 5 and 6. ε' of PVDF/LNO nanocomposites increases with increasing f_{LNO}. ε' of PVDF/LNO nanocomposites with $f_{LNO} \leq 0.2$ is nearly independent on frequency in the range of 10^2–10^6 Hz. It is observed that ε' of the PVDF/LNO nanocomposite