Applied Surface Science xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Enhanced dielectric permittivity with retaining low loss in poly(vinylidene fluoride) by incorporating with Ag nanoparticles synthesized *via* hydrothermal method

Nutthakritta Phromviyo [a,*], Narong Chanlek [b], Prasit Thongbai [c], Santi Maensiri [a]

[a] School of Physics, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand
[b] Synchrotron Light Research Institute (Public Organization), 111 University Avenue, Muang District, Nakhon Ratchasima 30000, Thailand
[c] Integrated Nanotechnology Research Center (INRC), Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

ARTICLE INFO

Article history:
Received 15 October 2017
Revised 15 February 2018
Accepted 19 February 2018
Available online xxxx

Keywords:
PVDF
Dielectric polymer composite
Silver nanoparticles
Percolation
Hydrothermal method
Aloe vera plant–extracted solution

ABSTRACT

The dielectric properties of poly(vinylidene fluoride) (PVDF) polymer incorporating with silver (Ag) nanoparticles, which were successfully prepared *via* a hydrothermal method using Aloe vera plant–extracted solution as surface stabilizer and reducing agent (Ag@Ale–NPs), were investigated. Ag@Ale–NPs/PVDF polymer nanocomposites were prepared by a liquid–phase assisted dispersion and hot–pressing methods. The microstructures of the Ag@Ale–NPs and Ag@Ale–NPs/PVDF nanocomposites were characterized. The modification of the Ag@Ale–NPs surface was confirmed using X–ray photoelectron spectroscopy. Interestingly, by using a filler volume fraction of 0.18, the composite exhibited a high dielectric permittivity of ≈92.5 with very low loss tangent of 0.049 at room temperature and 1 kHz. With further increasing a filler volume fraction to 0.22, a greatly enhanced dielectric permittivity of ≈257.2 was obtained with low loss tangent ($\tan\delta \approx 0.26$). Excellent dielectric properties of the Ag@Ale–NPs/PVDF nanocomposites were described by the interfacial polarization effect and the formation of micro–capacitor in the PVDF polymer matrix.

1. Introduction

The improvement of electrical and dielectric properties of polymer has been intensively investigated because flexible polymer with high dielectric permittivity can be desired in high–density electronic packaging technology [1–3]. Flexible polymer can be incorporated with organic substrates for many technologies such as electronic devices and high–density energy storage, in which the dielectric permittivity (ε') of polymer used must be as high as possible to reduce size of an electronic component. Unfortunately, the dielectric permittivities of all polymers are very low ($\varepsilon' < 10$) compared to that of dielectric oxides ($\varepsilon' > 10^3$) [1,4]. Therefore, fabrication of polymeric composites containing inorganic fillers to increase the dielectric permittivity of polymer has opened a scope for applications in electronic devices and energy storage.

One of the promising strategies to enhance the dielectric permittivity of polymer is to incorporate nanoparticles of dielectric oxides that have a high dielectric permittivity (e.g., $BaTiO_3$, $(Ba,Sr)TiO_3$, $CaCu_3Ti_4O_{12}$ and related compounds, $Ba(Fe_{0.5}Nb_{0.5})O_3$, etc.) into polymer matrix, which is a general method that has been widely studied in recent years [5–15]. Significantly enhanced dielectric response with good mechanical properties of the dielectric polymer composite is expected to accomplish because of a very large dielectric permittivity of a dielectric oxide coupled with excellent flexibility and good dielectric strength of a polymer used. Interesting dielectric properties of many dielectric oxide/polymer composite systems have been reported [5,7–9,14,16,17]. For most of these polymer composite systems, a high loading of ceramic filler (≥50 vol%) is usually used to achieve a greatly enhanced dielectric permittivity to be larger than 80 at 1 kHz. This can cause degradation of the flexibility of polymer. Moreover, an increase in dielectric permittivity of composites is usually accompanied with an increase in the dielectric loss tangent ($\tan\delta > 0.1$).

Besides dielectric oxide/polymer composites, to overcome a high filler loading used, many semi– or conductive materials such as $La_{0.5}Sr_{0.5}CoO_{3-y}$, carbon nanotube, and metallic nanoparticles have been used as fillers to enhance the dielectric properties of polymers [18–24]. In these cases, the great increase in the dielectric permittivity is associated with the strong interfacial polarization. However, such a greatly enhanced dielectric permittivity is usually accompanied with drastic increases in both of electrical

* Corresponding author.
E-mail address: nutthaphrom@gmail.com (N. Phromviyo).

https://doi.org/10.1016/j.apsusc.2018.02.188
0169-4332/

conductivity and related loss tangent, which are designable for many applications. The increases in dielectric permittivity, loss tangent, and conductivity are explained by the percolation theory. At a critical concentration value of conductive filler (percolation threshold, f_c), these three parameters are dramatically changed due to the formation of percolation network of conductive filler throughout the matrix [25]. The strong interfacial polarization is the primary cause of the dramatic increase in the dielectric permittivity, whereas the increase in conductivity is due to the formation of conductive pathway of conductive fillers (or percolation network). Generally, f_c of composites is dependent on several factors such as the conductivity of filler, size and shape of filler, and aspect ratio of filler [25,26]. The advantage of conductive/polymer composites is that a greatly enhanced dielectric permittivity of polymer composites can be achieved by using a small amount of filler, e.g., ≈16 vol% for spherical metal nanoparticles. If the percolation network can be confined in a specific region in polymer matrix (or suppression of long range of the percolation pathway), a large dielectric permittivity of a polymer composite can be achieved without increases in both the conductivity and loss tangent. Modification of the surface of conductive nanoparticles may be an effective way to improve the dielectric properties of polymer.

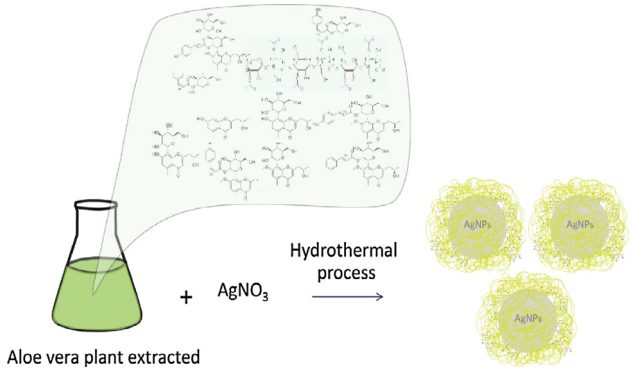

Fig. 1. Schematic illustration of the formation of Ag@Ale–NPs synthesized by a hydrothermal method using Aloe vera plant–extracted solution as surface stabilizer and reducing agent.

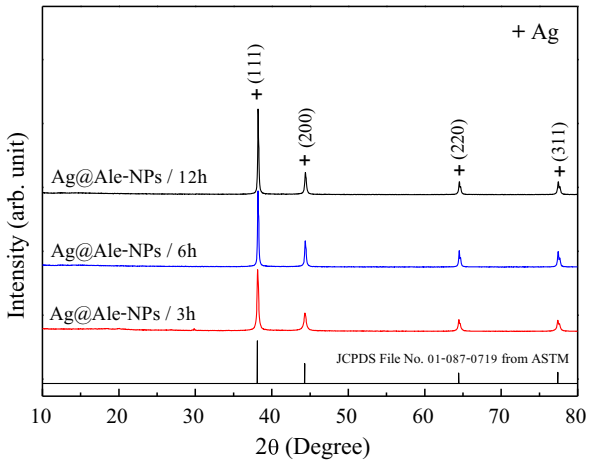

Fig. 2. XRD patterns of Ag@Ale–NPs prepared by a hydrothermal technique using Aloe vera plant–extracted solution for 3, 6, and 12 h.

In this work, silver nanoparticles (Ag–NPs), which were prepared by a hydrothermal method using Aloe vera plant–extracted solution as surface stabilizer and reducing agent (Ag@Ale–NPs), were used as filler to increase the dielectric response of poly (vinylidene fluoride) (PVDF). The hydrothermal method is an important technique for preparation of functional materials [27–30]. A PVDF polymer was used as a polymer matrix because of its superior dielectric properties (compared to other polymers) and high electric breakdown field [3,31,32]. It was found that the dielectric properties of Ag@Ale–NPs/PVDF were significantly improved because the Ag@Ale–NP surface was modified by forming hydroxyl functional and carboxyl groups during the preparation process. The mechanism for improving dielectric properties of the Ag@Ale–NPs/PVDF nanocomposites was discussed in details.

2. Experimental details

Ag–NPs were prepared *via* a hydrothermal method using Aloe vera plant–extracted solution as surface stabilizer and reducing agent. Surface of Ag–NPs was modified using Aloe vera plant–extracted solution (Ag@Ale–NPs). First, $AgNO_3$ (0.1 M) was dissolved in 20 ml of deionized water. Second, 20 ml of Aloe vera extract solution was mixed into the above solution under vigorous stirring at room temperature for 0.5 h. Third, the mixture was added to a sealed Teflon-lined vessel of 100 mL capacity (Parr, USA) and

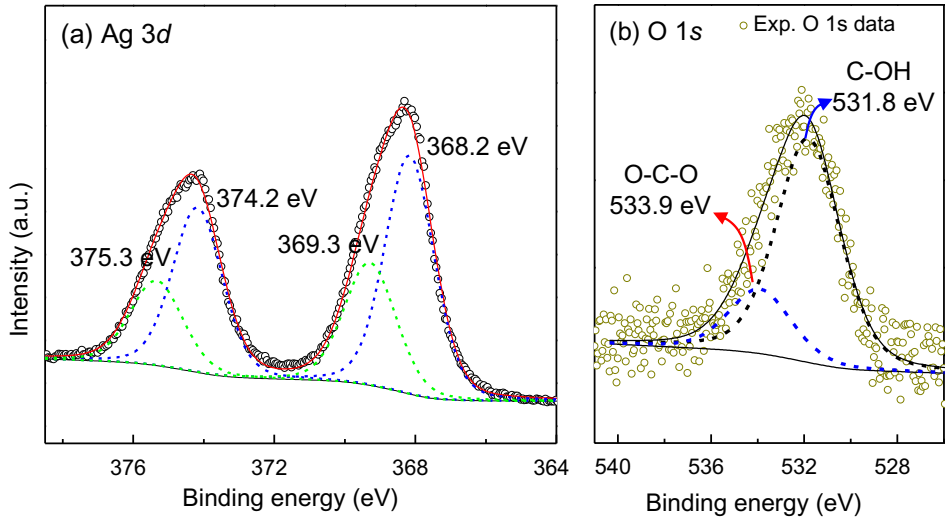

Fig. 3. XPS spectra of Ag@Ale–NPs; (a) Ag 3d and (b) O 1s.

Please cite this article in press as: N. Phromviyo et al., Enhanced dielectric permittivity with retaining low loss in poly(vinylidene fluoride) by incorporating with Ag nanoparticles synthesized *via* hydrothermal method, Appl. Surf. Sci. (2018), https://doi.org/10.1016/j.apsusc.2018.02.188