Applied Surface Science 421 (2017) 42–51

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Local mechanical and electromechanical properties of the P(VDF-TrFE)-graphene oxide thin films

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ARTICLE INFO

Article history:
Received 15 October 2016
Received in revised form 28 January 2017
Accepted 29 January 2017
Available online 31 January 2017

Keywords:
Ferroelectric polymer
Graphene oxide
Composites
Piezoelectricity
Piezoresponse force microscopy

ABSTRACT

Recently, many organic materials, including carbon materials such as carbon nanotubes (CNTs) and graphene (single-walled carbon sheet structure) were studied in order to improve their mechanical and electrical properties. In particular, copolymers of poly (vinylidene fluoride) and poly trifluoroethylene [P(VDF-TrFE)] are promising materials, which can be used as probes, sensors, actuators, etc. Composite thin film of the copolymer P(VDF-TrFE) with graphene oxide (GO) were prepared by spin coating. The obtained films were investigated using piezoresponse force microscopy (PFM). The switching behavior, piezoelectric response, dielectric permittivity and mechanical properties of the films were found to depend on the presence of GO. For understanding the mechanism of piezoresponse evolution of the composite we used models of PVDF chain, its behavior in electrical field and computed the data for piezoelectric coefficients using HyperChem software. The summarized models of graphene oxide based on graphene layer from 96 carbon atoms C: with oxygen and OH groups and with COOH groups arranged by hydrogen were used for PVDF/Graphene oxide complex: 1) with H-side (hydrogen atom) connected from PVDF to graphene oxide, 2) with F-side (fluorine atom) connected from PVDF graphene oxide and 3) Graphene Oxide/PVDF with both sides (sandwich type). Experimental results qualitatively correlate with those obtained in the calculations.

1. Introduction

In the recent years, significant interest has grown to find novel polar materials having low density, good elasticity, large piezoelectric and pyroelectric activity. Among these objects a special interest is focused on finding a composite material based on polymers and low-dimensional nanostructures of carbon (graphene, carbon nanotubes), as it exhibits an unusual electrical and mechanical characteristic. The study of such systems is dictated by the need to overcome the limitations in mechanical and electrical parameters of ferroelectric polymers. Composites containing nanostructured graphene in polymer matrix are promising materials due to their mechanical elasticity, low acoustic resistance, low dielectric constant and high piezoelectric and pyroelectric coefficients [1–3]. Furthermore, their properties can be varied by using different polymers and crystalline ferroelectrics, which gives an additional advantage for their use in functional devices such as pyro/piezo sensor, ultrasound transducers etc. In recent past, composites with ferroelectric polymer matrix based on polyvinylidene fluoride or copolymers have been explored by many researchers [4]. This is due to fact that, polar polymers base is characterized by high piezoelectric coefficients as compared to other polymer materials, and at the same time graphene particles embedded in a ferroelectric polymeric matrix is expected to provide highly unipolar state and a large electromechanical and pyroelectric activity. Furthermore, the polymer matrix doped with graphene can exhibit anomalous low coercive field without influencing its piezoelectric properties, which provides an additional degree of freedom for tailoring the properties of composites. In addition, it also allows the use of composite ferroelectric polymer-based materials in piezoelectric and pyroelectric sensor systems, as a relatively high conductivity of

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http://dx.doi.org/10.1016/j.apsusc.2017.01.291
0169-4332/

graphene offsets its low value for the polymer matrix, which in turn leads to significant enhancement in various vital parameters. Among the various methods to synthesize composite materials based on polymers and graphene, the most common ways are the crystallization from solution [5], hot pressing [6], centrifugation [7,8] etc. Many models have been proposed to explain the dielectric characteristics of such composites, which, in addition to the dielectric constant of the phases, also take into account of their concentration and depolarization factor. However, experimental and theoretical data till now did not give clear picture for the polarization behavior and changes of other physical properties of ferroelectric polymers as a function of graphene inclusion into the matrix [9]. Thus, to understand and control the functional properties of such ferroelectric composites, a detailed study regarding correlation of their property their composition, preparation conditions, microstructure must be addressed in detail.

2. Experimental and computational details

Graphene oxide (GO) was prepared by the chemical exfoliation of graphite (Graphite powder, <45 μm, ≥99.99%, Sigma-Aldrich). Briefly, it consists of the reaction of graphite flakes with concentrated H_2SO_4 and $KMnO_4$ in order to obtain individual sheets in an oxidized state. The resultant suspension was extensively washed with distilled water by filtration and centrifugation and finally subjected to dialyses to remove ionic contaminants. The resulting GO was dried by lyophilization to avoid aggregation.

For the composite sample preparation, poly (vinylidene fluoride-trifluoroethylene) copolymer with an TrFE content of 30% was used. The P(VDF-TrFE) copolymer was chosen because it favours crystallization from a solution or melt directly to the ferroelectric β-phase without additional stretching in comparison with the pure PVDF polymer. 4 g weight of the copolymer powder was added to 100 ml of a dimethyl sulfoxide (DMSO) and acetone mixture in 80/20 ratio. The powder was dissolved within 2 h at a temperature of 100 °C. The solution was then carefully filtered to remove impurities. Dried graphene oxide was added to the solution and then stirred magnetically for 30 min at 50 °C. For a homogeneous distribution of GO in the solution, this mixture was subjected to ultrasonic vibration for 1 h and stirred again for 3 h at 50 °C. The resulting composition was used to produce the thin composite films on the base of copolymer P(VDF-TrFE) as the matrix. Composite films of pure P(VDF-TrFE) and with GO (GO concentration of 1 wt%) were prepared by spin coating technique using P(VDF-TrFE)-GO solutions with film thickness of 400–500 nm. Glass with conductive coating of $InSbO_4$ was chosen as a substrate for the films deposition. Before the sample fabrication, the substrates were carefully cleaned with acetone and then dried.

The powder X-ray diffraction (XRD) patterns of the films were collected at room temperature in a continuous scanning mode (step 0.02° and time 10 s) on a Siemens D500 diffractometer with a secondary monochromator CuKα X-radiation in the range $2\Theta = 5°–60°$.

The nanoindentation measurements were performed using a three-sided pyramidal Berkovich diamond indenter having a nominal edge radius of 20 nm (faces 65.3° from vertical axis) attached to a fully calibrated nanoindenter (TTX-NHT, CSM Instruments).

Atomic Force Microscopy (AFM) measurements were carried out using a Veeco AFM Multimode Nanoscope (IV) MMAFM-2, Veeco microscopy. Piezoresponse force microscopy (PFM) was performed using AFM instrument with an external lock-in amplifier (EG&G 5205 Lock-in Amplifier), used to apply ac and dc voltages. Local piezoelectric properties of the films were visualized simultaneously by using AFM in contact mode and piezoresponse force microscopy (PFM) methods [10]. The PFM technique is based on the detection of the mechanical response of the sample to an applied electric voltage due to converse piezoelectric effect. A conductive Si cantilever (Nanosensors, nominal force constant of 15 N/m) was used to both apply the voltage to the surface and to measure mechanical response of the sample. The voltage applied to the sample was sine wave ($U_{ac}\sin(\omega t)$). Under this electrical field the piezoresponse signal $\Delta z(\omega) = d_{33eff}\, U_{ac}\, (\omega)$ were detected via vibration of the laser beam position on the photodiode due to sample deformation. The amplitude $A(\varpi)$ and phase difference $\Phi(\omega)$ of this vibration are measured with a lock-in amplifier. Domains with different orientation polarization obtained by PFM mode have different piezoresponse amplitude $A(\omega) \sim \Delta z(V_{ac})$ dependent on the orientation of the polarization and to the existence of difference phase $\Phi(\omega)$ between the two opposite domain 0 and 180°. So, using the function $A(\omega)\cos(\Phi(\omega))$ allows the mapping of piezoresponse signals on the sample surface as additional image. The amplitudes of the acquired signals are proportional to the effective vertical piezoelectric coefficients, d_{33eff}. In the poling experiments, the AFM conductive tip is fixed at a predefined position on the surface and the external bias pulse is applied. After poling, this area is scanned repeatedly to image the ferroelectric switching.

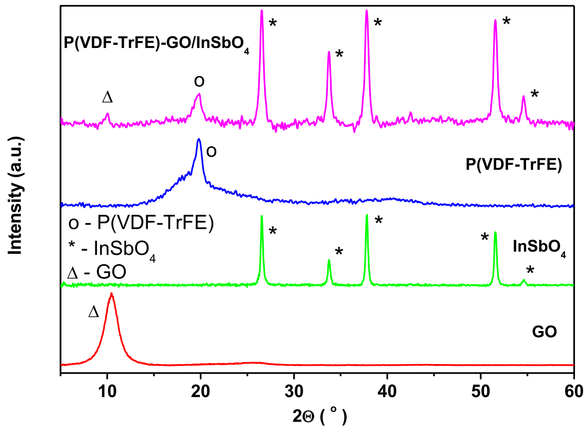

Fig. 1. X-ray diffraction pattern of P(VDF-TrFE) and P(VDF-TrFE)-graphene oxide thin films.

In this work, several versions of molecular models for PVDF (β–phase) – graphene oxide ferroelectrics systems were developed and investigated using HyperChem software ver.7.52 and 8.0. Various computational methods were used, including molecular mechanics (MM) methods (such as BIO CHARM), quantum mechanical (QM) self-consistent field (SCF) Hartree-Fock (HF) calculations based on density functional theory (DFT), as well as semi-empirical methods (such as PM3), in both restricted Hartree-Fock (RHF) and unrestricted Hartree-Fock (UHF) approximations. The main approach of both the MM and QM methods used for molecular modeling is to obtain the minimum of the total, or potential energy surface (PES), of a studied molecular system. The optimization of molecular geometry is executed using the Polak–Ribere (conjugate gradient) algorithm, which determines an optimized geometry at the minimum energy point (using PES) [11].

3. Results and discussion

Fig. 1 shows X-ray diffraction (XRD) pattern ($2\theta = 5–60°$ scan) for P(VDF-TrFE)-Graphene oxide/$InSbO_4$, P(VDF-TrFE)-Graphene oxide and $InSbO_4$ films. The strong diffraction peaks corresponding to three main phases of wiz. $InSbO_4$, P(VDF-TrFE) and Graphene oxide are observed. The XRD pattern of GO shows a broad diffraction peak at 10.5° corresponding to the interplaner distance (d_{200}) of 8.42 Å. In the mixed sample, three phase related to $InSbO_4$, P(VDF-TrFE) and GO was observed. In Initial P(VDF-TrFE) sample,