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# Poly(vinyl pyrrolidone)-coated graphene/poly(vinylidene fluoride) composite films with high dielectric permittivity and low loss

Hairong Li [b, c], Zongyi Chen [b], Lei Liu [b], Jianping Chen [b], Ming Jiang [a, **], Chuanxi Xiong [a, b, *]

[a] School of Materials Science and Engineering, Wuhan Textile University, Wuhan 430200, People's Republic of China
[b] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, People's Republic of China
[c] Hubei Institute of Measurement and Testing Technology, Wuhan 430223, People's Republic of China

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## ABSTRACT

A novel nanocomposite with significantly enhanced dielectric properties is reported. This nanocomposite consists of poly(vinyledene fluoride) (PVDF) and poly(vinyl pyrrolidone) anchored reduced graphene oxide (rGO@PVP) nanosheets. The microstructure and dispersion in this nanocomposite were studied by Fourier-transform infrared spectroscopy, thermogravimetric analysis, X-ray photoelectron spectroscopy, atomic force microscopy, X-ray diffraction and scanning electron microscopy. It was found that PVP layer was physically coated on rGO surface and rGO@PVP/PVDF composites exhibited multilaminate nanostructures. The resulted composite films showed high dielectric permittivity and low dielectric loss as well. The dielectric permittivity of the composite reached 622 whereas the dielectric loss was around 0.2 near the percolation threshold at 100 Hz. The PVP surface-functionalized layers were revealed to play important role on enhancing dielectric permittivity and suppressing dielectric loss in this nanocomposite. These results enable the preparation of the percolative dielectric composites with a facile method to exhibit desirable dielectric performances for the highly integrated electronic energy storage applications.

## 1. Introduction

Percolative composites of conductive particles and polymers such as poly(vinyledene fluoride) (PVDF) and its copolymers are highly attractive for their broad range of energy storage applications due to their ability to combine the high dielectric permittivity with low filler concentration and facile processability of polymer dielectrics [1–5]. In order to realize efficient electronic energy storage, the composites must possess low dielectric loss as well as high permittivity. Indeed, the dielectric properties of the composites strongly rely on the interfacial area, interfacial structure and electrical conductivity of fillers [6–11]. Graphene has distinct advantages compared with most of conductive particles; for example, it possesses a flake shape with atomic or molecular thickness, ultrahigh aspect ratios and extremely high electron mobility. Greatly enhanced dielectric permittivity has been observed at extremely low graphene concentration in PVDF-based composites [12,13]. Albeit with this great promise, poor compatibility between the bare graphene without any polar group and polar PVDF impedes the formation of a homogeneous composite system which leads to an adverse excessive agglomeration of graphene and vacancies at interfaces; another problem is the random distribution of the graphene nanosheets in PVDF matrix, which easily form conductive network so that it is difficult to simultaneously achieve a low dielectric loss and high permittivity. Therefore, several methods have been developed to modify the surface of graphene and to improve the dispersion in the composite materials, mostly through chemical functionalization of oxidized graphene surfaces [14–16]. Unfortunately, most of covalently functionalizing methods are difficult to preserve the structure integrity of the graphene, due to the $sp^2$ bond breaking within graphene. These methods also significantly raise the production cycle and costs, and thus make

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* Corresponding author. School of Materials Science and Engineering, Wuhan Textile University, Wuhan 430200, People's Republic of China.
** Corresponding author.
*E-mail addresses:* mjiang@wtu.edu.cn (M. Jiang), cxiong@whut.edu.cn (C. Xiong).

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them unfeasible to be produced on large scale. Moreover, the chemical reduction of graphene oxide (GO) to produce graphene often results in irreversible agglomeration [17]. Recently, researchers reported the graphene-based composites with $SiO_2$ or poly(vinyl alcohol) (PVA) as coatings on reduced graphene oxide (rGO) surfaces with greatly reduced dielectric loss as compared to the respective composites containing bare rGO nanosheet fillers [2,13]. $SiO_2$ or PVA layers between rGO and polymer host can stabilize the dispersion of nanofillers and also prevent the direct contact of conductive rGO nanosheets, and thereby reduce the leakage current and dielectric loss. However, decrement in loss tangent constantly meet with relatively low dielectric permittivity, so obtaining composites integrating both low dielectric loss and high permittivity is still challenging. To address these challenges, the optimized surface treatment of graphene nanosheets and ordered assembly structure of composites have to be taken into account. Along this line, here we propose a novel nanocomposite system consisting of PVDF and unfolded poly(vinyl pyrrolidone)-anchored rGO (rGO@PVP) nanosheets. PVP has comparatively less hydrophilic effect compared with highly hydrophilic PVA, thus water-induced loss increment could be effectively depressed. Prior studies [18,19] indicate that PVP with polar groups is miscible with PVDF, can form stable intermolecular bonds between the polar groups on PVP and PVDF chains. The polar interaction between PVP and PVDF can enhance interfacial polarization and stabilize the dispersion of nanofillers in polymer host. In addition, PVP has a propensity to coat graphene surfaces, which ensure the strong affinity between PVP and graphene. More importantly, the interaction between PVP and graphene is noncovalent, averting the $sp^2$ bond breaking within graphene. The rGO@PVP/PVDF composites exhibit superior dielectric performances as compared to the respective composites containing bare rGO nanosheets and those current available techniques.

## 2. Experimental

### 2.1. Materials

PVP (K30, $M_W$ = 40,000) was obtained from Sinopharm Chemical Reagents (China). Poly(vinylidene fluoride) (PVDF) with a melt flow index of 10 g/min was purchased from Shanghai 3F New Materials (China) and used as-received. Graphite flakes were purchased from Beijing Nanopowder Science & Technology (China). Other chemical reagents such as sodium nitrate, concentrated sulfuric acid, potassium permanganate and hydrazine were of analytical grade purchased from Sinopharm Chemical Reagents (China) and used as received.

### 2.2. Synthesis of rGO@PVP nanosheets

Firstly, GO was synthesized through a modified Hummers method from graphite flakes. The detailed synthesis process was enclosed elsewhere [20,21]. Afterwards, 100 mg of GO was dispersed in 160 mL DMF with the aid of sonication (200 W, 40 kHz, 0.5 h) to form a homogeneous dispersion. 400 mg of PVP was dissolved in 40 mL DMF and then the solution was mixed with GO dispersion under sonication before stirring in a 500 mL three-neck flask. Subsequently, 1 mL of hydrazine was added to the mixture under stirring and refluxing for 6 h at 80 °C. Afterwards, the aforementioned mixture was filtered through a PTFE filter membrane (0.22 μm pore size) and washed three times with DMF. After drying at 70 °C in a vacuum for 12 h, rGO@PVP was obtained.

### 2.3. Preparation of rGO@PVP/PVDF composite films

The rGO@PVP dispersion was first prepared at a concentration of 4 mg/mL in DMF by sonication (200 W, 40 kHz, 0.5 h). PVDF solution in DMF was mixed in the required ratio with the dispersion under sonication (200 W, 40 kHz) to give a homogeneous dispersion which was then dropcast on glass plates. The cast films were first dried at 60 °C for 6 h, and subsequently peeled off the glass plates for further drying in vacuum at 80 °C for 48 h. The solution-cast films were hot pressed at 180 °C and 20 MPa for 20 min to ensure the formation of uniform thin films around 0.15 mm in thickness, and then cooled to room temperature at a rate of 3 °C/min. The final film diameter was 12 mm.

### 2.4. Characterization

Infrared spectrometry measurements were carried out on a Fourier transform infrared (FTIR) spectrometer (Thermo Nicolet Nexus, USA) using KBr pellets. Thermogravimetric analysis (TGA) measurements were performed with a simultaneous thermal analyzer (Netzsch, STA 499C, Germany) under nitrogen flow of 20 mL/min from 25 °C to 800 °C at a heating rate of 10 °C $min^{-1}$. X-ray photoelectron spectroscopy (XPS) experiments were performed using a VG Scientific VG Multilab2000 photoelectron spectrometer (UK), and Al Ka X-rays were used as the source ($h\upsilon = 1486.6$ eV). Atomic force microscopy (AFM) measurements were performed using a DI Nanoscope IV (Veeco, USA) equipped with a tapping probe, and the samples were prepared by drop-casting onto a freshly cleaved mica surface and kept at room temperature overnight to let the solvent evaporate. The dielectric properties of the composite films at various rGO volume fractions were determined using a Hioki 3532-50 LCR meter (Japan). At least three specimens were tested for each composition and each specimen was tested at least three times. The rGO@PVP volume ratio data in the rGO@PVP/PVDF composites shown in this paper exclude the volume of PVP. The films were polished mechanically and coated with a silver film on the top and bottom surface of the films. The X-ray diffraction (XRD) measurements were carried out on a Rigaku D/Max-IIIA X-ray generator (Japan) with Cu Kα radiation at a wavelength of 1.54 Å. Specimens were scanned from 5° to 80° with a scan rate of 0.02°/min. Scanning electron microscopy (SEM) measurements were performed with a Hitachi S-4800 field emission electron microscope (Japan). The surfaces of the samples were contrasted with platinum before SEM observation.

## 3. Results and discussion

### 3.1. Chemical composition and microstructure of rGO@PVP nanosheets

Fig. 1 shows FTIR spectra of GO, rGO, rGO@PVP and PVP. The absorption peaks appearing in the spectrum of GO at 1730 $cm^{-1}$, 1405 $cm^{-1}$ and 1040 $cm^{-1}$ represent the stretching vibration of C=O, C–OH and C–O of GO, indicating the existence of plenty of oxygen functional groups. In comparing, these absorption peaks disappear in the FTIR spectra of rGO due to the reduction. Further, in comparison to that of rGO, the FTIR spectrum of rGO@PVP displays pronounced additional absorbance at around 1662 $cm^{-1}$ and 1287 $cm^{-1}$ corresponding to the absorption peaks of C=O and N–OH from PVP. Moreover, no significant new peaks were observed other than characteristic peaks of PVP and rGO at FTIR spectrum of rGO@PVP, which proved that there is no chemical interaction between PVP and rGO, the interaction between PVP and rGO was physical in nature.

Fig. 2 shows the TG curves of the pure PVP, GO, rGO and