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Remarkably variable dielectric and magnetic properties of poly(vinylidene fluoride) nanocomposite films with triple-layer structure

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ABSTRACT

The variable dielectric and magnetic properties of poly(vinylidene fluoride) (PVDF) nanocomposite films with triple-layer structure and with electrically conductive multi-walled carbon nanotubes (MWCNTs) and magnetic iron oxide (Fe_3O_4) nanoparticles as fillers, and PVDF as polymer matrix are systematically investigated. The single layer of MWCNTs/PVDF, Fe_3O_4/PVDF, and pure PVDF is denoted as *A*, *B* and *P*, respectively. The multilayered films with different arrangements are prepared by a simple two-step method. Scanning electron microscopy (SEM) shows good adhesion between the layers after stacking. The experimental results indicate that triple layer *AAA* films have higher dielectric constant (ε) and lower dielectric loss ($\tan\delta$) than the single layer *A* film with the same thickness in the frequency range of 10^2–10^4 Hz due to the interfacial effect. The nanocomposite films with structure of *ABA* and *APA* keep low $\tan\delta$ when the filler content is high due to the intermediate *B* and *P* layer as an inter-barrier to prevent the formation of conductive network in these samples. To replace the intermediate *B* layer of *BBB* films by *A* layer produces much higher saturation magnetization (M_s) for the filler content above 2.0 wt% due to the synergistic effect. But the replacement of the *B* layer by *P* layer causes nearly no significant change of M_s. This work demonstrates a new method to tune the dielectric and magnetic properties of nanocomposites.

1. Introduction

In recent years, polymer-based nanocomposites have attracted tremendous attention in academia and industry because of their unique properties and potential applications [1,2]. Most of the polymer nanocomposites possess both the advantages of polymer matrix such as light weight, easy processing, and low cost and those of inorganic nanofillers such as special functionalities and high thermal stability. Therefore, the physiochemical properties of nanocomposites can be adjusted by changing the type of polymers, the kind and size of fillers, the distribution of fillers in the system, and the interface features between polymers and fillers [2–11]. In most cases the specific needs of materials could be realized by tuning these parameters of the system [12–14].

So far, great success has been achieved to optimize the properties of the polymer-matrix nanocomposites. To obtain better comprehensive properties including multiple functionalities, hybrid fillers are often used [15,16]. For example, both high dielectric constant and low dielectric loss could be obtained by using cofillers of surface-functionalized graphene nanosheets and barium titanate ($BaTiO_3$) nanoparticles in poly(vinylidene fluoride) (PVDF) [15]. Besides, both high thermal conductivity and high electrical resistivity could be achieved by controlling the spatial distribution of hybrid fillers of multi-walled carbon nanotubes (MWCNTs) and silicon carbide (SiC) nanoparticles in immiscible PVDF/polystyrene (PS) 30/70 (vol%) blends [16]. However, it is usually hard to precisely control the spatial distribution of different fillers in the hybrid system to form a required micro-structure with high stability.

In addition, stacking of double and even multiple polymer nanocomposite films with different compositions and functions has emerged as a useful strategy to better control the dielectric properties of polymer nanocomposites in the past decade [17–19]. For example, compared with the single layer multi-walled carbon nanotube (MWCNT)/cyanate ester (CE) nanocomposites, higher

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dielectric constant and much lower dielectric loss were found in the double-layer materials with a layer of polyethylene (PE) and a layer of MWCNT/CE resin composite [17]. Besides, triple layer materials with carbon nanofiber (CNF)/PVDF nanocomposites intercalated by a pure PVDF layer have enhanced the dielectric constant and the low dielectric loss [18]. A versatile processing technique called coextrusion was used to fabricate PVDF/polycarbonate (PC) multilayer films with even thousands of nanolayers [19]. Such materials have a high energy density and low dielectric loss.

In this work, first MWCNTs with high electric conductivity and iron (II, III) oxide (Fe_3O_4) nanoparticles with excellent magnetic properties are added into PVDF matrix to form single layer functional materials, respectively. PVDF is used as the polymer matrix because of its unique chemical, mechanical, dielectric, and piezoelectric properties [20]. Then the single layers are stacked together in various ways to investigate the variation of the dielectric and magnetic properties. This work could shed some light on the better optimization of such polymer nanocomposites.

2. Experimental

2.1. Materials

PVDF (FR904) powders with a density of 1.78 g cm^{-3} and a melt flow index of 26.0 g (10 min^{-1}) were supplied by Shanghai 3F New Materials Co. (China). MWCNT (95% purity) with density of 2.10 g cm^{-3}, inner diameter of 5–10 nm, outer diameter of 10–20 nm, and length of 10–30 μm were purchased from Chengdu Organic Chemicals Co. Ltd. (China). $FeCl_2{\cdot}4H_2O$ (AR), $FeCl_3{\cdot}6H_2O$ (AR), Oleic acid (AR), nitric acid (AR) and $NH_3{\cdot}H_2O$ (AR) were purchased from Xilong Chemical Co. Ltd. (China) and used without further purification. *N*,*N*-dimethylformamide (DMF) (AR) with density of 0.95 g cm^{-3} at 25.0 °C was supplied by Beijing Chemical Works (China).

2.2. Preparation and surface modification of Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles were prepared by a conventional coprecipitation method and surface-modified according to the literature [21–23]. Firstly, 7.83 g $FeCl_3{\cdot}6H_2O$ and 2.87 g $FeCl_2{\cdot}4H_2O$ were dissolved in 100 mL deionized water in a 250 mL three necked round bottom flask in a water bath at 80.0 °C with mechanical stirring under N_2 protection. And then 30 mL 25 wt% $NH_3{\cdot}H_2O$ was quickly added to the solution. After a few seconds the solution turned black and it was further stirred for 1 h. Then a mixture of 6 mL ethanol and 6 mL oleic acid was added to the suspension and the system was further stirred for 2 h. The obtained precipitate was separated from the solution by using a magnet and washed with deionized water for three times and with ethanol twice. The cleaned precipitate was dried in vacuum oven at 70.0 °C for 24 h. The diameter of the obtained surface modified Fe_3O_4 nanoparticle was measured to be ca. 25–35 nm.

2.3. Surface modification of MWCNTs

The purchased MWCNTs were surface-modified according to the literature [24,25]. First ca. 3.0 g MWCNTs were soaked into a large amount of nitric acid in a round bottom flask for refluxing 6 h, and the mixture was separated by filtering and washed with deionized water for several times. Then the treated MWCNTs were dried in vacuum oven at 80.0 °C for 12 h.

2.4. Preparation of single layer and multilayer nanocomposite films

PVDF powders were dried completely in a vacuum oven at 80 °C overnight before use. First, MWCNTs or Fe_3O_4 nanoparticles with various weight ratios were added into 20 mL DMF, and the resultant solution was sonicated at room temperature for 2 h to form the suspension. Then ca. 3.2 g PVDF powders were also added into DMF solvent and the mixture was mechanically stirred in water bath at 70.0 °C for 3 h to ensure the complete dissolution of PVDF. The suspension was then cast into thin films on a clean glass plate by spin-coating at room temperature. The obtained films were kept in a vacuum oven at 70.0 °C for 12 h to completely remove any remnant solvent. The MWCNT/PVDF and Fe_3O_4/PVDF single layer nanocomposite films with different filler concentrations of ca. 1.0–5.0 wt% possessed a thickness of ca. 8 μm and ca. 24 μm and are denoted as A_8, B_8, A_{24}, and B_{24}, respectively. The pure PVDF films prepared with a similar procedure to the nanocomposites had a thickness of ca. 8 μm and are denoted as P_8. The prepared

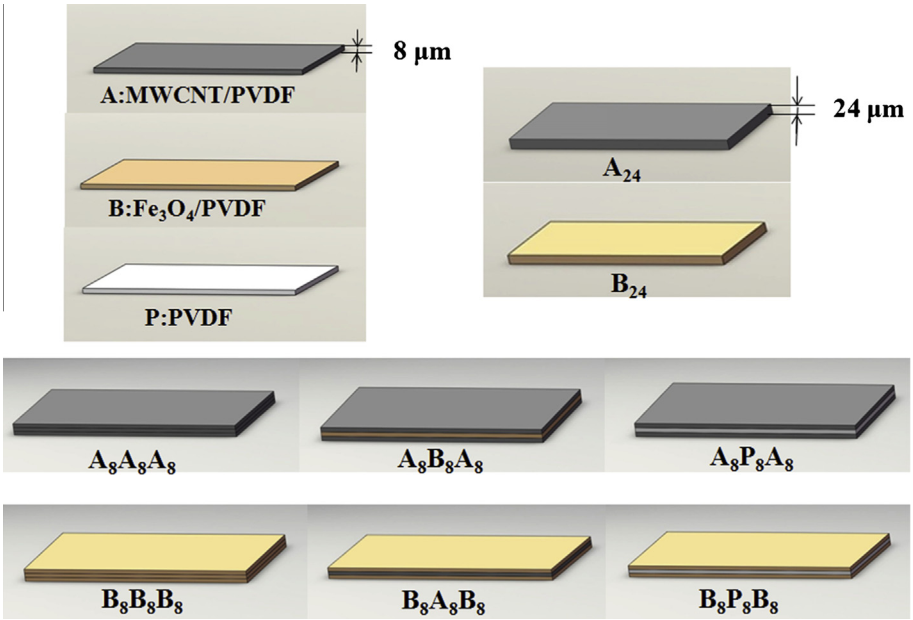

Fig. 1. Schematic presentation of different stacking to form multilayer structure.