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In-situ preparation of high dielectric poly (metal phthalocyanine) imide/MWCNTs nanocomposites

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ABSTRACT

The tetra-amino copper (zinc) phthalocyanine was copolymerized with the 4,4′-diaminodiphenyl ether and 4,4′-oxydiphthalic anhydride to synthesize the branched poly (copper phthalocyanine) imide [P(CuPc)I] and poly (zinc phthalocyanine) imide [P(ZnPc)I]. The P(CuPc)I and P(ZnPc)I exhibited higher dielectric constant than that of conventional polyimide due to the introduction of metal phthalocyanine. A series of P(CuPc)I/MWCNTs nanocomposites were prepared by in-situ composite method. The morphological study of nanocomposites by SEM suggested that the in-situ composite method was useful to achieve good dispersion of MWCNTs in P(CuPc)I matrix. A P(CuPc)I/MWCNTs nanocomposite containing 12 vol.% of MWCNTs prepared in this fashion had a high dielectric constant above 200 and a dielectric loss tangent of 2.2 at 1 KHz and room temperature.

1. Introduction

The most important property of the dielectric material is its ability to be polarized in the external electric field. The dielectric constant is an important index to represent one property of the dielectric material. With rapid development of the electronics industry, high dielectric constant materials with trapping carrier, store electricity, and uniform electric field, have very important applications in the dynamic random access memories, sensors, capacitors, photoelectric/electro-optical devices, and microwave devices, especially in the power capacitors and chip capacitors [1,2]. At present, most high dielectric constant materials are produced with the ferroelectric materials, especially the ferroelectric ceramic materials. Because of high processing temperature and relatively poor mutual bond force of ferroelectric materials, it is impossible to process the components in a large area [3,4]. However, conventional polymers are easy to process but generally suffer from a low dielectric constant (less than 10). An ideal high dielectric constant material should have high dielectric constant, low dielectric loss and good processibility. In fact, for one-component systems, it is hard to realize all these demands. In the past several decades, the composite approach, in which high dielectric constant particle were added to a polymer matrix, has been employed to increase dielectric constant of polymer. The polymer/ceramic, polymer/organic semiconductor, polymer/metal, and other polymer based composites [5–12] have been developed to improve the dielectric properties of composites including increasing dielectric constant, reducing dielectric loss, and enhancing dielectric strength, etc.

Carbon nanotubes (CNTs)/polymer composites had been extensively studied in past a few years, in which even a very small amount of CNTs can induce significant changes in the material's properties [16,7,17], because CNTs show good electrical and thermal conductivity, high mechanical strength, especially large aspect ratio. However, most of the reported studies were focused on the enhancement of mechanical properties and/or electrical conductivity of composites. Recently, as the potential application of the CNTs/polymer composites with high dielectric constant and good electromechanical properties, they have been paid more attention, for instance, super capacitors, on-chip capacitors, and microelectromechanical systems. Li [18] reported esterification reaction to modify the side wall, which enhanced the dispersion of multi-walled carbon nanotubes (MWCNTs) in poly (vinylidene fluoride) (PVDF). Dielectric constant of the obtained composite exceeds 200 with 6.5 vol.% of MWCNTs. Liu [19] prepared sulfonated poly (ary ether ketone) (SPAEK)/MWCNTs composites via solution blend. A percolation threshold of 3 vol.% and dielectric constant of 600 at 7 vol.% were obtained.

Metal phthalocyanines are a kind of macrocyclic compound with an electron hole which can carry metal ions such as copper, zinc, etc. They have been widely utilized in many different areas such as semiconductors, catalytic reactions, gas sensors [13], and the preparation of high dielectric materials and solar cells [14,15]. In this paper, the tetra-amine monomers of the

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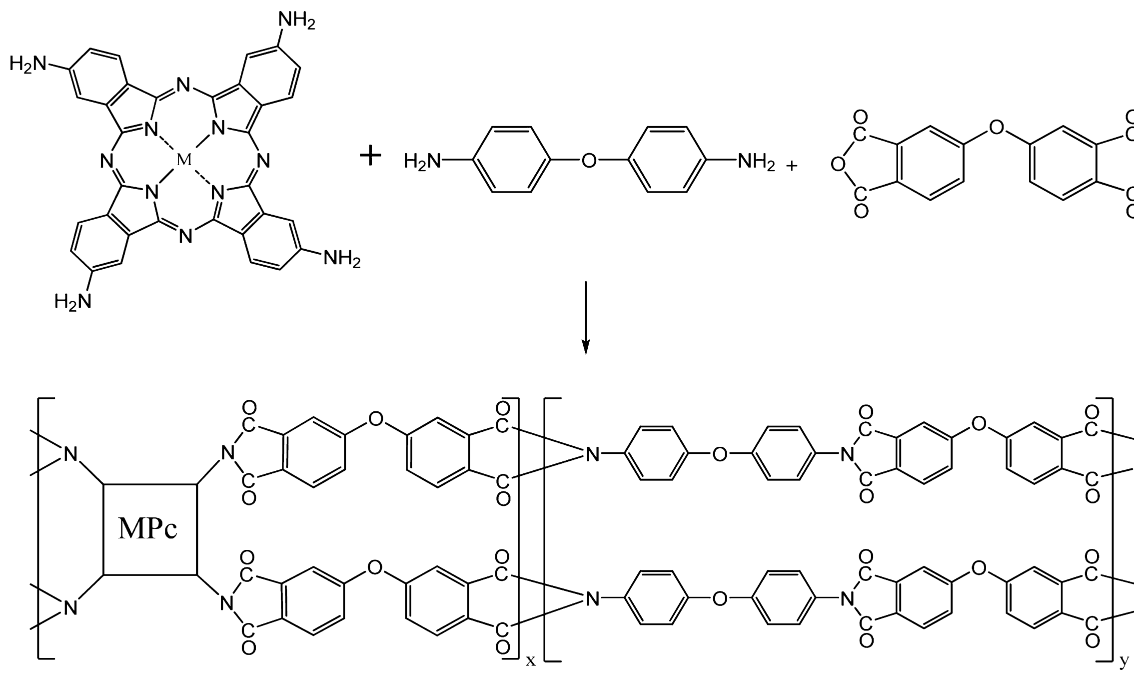

Scheme 1. Synthesis of P(MPc)I, M = Cu, Zn.

tetra-amino metal (copper, zinc) phthalocyanine were copolymerized with 4,4′-diaminodiphenyl ether and 4,4′-oxydiphthalic anhydride to synthesize the poly(metal phthalocyanine)imide [P(MPc)I]. A series of [P(MPc)I]/multi-walled carbon nanotubes (MWCNTs) nanocomposites were prepared by in-situ composite method. The morphologies and dielectric properties of the nanocomposites were systematically studied.

2. Experiment

2.1. Materials

The dimethylacetamide (DMAc) was purchased from Tianjin Tiantai Chemical Co., Ltd., China. 4,4′-Diaminodiphenyl ether (ODA) and 4,4′-oxydiphthalic anhydride (ODPA) were purchased from Aldrich and used without further purification. The MWCNTs (purity > 95%, diameter 2–20 nm, length about 30 μm, density 2.1 g/cm^3 synthesized by chemical vapor deposition were purchased from Chengdu Organic Chemistry Co., Ltd., Chinese Academy of Science, China. The tetra-amino metal (copper, zinc) phthalocyanine was synthesized following a procedure reported in Ref. [15].

2.2. Characterization

The UV–visible absorption spectrum was recorded on a UV2501-PC spectrophotometer. The SEM image was recorded using a JEOL JSM-6700F scanning electron microscope and iridium (IXRF Systems) software. The dielectric properties of the polymer films (diameter 10 mm and thickness 0.1 mm, and coated with golden by a vacuum evaporation method) were obtained using an HP 4294A impedance analyzer. The dielectric constant ε of the film was calculated by the formula of a parallel plate capacitor as:

$$\varepsilon = \frac{Ct}{\varepsilon_0 A}$$

where, C is the capacitance of the metal-insulator-metal element, ε_0 is the vacuum dielectric permittivity, A is the area of the electrode, and t is the thickness of the capacitor, respectively.

2.3. Synthesis of P(MPc)I

A three-necked flask was charged with 0.25 mmol of tetra-amino copper (zinc) phthalocyanine, 1.5 mmol of ODA and 25 mL of DMAc. The solution was stirred under a nitrogen atmosphere until amine dissolved completely, and then 2 mmol of ODPA was added. The reaction mixture was stirred at ambient temperature for 2–3 h under a nitrogen atmosphere to form poly (metal phthalocyanine) amide acid [P(MPc)AA] solution. The solution was then poured onto a glass slide and was dried in air at 80 °C for 3 h. Finally, the P(MPc)I films were obtained by sequential heating at 120 °C for 1 h, 200 °C for 1 h, and 250 °C for 1 h. The reaction formula was shown in Scheme 1.

2.4. Preparation of acidified carbon nanotubes [20]

MWCNTs was treated in mixing acid (H_2SO_4 : HNO_3 = 3:1) under sonication for 4 h in order to remove the impurities and the amorphous carbon, and to generate carbonyls on the surface of the MWCNTs. This mixture was diluted and washed by deionized water, the acidified MWCNTs were obtained after dried in vacuum oven at 50 °C.

2.5. Preparation of P(CuPc)I/MWCNTs nanocomposites

ODPA (2 mmol) was added into a stirred solution of tetra-amino copper phthalocyanine (0.25 mmol) and 4,4′-ODA (1.5 mmol) in DMAc under nitrogen at ambient temperature for 2–3 h, and the P(MPc)AA solution was obtained.

The acidified MWCNTs were dispersed in the DMAc with ultrasound for 2 h. Take a certain amount of the suspension in an appropriate amount of P(MPc)AA solution and continue to stir for 1 h to obtain the MWCNTs/P(MPc)AA mixture with the volume fractions (Volume fraction is calculated according to loading mass fraction of MWCNTs and densities of polymer and MWCNTs) being 5, 6, 7.5, 9.5, 11, and 12 vol.%, respectively. The mixture was then poured onto a glass slide and was dried in air at 80 °C for 3 h. Finally, the P(CuPc)I/MWCNTs nanocomposite films were obtained