



Tunable permittivity in polymer composites filled with Si-based semiconductors by regulating induced polarization

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ABSTRACT

Induced polarization shows a significant influence on dielectric permittivity of 0–3 polymer composites containing Si-based semi-conductive fillers. The nature of induced polarization is the increased electric conductivity or decreased band gap in Si-based semi-conductive fillers. In this work, the dependence of induced polarization onto particle size of α -SiC filler together with polarity of polymer matrix and Si-based semi-conductive filler has been elaborately investigated by detecting the permittivity of composites. It was found that increasing the grain size of SiC filler, improving the polarity of polymer matrix and reducing the band-gap of Si-based semi-conductive filler could favor the enhancement of the overall induced polarity in the composites. As a result, the significantly improved dielectric permittivity of composites higher than both of the neat polymer and filler was observed depending on the constituents of the composites. The highest dielectric permittivity of $\sim 215 \pm 1$ kHz was achieved in poly(vinyl alcohol) based composite filled with 60 vol% of 12 μm SiC particles. The dielectric permittivity of these 0–3 composites could be well tuned in a wide range through altering their constituents. This work might open a facile route to obtain the promising high-performance dielectric composite materials by regulating the degree of induced polarization.

1. Introduction

With the rapid development of electronic and electric power devices, electronic components such as capacitors are developed towards the direction of high energy storage and miniaturization, which has boost the persistent research and preparation of high-dielectric-constant (high-k) composite materials [1–3]. Recently, two primary strategies are widely utilized to obtain high-k feature in 0–3 polymer based composites. One is introducing the high-k ferroelectric ceramic fillers [4–7] such as barium titanate and lead titanate into polymer matrix, and the other is dispersing the high conductive fillers such as metals conductors [8–12], carbon materials [13–18] and conducting polymers [19–24] into polymer matrix.

In the former tactics, the high-k properties of obtained 0–3 composites are mostly originating from the inherit high-k performance of ferroelectric ceramic fillers scattered in polymer matrix. Based on current binary effective dielectric models, for instances, series/parallel equation, Maxwell-Garnett equation [25,26], Bruggeman equation [27,28], Jaysundere-Smith equation [29] and Lichtenker rule [30], the dielectric permittivity (ϵ_r) of this type of composite materials can

be finely predicted and further interpreted as the dielectric permittivity and volume content of both of high-k ferroelectric ceramic and polymer are known. In order to achieve a higher permittivity of composites, a rather high volume content of high-k ceramic fillers is indispensable according to binary dielectric models.

With regard to the latter route, the high-k trait of the 0–3 composites bearing the high conductive fillers is dominantly attributed to the electric percolative threshold [31] and interfacial polarization [32,33]. That is another convenient and practical approach to achieve high-k performance in 0–3 composites. In percolative threshold theory, the composites can undergo a transition from insulator to conductor as the volume content of high conductive fillers is increased to a critical value. At the critical content, the dielectric and conductive properties of the 0–3 composites can be dramatically elevated ascribed to the formation of a large 3D conductive network and the proposed massive micro-capacitors across the composites. Furthermore, in interfacial polarization theory, abundant charge carriers in the format of stable electric bi-layer can be accumulated in the filler/polymer interface zones due to the prominent discrepancy of the conductivity/permittivity in both of filler and polymer, which contributes to the significantly

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promoted permittivity of 0–3 composites. To address the contribution of interfacial layer, the modified models such as multi-core model [34], theoretical interlayer model [35] and double-inclusion model [36] have been presented. In these cases, the interface layer is deemed as the third component with a rather high permittivity depending on its thickness to clarify the abnormally high permittivity measured in some composites.

In our previous work [37], another route of fabricating the 0–3 high-k composites was presented. By constructing the strong induced polarization between Si-based semi-conductive filler and high polar polymer matrix such as poly(vinylidene fluoride) (PVDF), the high-k performance was achieved in composites although both of α -SiC filler and PVDF based copolymer matrix possessed rather low dielectric permittivity and electric conductivity. The permittivity of the composites was much higher than either of the sole components. Different from the above two strategies, the origination of high-k performance in these composites is attributed to the strong interaction between electron-withdrawing polymer and electron-donating Si-based semiconductor. A large number of electron-hole dipole pairs were expected to be formed in SiC, which made a remarkable contribution to the high-k properties of composites. To confirm that, a series of 2-2 composites were fabricated based on polymer layers and Si-based semiconductor layers with varied polarity [38]. The results confirmed that the nature of induced polarization should be from the enhanced electrical conductivity or the decreased percolative electric field in Si-based semiconductors. The induced polarization could lead to a notably increased permittivity in Si-based semiconductor but little change in polymer. It has been recently demonstrated that increasing the compatibility between the SiC particles and polymer matrix by modifying the surface of SiC with Si based coupling agents to further improve the dielectric performance of composites both under low and high electric field [39]. That strongly suggests that regulating the induced polarization between polymer matrix and filler might be an effective way to fabricate high-k composites consisting of low-k components.

To profoundly disclose how to regulate the induced polarization and its influence on the dielectric permittivity in Si-based semiconductor filled polymer based composites, in this work, a family of 0–3 polymer based composite films were fabricated. The influences of the grain size of α -SiC fillers, the polarity of polymer matrix and the polarity (band gap) of Si-based semi-conductive filler on the permittivity of the resultant composites have been well discussed. The larger filler size, the higher polymer polarity and the lower filler polarity would be more helpful to the formation of the strong induced polarization and the higher elevated permittivity in these 0–3 composites. The promising high permittivity as well as the low dielectric loss obtained in the resultant 0–3 composites suggested this work might offer another facile and valid strategy for fabricating the high-k composite materials by tuning the induced polarization between both components.

2. Experimental procedure

2.1. Materials

α -SiC fillers with particle sizes of 12 μm , 7 μm and 500 nm were kindly provided by Xi'an Tongxin Semi-conductor Accessory Co. Ltd. β - Si_3N_4 and mono-crystalline Si (*m*-Si) fillers with particle size of 12 μm were purchased from Shanghai Yunfu Nanotechnology Co. Ltd. All of Si-based fillers were washed with anhydrous alcohol for three times to remove impurities and then dried thoroughly at 200 $^\circ\text{C}$ for 10 h before used. Poly(vinylidene fluoride-co-chlorotrifluoroethylene) containing internal double bonds (P(VDF-CTFE-DB)) (80/10/10) with 10 mol% CTFE and 10 mol% DB, and poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) (80/20) with 20 mol% TrFE were directly used because they had been prepared in previous work of our group [37–40]. Universal polystyrene (PS) particles were brought from Maoming

Table 1

Name abbreviations of some utilized materials.

Material names	Abbreviations
12 μm α -SiC	SiC-12
7 μm α -SiC	SiC-7
500 nm α -SiC	SiC-500
12 μm β - Si_3N_4	Si_3N_4 -12
12 μm <i>m</i> -Si	Si-12
P(VDF-CTFE-DB)	PVDF

Yexiang Plastic Co. Ltd. and they were firstly dissolved in N,N -dimethylformamide (DMF) and then precipitated in deionized (DI) water to remove impurities before used. Poly(ethyl methacrylate) (PEMA) were purchased from Tianjin Heowns Biochemistry Technology Co. Ltd. Polyacrylonitrile (PAN) P60C was obtained from Shanguyu Baisheng Chemical Sales Department. Poly(vinyl alcohol) (PVA) 17–88 with a polymerization degree of 1700 and hydrolysis percentage of 88 mol% was purchased from Shanxi Sanwei Co. Ltd. Acetone (Tianjin Reagents Co. Ltd, AR grade), DMF (Tianjin Reagents Co. Ltd, AR grade) and tetramethylene oxide (THF, Tianjin Reagents Co. Ltd, AR grade) were used as received. The name abbreviations of some utilized materials were shown in Table 1.

2.2. Preparation of 0–3 composites

The composites (P(VDF-CTFE-DB)/12 μm SiC composites, P(VDF-CTFE-DB)/7 μm SiC ones, P(VDF-CTFE-DB)/500 nm SiC ones, PVA/12 μm SiC ones, PAN/12 μm SiC ones, PEMA/12 μm SiC ones, PS/12 μm SiC ones, P(VDF-TrFE)/12 μm SiC ones, P(VDF-CTFE-DB)/12 μm Si_3N_4 ones, PVA/12 μm Si_3N_4 ones and P(VDF-CTFE-DB)/12 μm Si ones) were prepared through solution casting method [41] from a suspension containing designed volume fraction of filler in high viscosity polymer solution (avoiding the sedimentation of high density filler during solvent evaporation) on glass slides. The various solvents for P(VDF-CTFE-DB) based composites, PVA based composites, PAN based composites, and PS, PEMA and P(VDF-TrFE) based composites were utilized, respectively. The different film forming temperatures (namely the solvent evaporation temperatures) were set for various composite systems. After kept at various post-treatment temperatures under reduced pressure for 4 h, these films (about 200 μm thickness) were peeled off followed by sputtering with Au on both surfaces as electrodes for electric properties measurements. The fabrication conditions of all 0–3 composites including the solvent, the film forming temperature and the film post-treatment temperature were clearly shown in Table 2.

Table 2

Fabrication conditions of all 0–3 composites.

Composites	Solvent	Forming temperature ($^\circ\text{C}$)	Post-treatment temperature ($^\circ\text{C}$)
SiC-12/PVDF	acetone	25	160
SiC-7/PVDF	acetone	25	160
SiC-500/PVDF	acetone	25	160
SiC-12/PVA	DI water	50	100
SiC-12/PAN	DMF	70	100
SiC-12/P(VDF-TrFE)	THF	25	180
SiC-12/PEMA	THF	25	100
SiC-12/PS	THF	25	100
Si_3N_4 -12/PVDF	acetone	25	160
Si-12/PVDF	acetone	25	160
Si_3N_4 -12/PVA	DI water	50	100

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