Influence of ZnO varistor fillers on the nonlinear dielectric and conductivity properties of silicone rubber polymer composites

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ABSTRACT

In this paper, ZnO varistor/rubber composites with nonlinear dielectric and conductivity properties were fabricated and investigated in detail. As composites with adjustable dielectric and conductivity properties are highly desired for various applications, two methods were employed to adjust the electric properties of the composites. Results show that composites with large amount of ZnO (more than 30vol%) exhibit good nonlinear properties with the electric field. Moreover, the size and formula control of the ZnO varistor filler show the potential of decoupled control of the dielectric and conductivity properties. The results indicate potential applications for HVDC cables and accessories.

KEYWORDS

ZnO varistor/rubber composites, nonlinear dielectric properties, nonlinear conductivity properties, adjustable electric properties

INTRODUCTION

In power systems, the unexpected high electric fields often appear in the insulation parts of electrical devices, such as the accessories of cables, which are normally caused by externally applied high voltage or accumulated space charges and will accelerate the aging and breakdown of insulation materials. Metal conductors and semiconductors or high dielectric permittivity materials can make spatial distribution of electric field more balanced without meeting the insulation requirement, while polymers can only act as insulators without improving the distribution of the electric field. As a result, the design of the accessories of cable become very complex through traditional materials as each material can only act as insulator to withstand the electric field or conductor to balance the electric field. Thus, from the view of materials, it is highly desired to develop a kind of polymer composite with nonlinear dielectric and conductivity properties, which can serve as insulator or conductor according to the externally applied field, i.e. under low electric field, the polymer composite should be insulating to avoid the unnecessary leakage current, while under high electric field, it should have large conductivity and dielectric permittivity, which can reduce the non-uniformity of electric field distribution.

In recent years, composite dielectric materials with high dielectric permittivity have received increasing attention due to their potential application in HVAC. Using the high dielectric permittivity materials to compound with organic materials with good insulation and flexibility, researchers can achieve composites having the advantages of both materials. Being employed in the cable accessories or the insulator ends, composites with high dielectric permittivity can balance the AC electric field, thereby increasing the breakdown voltage and reducing the corona.[1]

The traditional high dielectric permittivity composites use silicon rubber, polyethylene or PVDF as matrixes, and BT, CNF or CCTO as function fillers.[2-3] Although the dielectric permittivies of these composites vary with the content of the fillers, the conductivity only changes slightly. As the distribution of the stable DC electric field depends on conductivity, the above-mentioned method is not effective for HVDC applications. However, it is also necessary to consider the dielectric permittivity due to the charge accumulation at the interface of two different insulation materials which is a result of the mismatch of the dielectric permittivity and conductivity at each side.[4-7] Moreover, the electric distribution during the transient process in HVDC systems is also relative to both the dielectric permittivity and conductivity. Thus, if the composite's dielectric permittivity and conductivity can automatically change and fit with the electric field, above problems will no longer exist in HVDC applications.

ZnO varistor is a kind of ceramic with nonlinear electrical properties, whose conductivity and dielectric permittivity can change with electric field.[8-10] Under low electric field, the conductivity and dielectric permittivity of ZnO varistor are almost unchanged. Under high electric field above the breakdown field of ZnO varistor, its dielectric permittivity will increase quickly, as well as its conductivity. Researchers have already used ZnO varistor powders as fillers in insulating polymer matrix to impart the nonlinear conductivity directly to the composites.[11-13] However there have been no reports about doping ZnO varistor fillers into composites for both the nonlinear conductivity and nonlinear dielectric permittivity.

In this study, we have combined the ZnO varistor fillers with the silicon rubber to prepare the desired composites. The nonlinear dielectric and conductivity properties of the polymer composite samples composed of different types of ZnO varistor fillers were investigated and discussed in detail. The experiment results show that the bulk nonlinear electrical properties of the silicone rubber polymer composites can be well controlled by doping ZnO varistor fillers with special characteristics, indicating potential use in HVDC cables and accessories.

EXPERIMENTAL SECTION

Material: the preparation of ZnO varistor filler followed a conventional solid-states sintering method. Analytical-grades raw materials with the composition of 96.1mol% ZnO, 1mol% Bi_2O_3, 0.5mol% MnO_2, 1mol% Co_2O_3, 0.4mol% Cr_2O_3, 1mol% Sb_2O_3, and 0.01mol% $Al(NO_3)_3$ were mixed by a planetary ball mill, and calcined at 1000℃ for 10h. Then the sintered ZnO varistor fill er was crushed and sieved to tiny particles with size of about 20~50µm. The high-temperature vulcanized silicone rubber with average molecular weight of 500000~600000 was used as the matrix of the composite. The volume fractions of ZnO varistor fillers in the mixture were 5%,

Close and Return

10%, 20%, 30%, 40% respectively. To avoid the uneven distribution in the mixture, tetrahydrofuran was introduced as solvent. The mixture was dried in 60℃ till the tetrahydrofuran had completely evaporated. The composites were then hot pressed into a disc shape in 70℃.

Composition and Morphology: The SEM morphology was obtained by JSM 6301F scanning electron microscope, JEOL Ltd.

Dielectric and Conductive Properties: The composite samples were 20mm in diameter and about 1mm in thickness. The dielectric characteristics were measured by Concept 80 Broadband Dielectric Spectrometer, Novocontrol Technologies GmbH & Co. KG., Germany. The results were obtained under the DC bias voltage from 0V to 2000V and the testing AC voltage is 50Hz, 1V. The conductive properties were measured by Model 2410 digital source meter, Keithley Instruments, Inc., Cleveland, OH, USA.

RESULTS AND DISCUSSION

Fig. 1 shows the scanning electron microscope(SEM) morphology of the samples. The areas with lighter color are the ZnO varistor particles. Inside the particles, the ZnO grain size is about 2-5m, and tens of grains form a tiny particle, which is about 20-50m in size. The ZnO varistor particles are dispersed into the silicon rubber, and there is almost no pore in the samples, which indicates that the ZnO varistor particles and the organic matrix are in close contact.

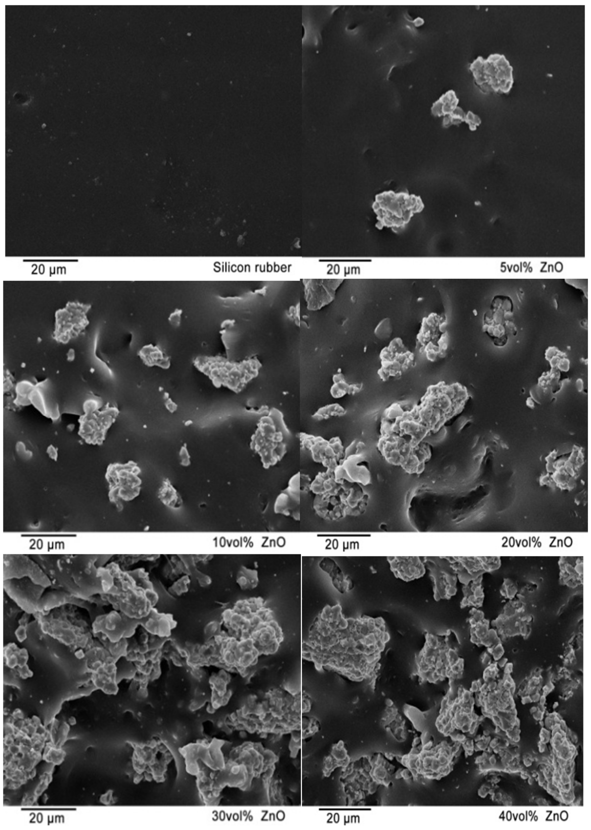

Fig. 1: The SEM morphology of the fresh surfaces of the silicon rubber and the composites with different volume fractions of ZnO varistor fillers

Nonlinear Conductivity and dielectric properties of the composites

Nonlinear Conductivity properties

ZnO varistors have nonlinear current density–electric field (*J*–*E*) characteristics, which are controlled by grain boundaries. The nonlinear coefficient α is expressed as:

$$\alpha = \frac{\log(J_2/J_1)}{\log(E_2/E_1)} \qquad [1]$$

where J_2, J_1 are the current density under the applied electric field E_2, E_1 respectively. The breakdown electric field E_b is considered as the electric field where the nonlinear coefficient α reaches a maximum value. When the applied electric field E is higher than the breakdown value E_b(always more than hundreds of V/mm), the electric field E will change slowly while the current density J increases quickly.

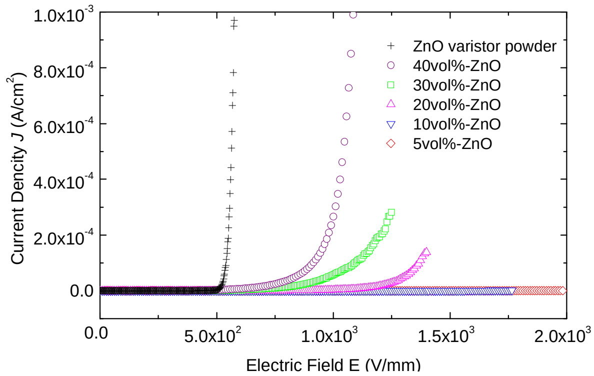

Fig. 2: The current density–electric field (*J*–*E*) characteristics of the composites with different volume fractions of ZnO varistor fillers.

Fig. 2 shows the electric field-current density (*E*–*J*) characteristics of the prepared samples, and Table 1 gives the detailed parameters of the samples' nonlinear conductivity properties, which highly depend on the filler contents. Increasing the filler content leads to decreased breakdown field. The difference in the breakdown electric field can be attributed to the interparticle distance of the filler particles inside the composites. The composites with ZnO varistor fillers less than 10 vol% almost don't exhibit the nonlinear conductivity properties, while the nonlinear coefficient α of the composites with ZnO varistor filler faction of 30vol% and 40vol% can be 16.9 and17.4 respectively. This phenomenon can be explained by the percolation threshold theory.

Table 1.The parameters of nonlinear conductivity properties of the composites with different volume fractions of ZnO varistor fillers.

ZnO fractions	5vol%	10vol%	20vol%	30vol%	40vol%	ZnO powder
α	~1	~1	13.1	16.9	17.4	45.3
E_b(V/mm)	—	—	1366	1223	1085	575

Nonlinear Dielectric Properties

Fig. 3 shows the dependences of the composites' dielectric permittivities on the electric fields and the volume fractions of ZnO varistor fillers, and the detailed data of dielectric permittivities in this figure are given in Table 2.The pre-breakdown dielectric permittivity ε_{pre} is gained under the electric field of $0.5E_b$, while the breakdown dielectric permittivity ε_b is under the electric field of E_b.

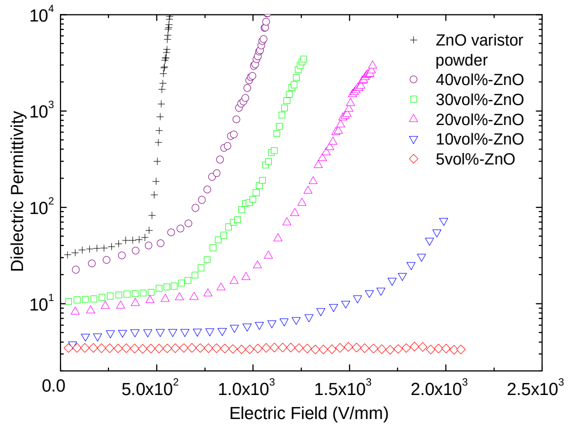

Fig. 3.The dependences of the composites' dielectric permittivities on the electric fields and the volume fractions of ZnO varistor fillers.

The dielectric permittivity almost does not change with the applied electric field when the volume fraction of ZnO varistor fillers is 5vol%. Once the volume fraction of the ZnO varistor fillers reaches 10vol%, the dielectric permittivity changes a little under a low electric field, but rises dramatically when the electric field reaches the breakdown field of the composite. When the volume fraction of ZnO varistor fillers reaches 20vol%, 30vol%,and 40vol%, the breakdown dielectric permittivity is about 29.5, 152, and 311 times of that in the pre-breakdown region respectively. For composites with low ZnO content (< 10%), the dielectric permittivity is determined by both the rubber matrix and the ZnO fillers, while for composites with high ZnO content, the dielectric permittivity is mainly controlled by the ZnO fillers and the nonlinear dielectric properties are related to the nonlinear conductivity properties of ZnO and the interface polarization of the composites.

Table 2.The dielectric permittivities of composites with different volume fractions of ZnO varistor fillers under different electric fields.

ZnO fractions	5vol %	10vol %	20vol%	30vol %	40vol %	ZnO powder
ε_{pre}	——	——	11.7	15.8	49.2	45.6
ε_b	——	——	341	2217	15284	20242
$\varepsilon_b/\varepsilon_{pre}$	——	——	29.1	140	311	443

Control of the electric properties of the composites

The nonlinear conductivity and dielectric properties of the composites make the materials self-adapted. However, different applications require adjustable electric properties. What's more, the conductivity and dielectric permittivity of the composites often change together, which limits the potential use of the composites as many applications needs to adjust the conductivity or dielectric permittivity only. Here, two methods were employed to adjust the electric properties of the composites.

Size Control of the ZnO fillers

Previous researches have shown that the properties of composites is influenced not only by the dispersion, surface morphology and geometrical shape of the fillers, but also by size of fillers.[14] In order to achieve fillers with different size, sieves with different mesh were employed. As shown in Fig. 4, five samples with an average diameter of 80µm, 57µm, 43µm, 30µm and 20µm were achieved, which was represented as Z100, Z200, Z300, Z400 and Z600. Composites with 5vol%, 10vol%, 20vol% and 30vol% of each sample was fabricated.

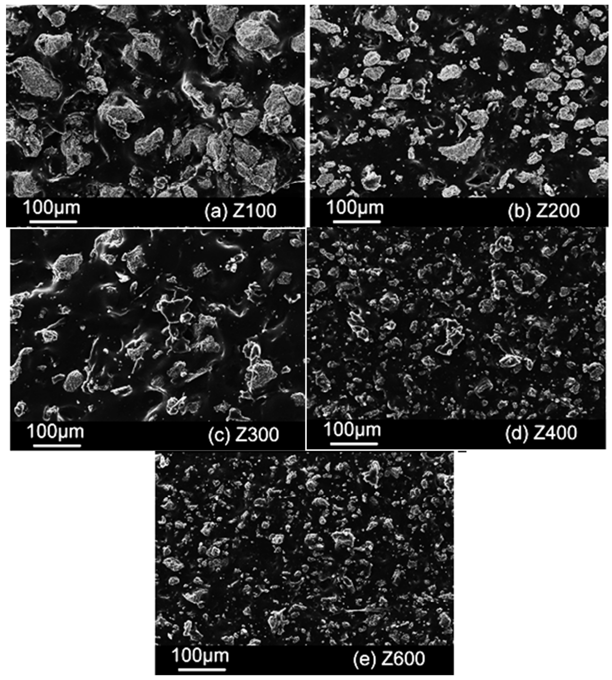

Fig.4 The SEM morphology of the fresh surfaces of the composites with fillers of varying sizes

The conductivity and dielectric properties were measured and the the detailed data were summarized in Table 3, where *l* is the average distance of ZnO fillers and other parameters have been explained above. For composites with fillers of a small diameter (smaller than 43µm), the nonlinear properties become poor, which exhibit nonlinear conductivity coefficients smaller than 4, nonlinear dielectric coefficients smaller than 10 and largely enhanced breakdown electric fields. Thus, those above mentioned composites are suitable for applications which need small nonlinear coefficients of conductivity and dielectric. However, for composites with fillers of a large diameter (larger than 43µm), the nonlinear conductivity properties are largely enhanced and become steady with the increase of the sizes of the fillers, while nonlinear dielectric coefficients grow up with the size of the fillers. Thus, those composites are applicable where high nonlinear properties are required. Besides, the nonlinear dielectric properties of those composites could be easily adjusted with a small change of the nonlinear conductivity properties, which indicates the potential of decoupled control of conductivity and dielectric permittivity.

Table 3. The nonlinear conductive parameters and dielectric permittivities of composites with fillers of varying sizes

Fillers fractions	Parameter	Z100	Z200	Z300	Z400	Z600
20 vol%	l(μm)	95	51	38	29	19
	α	11.1	11.6	11.6	3.8	—
	E_b(V/mm)	1229	1182	1128	1203	—
	ε_{pre}	6.4	6.5	—	—	—
	ε_{brk}	39.1	21.0	—	—	—
	$\varepsilon_{brk}/\varepsilon_{pre}$	6.1	3.2	—	—	—
30 vol%	l(μm)	51	28	20	16	10
	α	19.7	22.2	19	3.8	—
	E_b(V/mm)	1083	948	1098	1333	—
	ε_{pre}	9.9	9.4	9.3	9.6	9.8
	ε_{brk}	75.7	35.4	32.0	15.4	14.5
	$\varepsilon_{brk}/\varepsilon_{pre}$	7.6	3.8	3.4	1.6	1.5

Formula control of the ZnO fillers

ZnO varistors are composed of ZnO and small amount of elements such as Bi_2O_3, MnO_2 and Al_2O_3 etc. The electric properties of ZnO varistors can be adjusted through controlling the content of each element. As the electric properties of composites with large amount of ZnO fillers are determined by the ZnO fillers, it is possible to modify the conductivity and dielectric properties by changing the content of the elements.

MnO_2 can either segregate to the ZnO grain boundary, forming the interfacial state to raise the barrier height of grain boundary and endow the boundary with nonlinear electrical property, or dissolve in the ZnO grain to alter the resistivity of ZnO grain. Bi_2O_3 can also segregate to the grain boundary to form the interfacial state. Moreover, it can also adjust the grain size by forming liquid phase in the sintering process. Slight quantity of Al_2O_3 introduced into grain acts as the acceptor, which can decrease the grain resistivity. However opposite effect occurs, i.e. the aluminum ion acts as donor and increase the resistivity, when the amount of Al_2O_3 exceeds critical value.[15]

Table 4. the influence of the doped element on the electric properties of the composites

Doped element	conductivity properties			Dielectric properties		
	E_b	α	J_{pre}	ε_{pre}	ε_b	$\varepsilon_b/\varepsilon_{pre}$
MnO_2	--	↑↓	--	↑↓	↑↓	↑↓
Bi_2O_3	↓	--	--	↑	↑	↑
Al_2O_3	↑	--	↑	↓	↓	↓

By adjusting the content of Bi_2O_3, MnO_2 and Al_2O_3 in ZnO, the electric properties of the composites is changed and the results are shown in table 4, where '↑' means that the parameter is enhanced with the element content, '↓' represents that the parameter decreases with the element content, '--' means that the parameter has no relationship with the element content, and '↑↓' indicates that the parameter increases first and then decreases with the element content. Each element shows different impact on the electric properties of the composites. The amount of MnO_2 affects the nonlinear conductivity and dielectric properties at the same time, while the content of Bi_2O_3 and Al_2O_3 only influences the nonlinear dielectric coefficient, which exhibits another way to decouple the control of conductivity and dielectric permittivity.

SUMMARY

The nonlinear electrical properties of the silicone rubber polymer composites highly depend on the volume fractions and characteristics of doped ZnO varistor fillers. According to the different application requirements in power systems, the silicone rubber polymer composites with various nonlinear parameters are generally expected. In this paper, ZnO varistor fillers with different breakdown voltages and nonlinear coefficients were produced by changing the formula and sintering process. Then the ZnO varistor fillers were doped into the silicone rubber matrix, in order to gain the polymer composites with various nonlinear parameters. The nonlinear dielectric and conductivity properties of the polymer composite samples composed of different types of ZnO varistor fillers were investigated and discussed in detail. The experiment results show that the nonlinear electrical properties of the silicone rubber polymer composites can be well controlled by doping ZnO varistor fillers with special characteristics. There is also a potential of decoupled control of the nonlinear conductivity and dielectric properties by size or formula control, which is important to HVDC applications due to their requirements of both conductivity and dielectric properties.

Acknowledgments

This work is supported by the National Science Foundation of China (NSFC), Grant 51007046.

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