

Dielectric and thermal properties of micro/nano boron nitride co-filled EPDM composites for high-voltage insulation

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Ethylene propylene diene monomer (EPDM) is a polymeric material widely used for high-voltage insulation. This work reports the dielectric and thermal properties of EPDM co-filled with micro- and nano-BN particles. EPDM composite samples with different micro and micro/nano co-filled contents are prepared by melt-blending and followed by hot press application. Measurements were made including broadband dielectric spectroscopy, thermogravimetric analysis and thermal conductivity. Experimental findings indicate that Micro-25 wt% + Nano-5 wt% performs better in terms of dielectric loss and conductivity whilst the dielectric constant is measured lower in Micro-29 wt% + Nano-1 wt% relative to the equivalent micron filled Micro-30 wt%. Moreover, the initial degradation temperature and final residual masses of co-filled composites are found considerably higher. The thermal conductivity of EPDM is highly influenced by the introduction of co-filled set of particles and it is measured about 0.465 W/m.K in Micro-29 wt% + Nano-1 wt% which is 18% higher than Micro-30 wt%. It is likely that the denser packing geometry due to co-filled set of particles inside the EPDM matrix improves the dielectric and thermal properties which make such composites more attractive for electrical insulation applications.

1. Introduction: In early development of polymeric insulation, pristine form of polymers was engaged for high-voltage (HV) insulation. Later on, it was observed that conventional and pure polymers did not meet the HV insulation requirements and the trend of introducing filler particles was started to enhance the electrical and mechanical properties of insulators [1, 2]. Initially, micro-fillers were introduced and such addition enhanced resistance against electrical tracking, erosion, long-term damage by partial discharge and also improved thermal performance [3].

In recent years, polymeric nanocomposites insulation with excellent insulating properties has been introduced for HV applications [4, 5]. Ethylene propylene diene monomer (EPDM) is a leading polymer after silicone rubber for HV outdoor insulators [6, 7]. EPDM is widely used in electrical insulators because of superior electrical properties, flexibility over a wide temperature range and resistance to moisture and weather [3, 8]. In addition to that, EPDM-based cables are often used for power delivery and control of power components. In harsh operating environments such as nuclear power plants, EPDM is used for the required insulation of cables which are exposed to thermal and nuclear radiations [9].

A combination of both micro- and nano-fillers is another approach to improve the dielectric and thermal performance of insulation and to reduce the overall cost [10, 11]. Enhanced partial discharge resistance was earlier reported by the authors, achieved by adopting the micro and nano co-filled composite topology [12, 13]. Moreover, excellent electrical tracking performance of micro and nanohybrid particles addition in silicone rubber with surfactant against dry band arcing was also reported [14]. Recently, Khattak *et al.* [15] investigated the impact of multi-stresses on the dielectric strength, material properties and leakage current parameters of EPDM micro and nanocomposites and life estimation statistics was described using the leakage current data of composites.

To date, studies in order to explain the dielectric and thermal properties of EPDM with co-filled set of particles are sparse. This Letter presents the experimental work and findings on the

dielectric properties, thermal stability and thermal conductivity of micron and micro + nano boron nitride (BN) filled EPDM composites.

2. Experimental: Keltan@2470-EPDM with Mooney viscosity of 22 MU and density of 0.86 g/cm³ was used for composite fabrication. This raw EPDM contains 69% of ethylene and 4.2% of ethylenenorbornene which is a bicyclic monomer. BN particles (5 µm and 50 nm) were procured from Beijing DK Nano Technology, China. Both BN particles were modified with silane coupling agent γ -methacryloxypropyl trimethoxy silane KH570 and its chemical structure is $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$. Dicumyl peroxide (98% active) was used as curing agent and obtained from Weng Jiang Reagent, China.

Initially, the required amount of EPDM was melted at 90°C at a moderate speed of 20 rpm for 2 min in HAAKE PolyLab QC torque rheometer. After that, pertinent amount of micron particles was mixed for 10 min and the rotational torque was increased to 120 rpm. Subsequently, nanoparticles were added and mixed for the next 10 min. The curing agent Dicumyl peroxide (DCP) (2 wt%) was mixed for 8 min in the cross-composite compound in the last stage of the fabrication. Finally, the cross-composites were hot pressed by compression moulding at a temperature of 170°C with a pressure of 10 MPa for 30 min.

The dielectric response was recorded with the help of a Novocontrol broadband dielectric spectrometer operating at room temperature and 1.0 Hz–1.0 MHz frequency range. For dielectric response, disc-shaped samples with diameter of 40 mm were prepared. All the composites were sputter-coated and overlaid with a gold electrode of 30 mm diameter. The dielectric permittivity (real and imaginary), equivalent capacitance and conductivity of the samples were obtained using the dielectric spectroscopy over the broadband of frequency. The real and imaginary parts of permittivity which form the complex permittivity are given below:

$$\epsilon_r = \epsilon'_r + j\epsilon''_r \quad (1)$$

where ϵ' and ϵ'' are the real and imaginary parts of the relative permittivity of the samples. Moreover, the dielectric loss tangent ($\tan \delta$) can be computed by the following expression:

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (2)$$

Furthermore, the equivalent parallel capacitance of the samples was recorded over the wide frequency spectrum and the dielectric constant (k) was obtained through the parallel-plate capacitance using the following equation:

$$k = \frac{C_p \cdot d}{\epsilon_0 \cdot \pi \cdot r^2} \quad (3)$$

here, C_p is the measured equivalent parallel capacitance, d denotes the thickness of the test sample, ϵ_0 is the permittivity of vacuum and r is the gold overlaid electrode radius.

Moreover, thermogravimetric analysis (TGA) was performed using a Mettler Toledo TGA-851 instrument. The sample mass was controlled in a ceramic crucible at around 12 mg and heating was ramped up at the rate of 20°C/min from 50 to 800°C. Furthermore, thermal conductivity experiments were completed using a Netzsch LFA 447 NanoFlash instrument and 10 mm × 10 mm × 1 mm specimens were used for such measurements.

3. Results and discussion: The results of real permittivity and dielectric loss tangent of all samples are shown in Fig. 1. Figure 1 shows that the real permittivity values of the filled composites are measured higher relative to the unfilled EPDM sample and related to the particle contents. Dielectric spectroscopy results show that real permittivity values increase with increasing particle content over frequency range from 1 MHz to 1 Hz. It can be due to interfacial polarisation and insufficient time for orientation to follow the changing field direction [2]. As seen from Fig. 1, the dielectric loss tangent of composites increases with increasing particle content. Moreover, it is measured relatively high in the low frequency band, especially in unfilled sample. It could be due to moisture uptake ability of EPDM polymer. Micron-10 wt%, Micro-20 wt% and their co-filled counterparts exhibit marginal

increment in the loss tangent values in the low-frequency band. Conversely, this increment is seen significantly higher in the Micro-30 wt% and its compeers.

In order to explore the relative performance of samples, the dielectric constant, tan delta and conductivity results of composites are compared at $f=1$ kHz as shown in Table 1. It shows that these parameters decreased with the nano-BN doping in the co-filled composites. All three measurements are observed lower in Micro-5 wt%+Nano-5 wt% compared to Micro-10 wt%. Furthermore, the dielectric constant and conductivity of Micro-17.5 wt%+Nano-2.5 wt% are seen noticeably lower but the dielectric loss tangent is marginally higher relative to Micro-20 wt%. The tan delta and conductivity of Micro-25 wt%+Nano-5 wt% are noticed substantially lower by 24 and 42% relative to Micro-30 wt% while the dielectric constant of Micro-29 wt%+Nano-1 wt% is measured 18% lower than Micro-30 wt%.

From the experimental findings, it can be clearly noticed that the dielectric performance of co-filled samples is enhanced as compared to their micron filled counterparts. For micron+nano BN co-filled EPDM composites, nano-BN can fill the gaps among micron-BN particles and act as a bridge between EPDM and micron particles. This may produce a phase interface which can significantly impact on the dielectric performance [16].

The TGA curves of the selected composites are compared in Fig. 2. The initial degradation temperature (IDT) is measured at 320, 325, 325 and 327°C for 0 wt%, Micro-10 wt%, Micro-20 wt% and Micro-30 wt%, respectively. A noticeable increment is seen in the IDT with increasing micron contents. It suggests that the addition of particles in the pure EPDM matrix can enhance the thermal stability characteristics. For the co-filled composites, the IDT of Micro-17.5 wt%+Nano-2.5 wt% and Micro-27.5 wt%+Nano-2.5 wt% are 342 and 340°C which are higher by 17 and 13°C relative to their micron-filled counterpart (Micro-30 wt%). Moreover, the residual mass of the samples at the final temperature of 800°C is another metric for the estimation of thermal stability [17]. The final residual mass of 0 wt%, Micro-10 wt%, Micro-7.5 wt%+Nano-2.5 wt%, Micro-20 wt%, Micro-17.5 wt%+Nano-2.5 wt%, Micro-30 wt% and Micro-27.5 wt%+Nano-2.5 wt% are 8, 15, 23, 26, 33 and

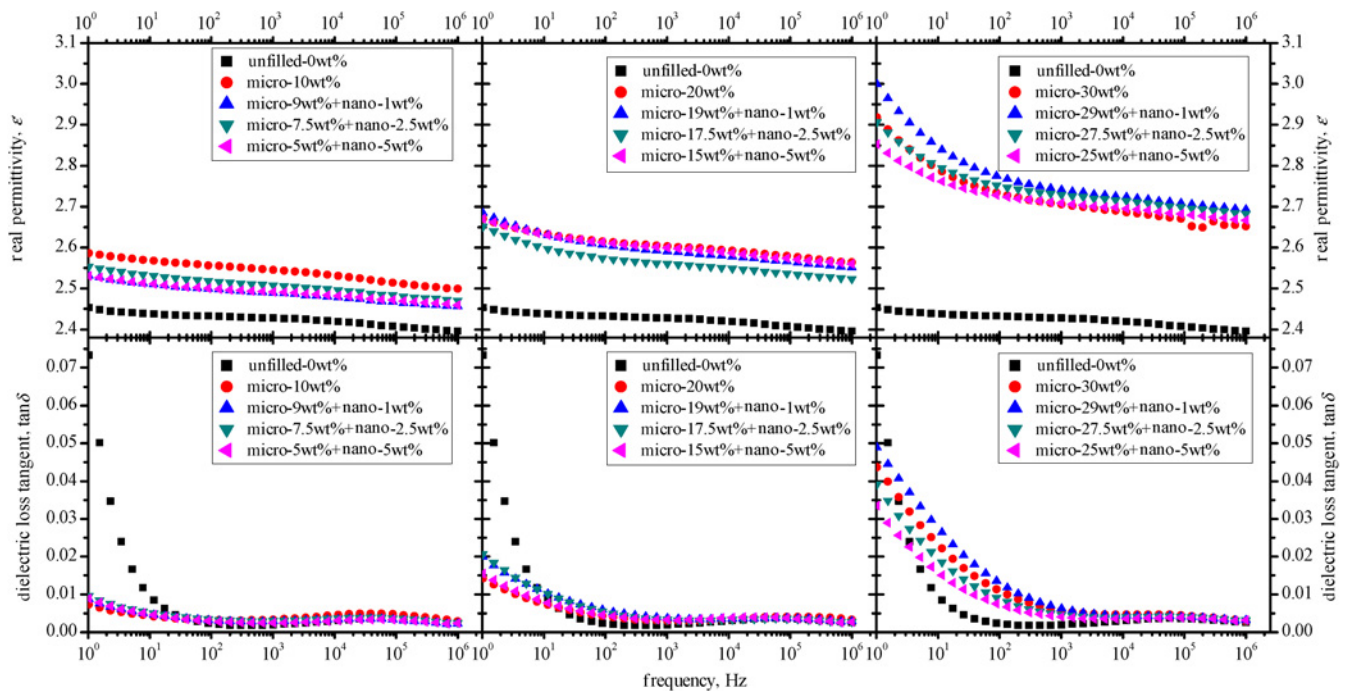
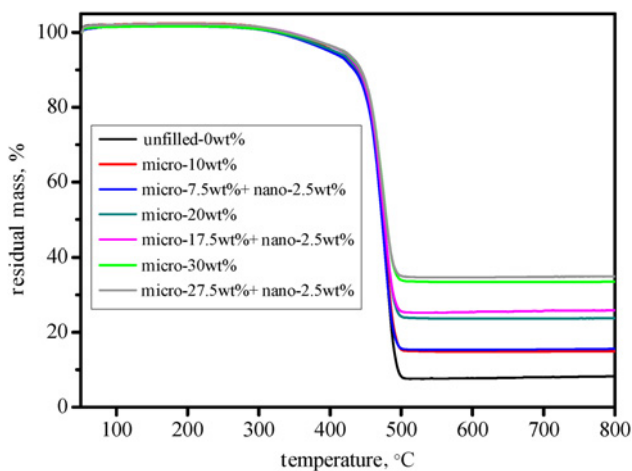


Fig. 1 Real permittivity and dielectric loss tangent of samples over the broadband range of frequency

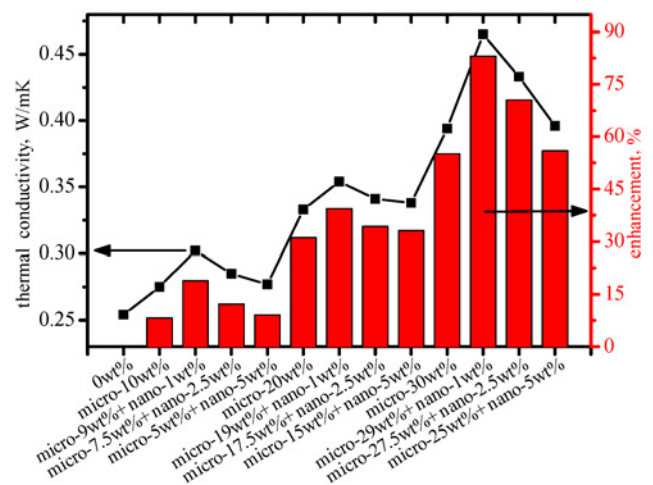
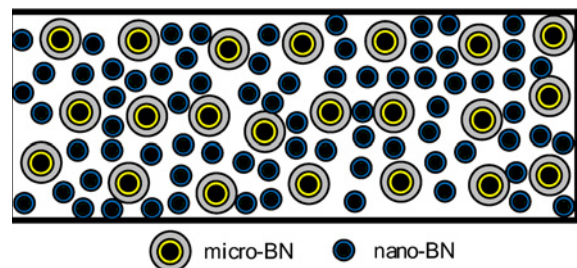
Table 1 Different parameters of dielectric properties at 1 kHz frequency

Sample	Real permittivity (ϵ')	Imaginary Permittivity (ϵ'')	Capacitance (C_p), F	Tan δ	Dielectric constant (k)	Conductivity, S/cm
0 wt%	2.42641	5.08×10^{-03}	1.34×10^{-11}	0.00209	2.4333	3.78×10^{-12}
micro-10 wt%	2.54307	8.80×10^{-03}	1.45×10^{-11}	0.00346	2.5443	6.54×10^{-12}
micro-9 wt% + Nano-1 wt%	2.4889	7.00×10^{-03}	1.21×10^{-11}	0.00281	2.5690	3.95×10^{-12}
micro-7.5 wt% + Nano-2.5 wt%	2.50822	7.60×10^{-03}	1.23×10^{-11}	0.00303	2.5128	4.29×10^{-12}
micro-5 wt% + Nano-5 wt%	2.49137	6.14×10^{-03}	1.18×10^{-11}	0.00246	2.4926	3.47×10^{-12}
micro-20 wt%	2.60105	7.62×10^{-03}	1.43×10^{-11}	0.00293	2.6023	5.67×10^{-12}
micro-19 wt% + Nano-1 wt%	2.59015	9.61×10^{-03}	1.39×10^{-11}	0.00371	2.5914	5.43×10^{-12}
micro-17.5 wt% + Nano-2.5 wt%	2.56049	8.60×10^{-03}	1.39×10^{-11}	0.00336	2.5617	4.80×10^{-12}
micro-15 wt% + Nano-5 wt%	2.59926	8.50×10^{-03}	1.35×10^{-11}	0.00327	2.6005	4.86×10^{-12}
micro-30 wt%	2.70165	1.43×10^{-02}	1.82×10^{-11}	0.00528	2.7029	1.06×10^{-11}
micro-29 wt% + Nano-1 wt%	2.74089	1.70×10^{-02}	1.21×10^{-11}	0.00622	2.2197	9.62×10^{-12}
micro-27.5 wt% + Nano-2.5 wt%	2.72924	1.27×10^{-02}	1.20×10^{-11}	0.00464	2.7305	7.15×10^{-12}
micro-25 wt% + Nano-5 wt%	2.70834	1.09×10^{-02}	1.27×10^{-11}	0.00401	2.7096	6.14×10^{-12}

**Fig. 2** TGA profiles of selected composites

35%, respectively. From TGA results, it can be conclusively said that thermal stability is considerably enhanced by addition of particles. Moreover, nano-BN addition in the micron-filled samples also improves the interactions of EPDM with micron-particles which restricts the thermal depolymerisation mechanism of EPDM and enhances the thermal stability.

Fig. 3 shows the effects of particle loading on the thermal conductivity of EPDM micron and micron/nano co-filled composites. It is obvious that addition of particles significantly enhanced the thermal conductivity of the resultant composites. The thermal conductivity of Micro-10 wt%, Micro-20 wt% and Micro-30 wt% is enhanced by 8.3, 31 and 55%, respectively, as compared to unfilled-0 wt% EPDM. As far as co-filled composites are concerned, the thermal conductivity results are much improved relative to their equivalent micron-filled composites. It can be seen that the thermal conductivity of Micro-29 wt%+Nano-1 wt% is about 0.465 W/m.K which is higher by 83 and 18% relative to 0 wt% and Micro-30 wt%, respectively. The use of co-filled particle system may result in a more compact packing pattern in the EPDM and formation of random networks from conductive BN particles and this may assist phonon transfer leading to higher thermal conduction ability [18]. Hence, the denser the packing geometry inside the EPDM matrix, the higher the thermal conductivity is as illustrated in the package model of Fig. 4. Micro-29 wt%+ Nano-1 wt% offers the highest thermal conductivity relative to Micro-30 wt% and it could be due to the uniform dispersion of nano-BN particles. It is likely that the nano-particles at lower

**Fig. 3** Thermal conductivity of composites**Fig. 4** Packing model of micro- and nano-BN particles in co-filled composites

concentration are more effective in filling the gaps. Furthermore, successive enhancement in the doping of nano-BN contents may decrease the thermal conductivity due to agglomeration of nano-particles in the co-filled composites.

4. Conclusion: The enhanced dielectric and thermal properties of micron BN filled EPDM are achieved by fabricating its co-filled composite with addition of a small amount of nano-BN particles. The dielectric constant, dielectric loss tangent and conductivity of co-filled composites are significantly improved relative to micron-filled counterparts. The tan delta and conductivity of

Micro-25 wt% + Nano-5 wt% is observed significantly lower while Micro-29 wt% + Nano-1 wt% showed much lower dielectric constant relative to micron compeers. The IDT and residual mass of samples confirm excellent thermal stability of the co-filled composites. They also offer substantial enhancement in the thermal conductivity due to compact packing structure. Micro-29 wt% + Nano-1 wt% offers the highest thermal conductivity relative to Micro-30 wt%.

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