

Preparation and characterization of EPDM-silica nano/micro composites for high voltage insulation applications

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The rising market for substitute materials in high voltage insulation components is stimulated largely by the need to reduce overall costs. In this respect, polymer insulators offer significant advantages over old traditional materials. In the present research, efforts have been made to quantify the effect of silica (having different particle size nano, micro and hybrid) loading on the mechanical and thermal behaviors of Ethylene-Propylene-Diene Monomer (EPDM) based high voltage electrical insulations. The fabricated composites were subjected to mechanical, thermal and electrical properties measurements. The results of dielectric strength, surface and volume resistivities showed that all composites had insulator properties, while their mechanical and thermal properties improved considerably. EPDM was compounded with different types of silica in a two roll mill using sulphur cure system. The outcome achieved from the comparative study revealed that the EPDM nanocomposites had enhanced mechanical, thermal and electrical properties even at 5 % loadings.

Keywords: *EPDM; nanocomposites; thermal stability; surface and volume resistivity; dielectric strength*

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1. Introduction

Nanodielectrics are the fastest growing area of electrical insulation, in which nanoparticles filled composite materials improve the properties of the base polymer. Nanoparticles can enhance electrical, thermal and mechanical properties of the composite materials [1–3]. The nanoparticles have high surface area-to-volume ratio, which provides large interaction zone in nanocomposites as compared to microcomposites. The properties enhancements in nanocomposites are mainly attributed to this interaction zone and nanoparticles dispersion in the polymer matrix. This interaction zone is more widespread in nanocomposites than in conventional composites, due to which it has a noteworthy impact on their electrical, mechanical, thermal and other properties [4, 5]. The free volume in these interaction zones is altered by the addition of nanofillers. As interaction zones are likely to overlap at relatively low volume fractions in nanocomposites, a small loading of nanofiller has been found to

enhance the electrical properties [6, 7]. For good dispersion and distribution of nanoparticles in a polymer matrix, selection of appropriate processing parameters is very important [8].

In this work we have used a polymer matrix Ethylene-Propylene-Diene (EPDM), which belongs to the leading synthetic rubber's family, widely utilized in automotive weather-stripping and seals, radiators, electrical insulations, roofing membranes, tubing, belts, and other general purpose applications [9]. EPDM is a terpolymer, in which ethylene and propylene monomers provide a saturated backbone and non-conjugated diene monomers provide unsaturated chains.

The prominent characteristics of EPDM are excellent electrical properties due to its non-polar structure and its saturated backbone makes it resistant to oxidation and thermal aging and easy to process at low temperature [10]. This work was devoted mainly to developing EPDM composites for high voltage outdoor insulations. Inorganic fillers have a key role in enhancement of desired properties of polymers [11, 12]. Modification of inorganic fillers with organic materials results in improvement of dispersion properties [13]. Fillers used in

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this study were nano-sized silica (12 nm SiO₂) and micro-sized silica (5 µm SiO₂). Various samples of EPDM (virgin), EPDM microcomposites, EPDM nanocomposites and hybrid EPDM composites (micro + nano) were prepared. Mechanical properties, such as tensile strength, elongation at break and hardness were measured. TGA was carried out to study the thermal stability of the composites. Electrical properties, such as dielectric strength, volume and surface resistivity of the composites were investigated.

2. Experimental

2.1. Materials

Ethylene Propylene Diene Monomer (EPDM) was purchased from Kelton, Germany. Nanosilica (12 nm) was purchased from Degussa, USA, Micro-silica (5 µm) was purchased from Wuhan Newreach Chemical, China. Other ingredients, including zinc oxide (ZnO), stearic acid, mercaptobenzothiazole (MBT), sulfur (S), tetramethyl thiuram tetrasulfide (TMTD) and dioctyl phthalate (DOP) were of industrial grade products.

2.2. Preparation of EPDM composites

EPDM and fillers were prepared as per formulation recipes depicted in Table 1. The compounding of the EPDM composites was carried out in a two roll mill, according to ASTM D-3182-07 standard. The rolling mill had the rolls of 160 mm in diameter with variable nip gap ranging from 0.2 to 10 mm. The mill was equipped with a cooling water jacket to control the temperature of the rollers, in order to avoid early vulcanization. EPDM composites were prepared by compounding technique. The ingredients were added as per the sequence given in the Fig. 1.

Vulcanization of the compounds was carried out in a compression type hydraulic press under 10 MPa pressure and 170 °C temperature for 45 minutes according to ASTM D3182-89. The optimum curing time was determined using a disk rheometer.

NE = Neat EPDM, EMC = EPDM micro-composite, ENC = EPDM nano-composite,

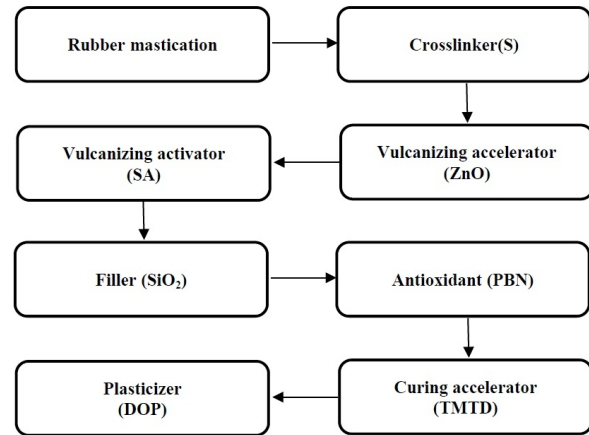


Fig. 1. Sequence of ingredients addition in compounding process.

Table 1. EPDM composites formulation recipes.

	NE	EMC	ENC	EHC
EPDM	100	100	100	100
S	2	2	2	2
ZnO	5	5	5	5
SA	1	1	1	1
PBN	1	1	1	1
MBTS	1	1	1	1
TMTD	1	1	1	1
DOP	2	2	2	2
Nano silica	–	–	6	6
Micro silica	–	23	–	23

EHC = EPDM hybrid composite; all ingredients were used in phr ratio.

3. Analysis and characterization

3.1. Mechanical properties

Tensile mechanical tests were performed on intentionally shaped composite samples using a universal testing machine, Instron (UK). The cross-head speed of machine was 100 mm/min, according to DIN 53504/ASTM D412 standard. For each formulation, 5 to 10 samples were tested and average values were calculated.

The hardness values of the composite samples were measured using a Shore-A durometer based on DIN 53505/ASTM D2240 standard. Hardness

values of each sample were measured at five different points and average results were reported.

3.2. Thermal properties

Thermal properties of pure EPDM and its composites were determined by thermogravimetric analyzer TGA Q50, TA Instruments (USA). The changes in weight at different temperatures were calculated from thermograms, measured under N₂ atmosphere at a scanning rate of 10 °C/min. The experiments were carried out from 25 °C to 600 °C.

3.3. Electrical properties

The dielectric strength measurements were carried out using an alternating voltage, which was gradually increased from zero to the breakdown value as per IEC-60243-1 [14]. The voltage was applied to the composite samples using high voltage generator and breakdown voltage values were recorded. For each formulation, 5 to 10 samples were tested and average values of dielectric strength were reported. Volume and surface resistivity of the composite samples were calculated as per ASTM D257/IEC 60093 standard [15].

4. Results and discussion

4.1. Mechanical properties

Physical and mechanical properties of the EPDM composites, such as ultimate stress, elongation at break and hardness improved by the incorporation of silica fillers, are collected in Table 2. The results of mechanical properties depend upon the particle size of silica.

Table 2. Mechanical properties of EPDM composites.

Code	Stress (kPa)	Elongation (%)	Hardness +
NE	1110.2	244.5	48.4
EMC	1901.2	223.4	57.3
ENC	2042.7	220.2	58.1
EHC	2345.2	216.1	59.2

Considerable enhancement in the tensile properties of all EPDM composites was observed with

respect to different filler loadings. This enhancement was 71.25 % in case of EMC, while 83.99 % in case of ENC and 89.9 % in case of EHC.

This increase was attributed to the uniform dispersion, high surface area, nano/micro level interaction with the polymeric molecular chains and the filler-matrix compatibility of the silica. The ENC composites containing nano silica showed better mechanical properties as compared to the EMC having micro silica as filler even at lower loadings due to larger increase in surface area of the filler particles. The oxygen atoms on the silica surface contributed towards better mechanical properties due to the establishment of hydrogen bonding in the EPDM composites.

The stress values for different composites prepared by incorporation of nano, micro, and hybrid silica as filler are shown in Fig. 2.

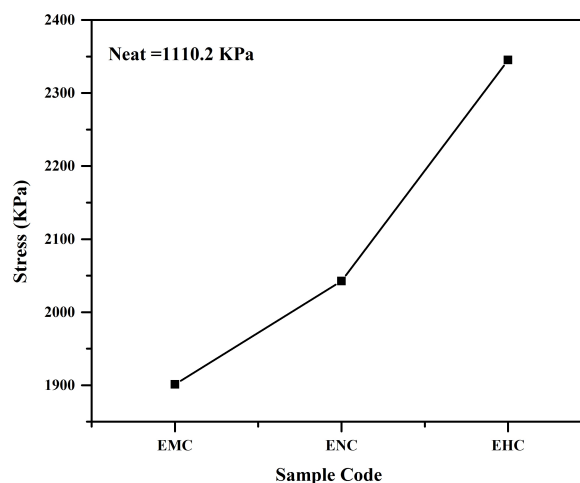


Fig. 2. Stress in various EPDM composites.

The elongation of EPDM composites decreased with the incorporation of fillers. This phenomenon became more prominent as the particle size of fillers decreased. The trend of elongation for different EPDM composites is depicted in Fig. 3.

The decreasing trend of elongation is attributed to the stiffness of composites imparted by the added fillers, which reduced the flexibility of the EPDM composites.

The physical properties, such as hardness of EPDM composites increase with the filler loading.

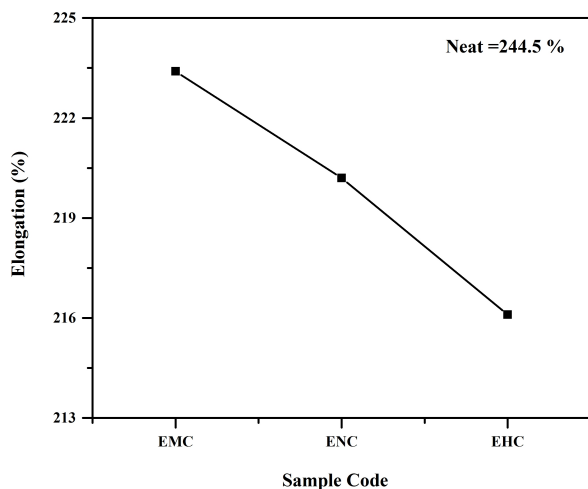


Fig. 3. Elongation for various EPDM composites.

This increase in hardness values is due to the fact that fillers restrict the mobility of polymeric chain, which results in stiffening of rubbers. The ENC composites have greater hardness than EMC composites due to more intensive interaction of filler-polymer network, which reduces the flow ability of polymer matrix. The behavior of hardness for different composites is illustrated in Fig. 4.

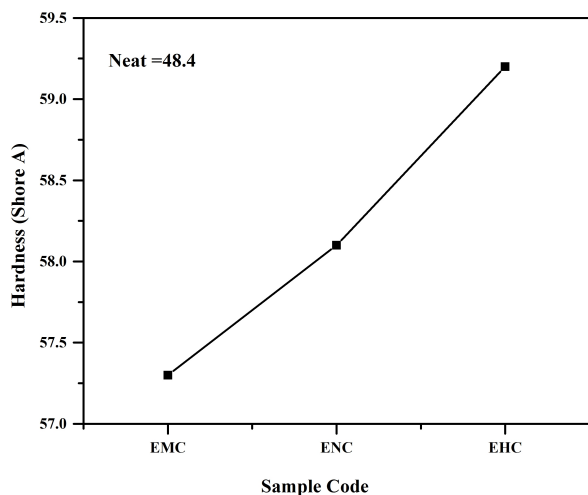


Fig. 4. Hardness for different EPDM composites.

4.2. Thermal properties

The effect of silica fillers on the thermal properties of EPDM composites, such as 10 % weight

loss temperature, polymer decomposition temperature of composites and char yield, was calculated from the thermograms obtained by TGA under the conditions mentioned before. The results of thermal properties are presented in the Table 3.

Table 3. Thermal properties of EPDM composites.

Code	T ₁₀ (°C)	T ₅₀ (°C)	PDT (°C)	Char yield (%)
NE	290	440	467	5.70
ENC	293	447	472	10.18
EMC	297	452	474	16.42
EHC	304	454	475	19.2

The temperature at which 10 % weight loss occurs showed an increasing trend with the reinforcement of fillers in the rubber matrix. The filler-polymer networks minimize the permeability of volatile components in the polymer matrix [16].

The comparison of EPDM composites fabricated using micro, nano and hybrid sized silica demonstrated an increase of T₁₀ as the particle size of silica decreased. The behavior of T₁₀ for various EPDM composites is illustrated in Fig. 5.

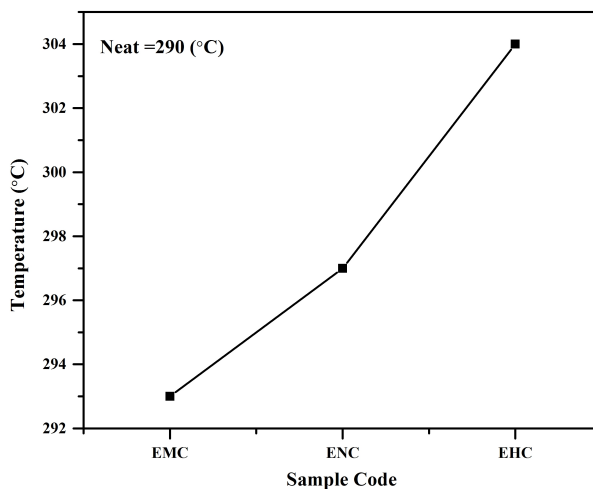


Fig. 5. T₁₀ for various EPDM composites.

The ENC, due to increased surface area, has higher T₁₀ value, even at 5 % filler loading, than EMC containing 20 % filler content.

The temperature, at which 50 % weight loss of polymer composites occurs, showed a similar trend as T_{10} , increasing with inclusion of silica fillers into the rubber matrix. The weight loss at this temperature was mainly caused by the loss of oil and volatile components.

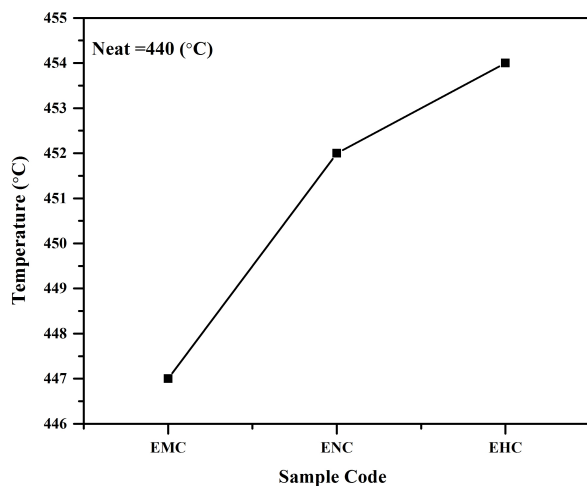


Fig. 6. T_{50} for various EPDM composites.

The T_{50} increases with a decrease of particle size of silica as shown in the Fig. 6, which is attributed to restriction of polymer chain mobility imparted by the filler particles.

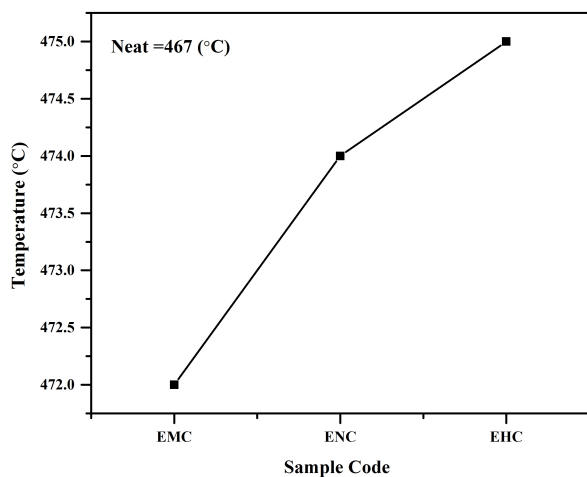


Fig. 7. PDT for various EPDM composites.

The polymer decomposition temperature (PDT) also shifted towards higher temperatures as presented in Fig. 7. This increase of polymer decomposition temperature is due to the silica filler ability

to suppress thermal degradation of the elastomers, which may be caused by barrier effects or a reduction of the pyrolysis rate due to the decrease of the polymer mobility. In fact, it has been shown that polymer chains restrained in the mesoporous structures show greater thermal stabilities [18].

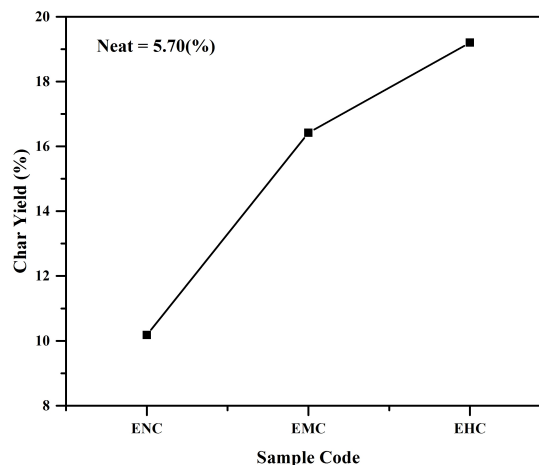


Fig. 8. Char yield for various EPDM composites.

The influence of silica loadings on the char formation of the EPDM composites shown in Fig. 8, shows that char formation of the samples increased with the increase of silica content in the samples. Silica, being a very stable compound, which has not decomposed in the experiment conditions, caused an increase in the char formation.

4.3. Electrical properties

The dielectric strength, surface resistivity and volume resistivity of the EPDM composites were examined and the results are shown in Table 4. The same trend of superior properties for the EHC and ENC has been preserved. This improvement may be attributed to the smaller interspacing distance between the filler particles [17].

The results of dielectric strength measurements were plotted for the EPDM composites having different particle sizes of silica filler. The plot shows that the dielectric strength increases with the decrease in the particles size of the filler as presented in Fig. 9. This behavior is attributed to better interaction of nano-fillers, with matrix and increased

Table 4. Electrical properties of EPDM composites.

Code	Dielectric strength (kV/mm)	Volume resistivity ($\Omega\cdot\text{cm}$)	Surface resistivity (Ω/sq)
NE	19	3E+14	2.1E+14
EMC	20.5	3.4E+14	2.3E+14
ENC	22.3	3.6E+14	2.5E+14
EHC	23.4	3.8E+14	2.6E+14

surface area of the nano fillers, providing strong polymer-filler network.

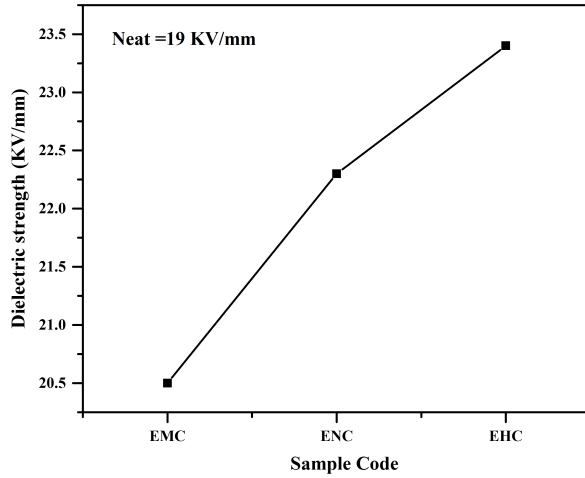


Fig. 9. Dielectric strength for various EPDM composites.

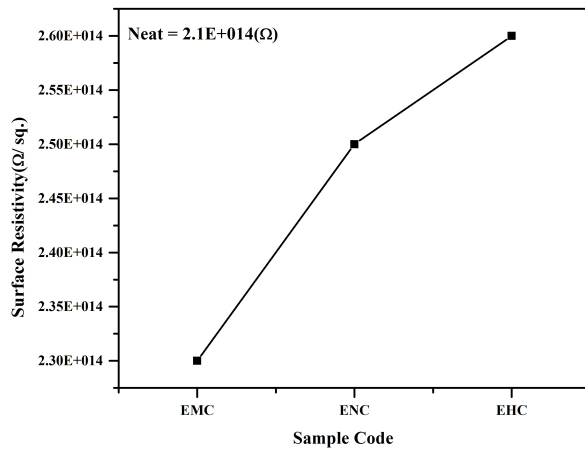


Fig. 10. Surface resistivity for various EPDM composites.

Surface resistivity of EPDM nanocomposite showed a similar trend of increase with the

decrease in the particle size of silica filler. The trends in surface resistivity are shown in Fig. 10. It could be due to the intercalation of nano fillers into the rubber matrix. The silica, having insulating properties, also imparted increasing effect on the surface resistivity of EPDM composites.

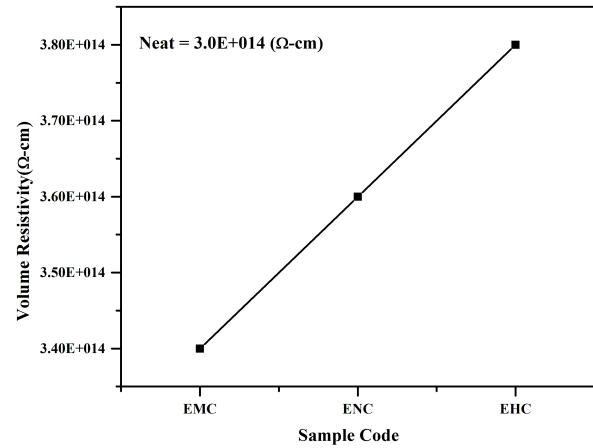


Fig. 11. Volume resistivity for various EPDM composites.

Volume resistivity of EPDM nanocomposite increases with an increase of silica contents as illustrated in Fig. 11. This could be due to the separation of polymeric chains as a result of introduction of silica. The effect is more pronounced in case of nano-fillers which form discrete phases within the EPDM matrix. This could also be attributed to the fact that nano fillers become intercalated in the EPDM matrix, leading to the increase of the electrical resistance of the polymer.

5. Conclusions

From this experimental work following conclusions can be made:

- The EPDM composites have been prepared using appropriately selected processing parameters, such as mixing time, temperature, mixing sequence and curing time.
- The mechanical, thermal and electrical properties of prepared EPDM (pure, micro, nano and hybrid) composites confirm the quality and uniform dispersion of the fillers in the fabricated polymer matrix.
- The EPDM composites demonstrate improved thermal and mechanical properties.
- All prepared composites have insulator properties, which makes them good candidates for high voltage insulation applications.

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