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# Effect Of Nanosilica On Ethylene Propylene Diene Monomer Rubber Nanocomposites

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***Abstract:***

*EPDM nanocomposites based on Nano-silica in combination with other inter fillers in were prepared and studied. Mechanical, Electrical, Thermal and Morphology Characterization of EPDM – Nano Composites were studied. Incorporation of nanofillers in EPDM rubber compound found to increase the thermal resistance of nanocomposites and decrease the electrical resistance properties.*

***Key words****: EPDM, Nano-silica, SEM –EDS, Thermal resistance, Volume resistivity*

## 1.Introduction

In the recent years, polymer nano composites have been proved to be of great interest for researchers as they exhibit extraordinary properties which have many industrial applications. Materials with combination of nano-sized organic / inorganic materials and polymers expected to give the properties that are synergistic combinations of the individual components with the reinforcing components are mostly nano-clay, nano-silica, nano-graphite, carbon nano-tubes (CNT) etc. These are class of organic / inorganic hybrid materials, where the inorganic components are uniformly distributed in nanometer scale (10-100 nm) within the polymer matrix.

Elastomers happen to be reinforced with fillers to improve their performance by incorporating conventional fillers such as carbon blacks, silica, clay, talc and calcium carbonate etc. The nano fillers with very small amount could reinforce the polymer matrix. The resulting polymer nano composites thus comprise nano fillers embedded in a polymerized medium that can be subsequently cross-linked, to obtain vulcanized rubber nanocomposites. Nano-composites made out of nano fillers had shown to afford remarkable property enhancements compared to conventional micro composites [1–3] that were made using conventional fillers. Polymer nano-composites with layered silicates [4–9] and carbon nano tubes [10–12] have attracted major interest for the improvement of structural properties and the development of new materials having different functional properties. Nano-graphite is a layered material with high aspect ratio in its exfoliated state is also considered as one of the strongest materials per unit weight and has unique functional properties e.g. good electrical and thermal conductivities, and good lubricating properties. Acrylonitrile Butadiene Rubber (NBR)-Nano graphite polymer nano composites were found to increase its thermal stability [13]. Mechanical and tribological properties of NBR filled with graphite and carbon black were studied [14]. Effects of Radiation on SBR-EPDM Rubber based Carbon nanotubes composites were reported [15]. SBR – nanoclay based nanocomposites were optimized using face centered central composite design [16].

Ethylene – Propylene- diene monomer (EPDM) is a saturated, non-polar rubber (i.e very low –C=C- content) and it exhibits several properties including balanced heat stability, ageing resistance, water resistance etc. The incorporation of nano silica in polymers found to increase the thermal resistance properties. In this present study, effect of nano silica on thermal properties of EPDM rubber compound was studied.

## 2 Materials and Methods

### *2.1 Materials*

Ethylene Propylene Diene Monomer Rubber (EPDM), Nano silica and other ingredients (like curatives [DCP 40], fillers like vapourlink, clay, Calcium Carbonate, Aluminum trihydride, ZnO, paraffinic oil were obtained from reputed manufacturers and used for studies.

| **Compounding Ingredients** | **ENS 0** | **ENS 3** | **ENS 5** | **ENS 7** |
|---|---|---|---|---|
| EPDM- Vistalon 7500 | 100 | 100 | 100 | 100 |
| Zinc Oxide | 5 | 5 | 5 | 5 |
| Clay | 100 | 100 | 100 | 100 |
| Vaporlink | 20 | 20 | 20 | 20 |
| Calcium Carbonate | 30 | 30 | 30 | 30 |
| Aluminum Trihydroxide | 20 | 20 | 20 | 20 |
| Paraffinic oil | 5 | 5 | 5 | 5 |
| Nano silica | 0 | 3 | 5 | 7 |
| Di- cumyl Peroxide - 40 | 4 | 4 | 4 | 4 |

*Table 1: Compound Formulations*

### *2.2 Methods*

**2.2.1.**Preparation of EPDM-Nano composites

Mixing of Nano silica in EPDM Rubber was carried out along with other rubber compounding chemicals, as per the formulation given in table 1 such as activators, curatives etc in a laboratory two roll with the speed ratio of two rolls were kept at 1 : 1.2. Due care has been taken while mixing the nano fillers in polymer matrix to avoid fly loss. The mixing temperature was maintained at 70 deg C, to ensure good dispersion of nano fillers in polymer matrix.

2.2.2.Rheological Properties And Curing Behavior

Rheological properties were carried out using Rubber Process analyzer [RPA- 2000, Alpha Technologies, USA] at 150˚C as per the ASTM test method. The compound was cured to obtain test slab as per optimum cure time in Hydraulic Press at 150 ˚ C at a pressure of 3000 Psi.

2.2.3.Mechanical Properties

Mechanical properties were measured with a Universal Testing Machine [Zwick 1445, Germany] according to ASTM D 412 standard testing method using a cross head speed of 500 mm per min at 25 +/-2$^{o}$C. Shore Hardness was measured with a Durometer [Stech Engineers, India] as per ASTM D 2240. Tear strength was measured using UTM [Zwick 1445, Germany] as per ASTM D 624 and tested at a rate of 500 mm per min of cross head speed.

2.2.4.TGA Studies

Thermal analysis was carried out using TGA [Q-50, TA instruments USA] to obtain initial temperature of degradation and maximum thermal degradation temperatures. The heating rate was maintained at 20˚C per min over the range from 70 to 900˚C under N2 inert atmosphere.

2.2.5.XRD Studies

X-Ray patterns were recorded using X-Ray Diffractometer, [Shimadzu, Japan] with X ray tube Cu Kα having wave length of $\lambda$ = 1.54060 A, voltage of 40 KV and current of 30 mA, under continuous scanning mode at a scan speed of 2$^{o}$ / min in the range of 2ɵ from 0 to 30. The d spacing was calculated using the Bragg's Law formula $2d\sin\theta = n\lambda$ .

2.2.6.Thermal Ageing

Thermal ageing of polymer nanocomposites were carried out using air circulating ageing oven at 200˚C / 24 hrs. After ageing, the physical properties like Tensile strength, Elongation at break, Hardness were measured and compared with the original values of PNCs.

2.2.7.Volume Resistivity

Volume Resistivity of Vulcanized sheets obtained from polymer nanocomposites were measured using Million Mega Ohm meter as per ASTOM D 257, at a input voltage of 500 V.

2.2.8.SEM – EDS Analysis

Morphological studies of polymer nano composites were carried out using Scanning electron microscope [SEM, Zeiss Instrument] combined with EDS system.

## 3. Results and Discussion

### *3.1.Rheological Properties*

Vulcanization reaction studies were carried out using Rheometer. Rheological data obtained in this study reported in table 2. The scorch time and optimum cure time slightly increases with increase in dose of Nano filler concentration, which could be due to intercalation of nano filler between the polymer matrix restricts the free radicals to come closures to cross linking and leading to hinder the curative and matrix interaction.

| **Rheological Properties** | **ENS 0** | **ENS 3** | **ENS 5** | **ENS 7** |
|---|---|---|---|---|
| Scorch time, ts2, min | 1.6 | 1.7 | 1.8 | 1.8 |
| Cure time t 90, min | 21.5 | 22.6 | 22.8 | 22.4 |

*Table: 2: Rheological properties*

### *3.2.Mechanical Properties*

Stress –Strain properties of nanocomposites were studied at room temperature using Zwick Tensile Tester. The results obtained from these stress – strain studies are reported in table

| Properties | ENS 0 | ENS 3 | ENS 5 | ENS 7 |
|---|---|---|---|---|
| Tensile Strength (MPa) | 4.2 | 4.8 | 4.9 | 4.3 |
| Modulus @ 100 % (MPa) | 2.1 | 2.3 | 2.5 | 1.9 |
| Modulus at 300 % (MPa) | 2.6 | 2.7 | 2.9 | 2.3 |
| Elongation at break % | 640 | 620 | 610 | 600 |
| Hardness (Sh A) | 67 | 68 | 69 | 70 |

*Table: 3: Physico-mechanical properties*

The stress strain properties indicates that the nano filler improves the physical properties from 11 % to 20 % at an optimum level of 5 phr of nanosilica filler loading and then decreases with further loading (7 phr).Studies suggest that after a loading of certain phr of nanosilica fillers it acts as blocking agent between matrix and curing agent which reduces chemical interaction between two and consequently leads to weaken the strength and modulus of the cure compounds. The hardness was increasing from 67 to 70 as reported in **table 3** with the increase in nano filler loading from 0 to 7 phr. Thus the nano silica play a vital role in increasing hardness of the poymer nanocomposites without compromising other properties.

*3.3.Thermal Ageing*

The thermal ageing of polymer nano composites were carried out at $200^{o}$ C for 24 hrs. The results of changes in properties of polymer nanocomposites are reported in table 4.

| % Changes in properties | ENS 0 | ENS 3 | ENS 5 | ENS 7 |
|---|---|---|---|---|
| Tensile Strength | -52 | -44 | -30 | -23 |
| % Elongation at break | -83 | -81 | -81 | -80 |

*Table 4: Physical properties after thermal ageing at $200^{o}$ C for 24 hrs*

The retention of tensile strength found to improve almost 50 % with the nano filler loading with 7 phr compared to the unfilled composites. The ageing resistance found improving linearly with the incorporation of nano fillers. In general, it was also found that nano fillers improve the heat and thermal stability. This shows that the nano filler contributes considerably in improving thermal resistance of the composites. This can be again attributed to the filler incorporation which is considerably a thermally stable

material and this does not allow much molecular movement of rubbery chain against the temperature.

*3.4.TGA Studies*

Fig. 1 depicts the thermograms of EPDM nanocomposites. It was observed that there is an increase in initial and maximum degradation temperature of EPDM nanocomposites with increase of content of silica nano filler which is thermally more stable.

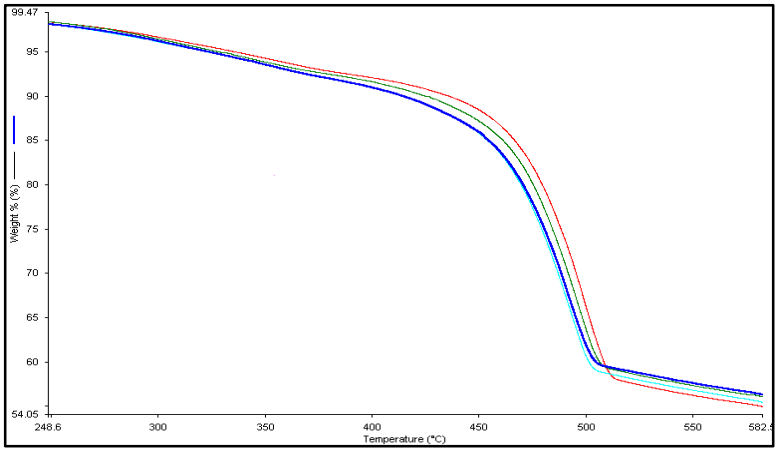


*Figure 1: Thermo gram of Polymer nano composites*

As the loading of nano fillers increases, there is an increase in thermal stability due to increase filler – polymer interaction and thereby occurring strong net works and bonds between the polymers and the fillers. Therefore, the initial and maximum degradation temperature increases with the increase of nano fillers as shown in the TG Graphs.

*3.5.XRD Studies*

The XRD studies revealed that incorporation Nano Silica particles in EPDM polymer matrix leading to reduction in d spacing. This could be due to the intercalation of silica nano particles between the EPDM polymer chains.

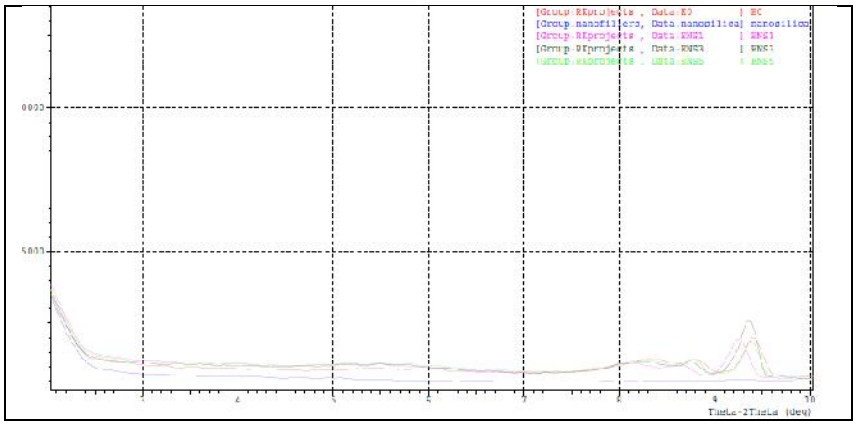

*Figure 2: XRD graphs of PNCs with different loading of nano silica*

*3.6 Volume Resistivity*

Fig.3 shows that Volume resistivity of EPDM Nanocomposite decreases with an increase of silica nanofillers. This could be due to the separation of polymeric chains due to the introduction of silica Nano fillers which form discrete phases within the EPDM matrix. This could also be attributed to the fact that Nano fillers gets intercalated in the EPDM matrix, leading to increase of the electrical resistance of the polymer.

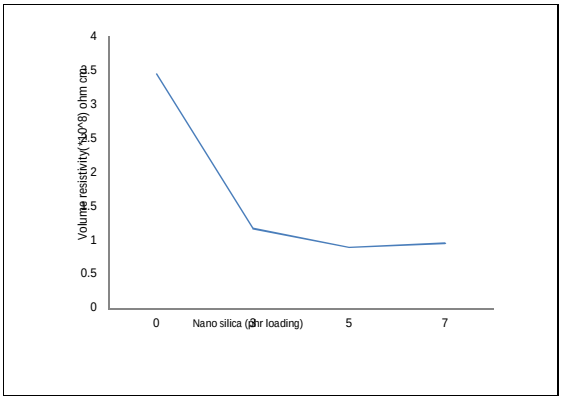


*Figure 3: Electrical properties of EPDM Based Nano silica composites*

*3.7. SEM – EDS Analysis*

Morphological characterization of the nanocomposites was carried out using a Carl Zeiss 5800 Digital Scanning Electron Microscope (SEM). Fractured surfaces of the nanocomposites were examined under the SEM. The images were obtained at a tilt angle of $0^o$ with an operating voltage of 20 kV. The fig. 5 a, 5c, & 5e depicts the SEM photographs of the EPDM nanocomposites in which the uniform dispersion of silica nano particles in polymer matrix.

Further to corroborate the above dispersion study, EDS spectroscopic studies were also taken on the scanned area of SEM micrographs to locate the dispersed silica Nano particles. The fig. 5b, 5d & 5f depicts the EDS spectra and these figures shows that as the loading of silica nano filler increases in the EPDM nanocomposites, the intensity of Nano Silica also found denser than that of the nano composite with the lower concentration of silica nano filler.

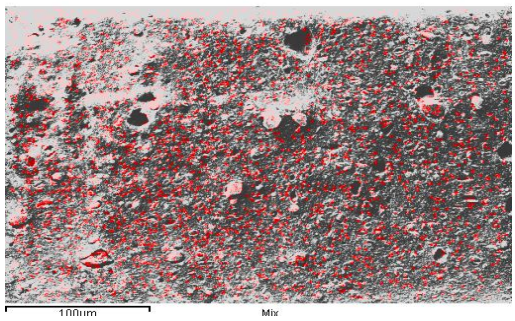


*Figure 5(a): SEM image of ENS with 3 phr loading*

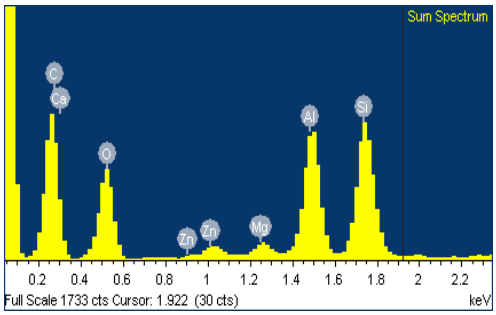


*Figure 5(b): EDS spectra of ENS with 3 phr loading*

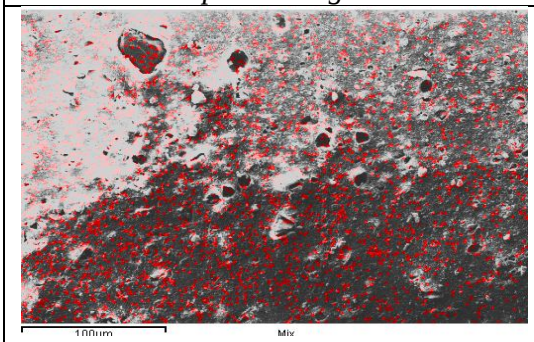


*Figure 5(c): SEM image of ENS with 5 phr loading*

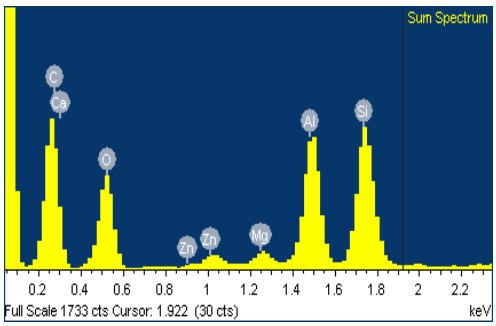


*Figure 5(d): EDS spectra of ENS with 5 phr loading*

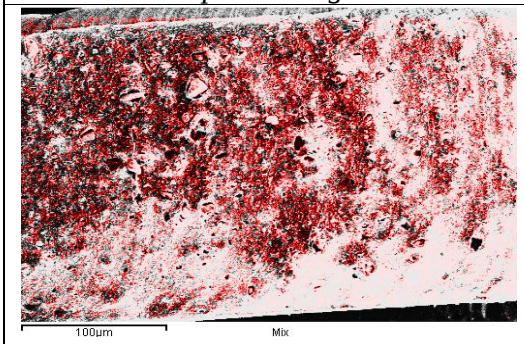


*Figure 5(e): SEM image of ENS with 7 phr loading*

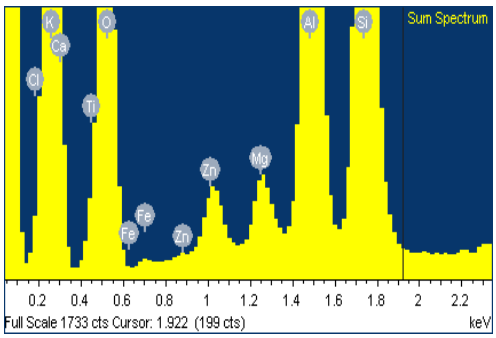


*Figure 5(f): EDS spectra of ENS with 7 phr loading*

*Figure 5: SEM-EDS Analysis of Nano Silica Mapping in EPDM Rubber*

**4.Conclusion**

Silica Nano particle fillers showed improvement in the physico-mechanical properties of EPDM nano composites with increasing loading of nanofillers. The increase in retention of physical properties was also found with the increase of loading of nano fillers in the EPDM nanocomposite. Thermo gravimetric analysis corroborated the above findings by way of increase in thermal stability of EPDM nano composites with an increase in loading of nano fillers. SEM –EDS studies revealed the uniform dispersion of silica nano particles within the EPDM polymer matrix. Further, the electrical resistance of EPDM nanocomposites found decreasing with an increasing dose of nanofillers.

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