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RESEARCH ARTICLE

Mechanical, Thermal, Electrical and Morphology Characterization of Ethylene Propylene Diene Monomer - Nanoclay Composites

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Abstract: The effect of nanoclay in combination with other inter fillers in ethylene propylene diene monomer (EPDM) rubber vulcanizate were studied. Curing characteristics were carried out using rubber process analyzer (RPA). Mechanical, thermal and morphology characterization of EPDM - nanoclay composites were studied.

Keywords: EPDM, Nanoclay, SEM - EDS, Thermal resistance, Volume resistivity

Introduction

In the recent years, polymer nanoclay composites are 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 (10-9 nm) within the polymer matrix.

Elastomers were 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 nanoclay in polymers found to increase the thermal resistance properties. In this present study, effect of nanoclay on thermal properties of EPDM rubber compound was studied.

Experimental

Ethylene propylene diene monomer rubber (EPDM), nanoclay powder 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.

Techniques

Preparation of EPDM-nanoclay composites

Mixing of nanoclay 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.

Table 1. Compound formulations

Compounding Ingredients	E 0	ENC 3	ENC 5	ENC 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
Nanoclay	0	3	5	7
Di- cumyl peroxide - 40	4	4	4	4

Rheological properties and curing

Rheological properties were carried out using rubber process analyzer (RPA- 2000, Alpha Technologies, USA). The compound was cured as per optimum cure time in hydraulic press at 150 ^{o}C at a pressure of 3000 Psi.

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.

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 ^oC per min over the range from 70 to 900 ^oC under N_2 inert atmosphere.

XRD studies

X-Ray patterns were recorded using X-ray diffractometer, (Shimadzu, Japan) with X ray tube Cu Kα having wave length of λ= 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 2θ from 0 to 30. The d spacing was calculated using the Bragg's Law formula $2d\sin\theta = n\lambda$

Thermal ageing

Thermal ageing of polymer nanocomposites were carried out using air circulating ageing oven at 200^o C for 24 h. After ageing, the physical properties like tensile strength, elongation at break were measured and compared with the original values of PNCs.

Volume resistivity

Volume resistivity of vulcanized sheet was measured using Million Mega Ohm meter as per ASTM D 257.

SEM-EDS analysis

Morphological studies of polymer nano composites were carried out using scanning electron microscope (SEM, Zeiss Instrument) combined with EDS system.

Results and Discussion

Rheological properties

Rheological data of compounds were tabulated in Table 2. The scorch time and optimum cure time slightly increases with increase in dose of nanoclay concentration (Table 2), which could be due to intercalation of nano filler between the polymer matrix restricts the free radicals to come closures to form cross linking.

Table 2. Rheological properties

Rheological Properties	ENC 0	ENC 3	ENC 5	ENC 7
Scorch time, ts2, min	1.6	1.7	1.8	1.8
Optimum cure time t 90, min	21.5	22.6	22.8	22.4

Mechanical properties

As the loading of nano filler increases, the 300% modulus increases as shown in the Table 3 which is due to the reinforcement of polymer - filler interaction. As the loading of nano filler increases, the tensile strength also increases initially and after an optimum level it decreases as shown in the Table 3, which is due to the reinforcement of polymer - filler interaction. The three dimensional net work increases and hence the tensile strength increases initially and after a level of optimum dose, the strength comes down. Unlike conventional filler, the loading of nano filler increases the elongation at break is increasing (Table 3). This is an interesting point to note that though the stiffness of the PNCs are increasing, with nano filler loading, the elastic properties are maintained which is unique. This could be due to low filler loading leading to chain slippage during stretching which is not the case with higher loadings of conventional filler.

Table 3. Physicomechanical properties

Properties	ENC 0	ENC 3	ENC 5	ENC 7
Tensile Strength (MPa)	4.2	4.8	4.9	4.3
Modulus at 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

The ageing resistance found to be improved with incorporation of nano fillers and hence the retention of physical properties (Table 4) was found better for the samples with increase in dose of nano fillers. Hardness is defined as the resistance to indentation. The durometer is an instrument that measures the penetration of a stress-loaded metal sphere into the rubber. As clear from the Table 3, the resistance to indentation of PNCs was increasing with an increase of nano filler loading.

TGA Studies

The thermograms of PNCs (Figure 1) show that there is an increase in initial and maximum degradation temperature of PNCs. For cross linking type of polymers, the thermal stability is expected to improve due to the formation of more compact three dimensional cross-linking networks, which is more thermally stable.

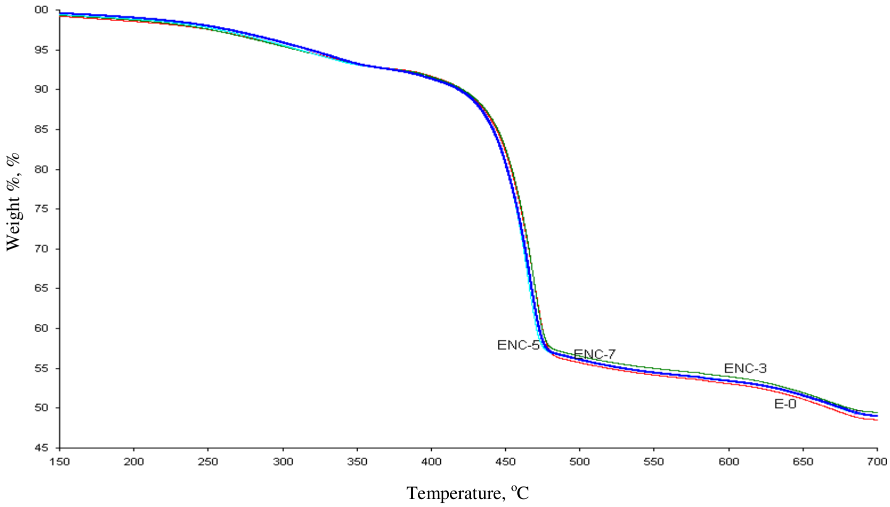

Figure 1. TGA of PNCs with different loading of nano clay in EPDM rubber matrix

Thermal ageing

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

Table 4. Physical properties after thermal ageing at 200 °C for 24 h

Properties	ENC 0	ENC 3	ENC 5	ENC 7
Change in Tensile Strength, %	-52.3	-46.3	-43.6	-26.8
Change in Elongation at break, %	-83.3	-82.0	-81.3	-82.3

XRD studies

The XRD studies reveals that the nano clay alone exhibits (Figure 2) a crystalline structure and upon incorporation in polymer structure the peak intensity reduced. This shows that the clay has intercalated between the polymer molecules.

Volume resistivity

Volume resistivity of vulcanizate decreases considerably (Figure 3) on introduction of nanoclay shows that the nanoclay intercalated within the polymer matrix and decreases the electrical resistance of the polymer.

SEM -EDS analysis

Morphological characterization of the nanocomposites was carried out using a Carl Zeiss 5800 digital scanning electron microscope (SEM). Cryo fractured surfaces were made conductive by sputter coating with gold and then examined under the SEM. The images were obtained at a tilt angle of 0^o with an operating voltage of 20 kV at 0 ^{0}C. Then the cut specimens were suspended in a copper grid.

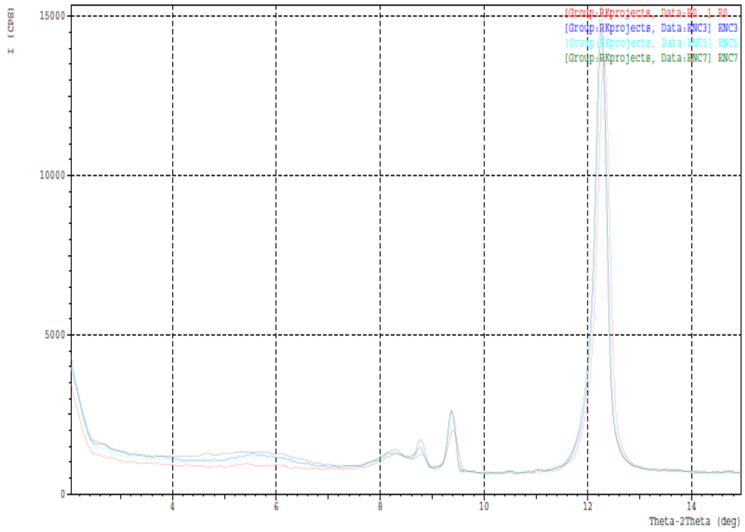

Figure 2. XRD graphs of PNCs with different loading of nano fillers

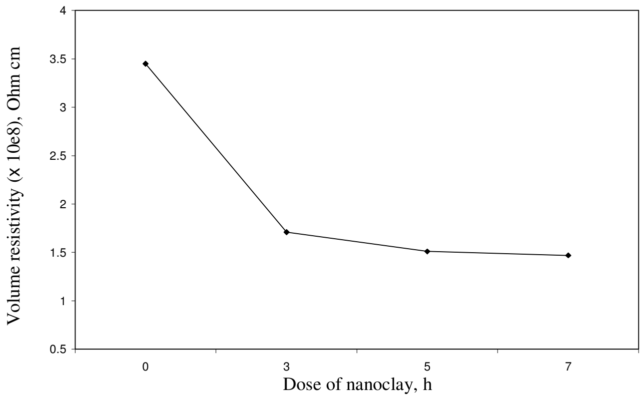

Figure 3. Electrical properties

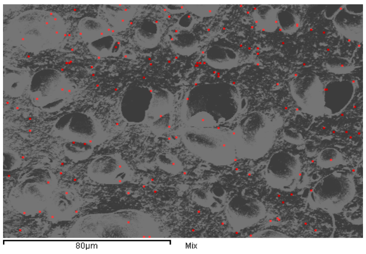

Figure 4. SEM of ENC-3

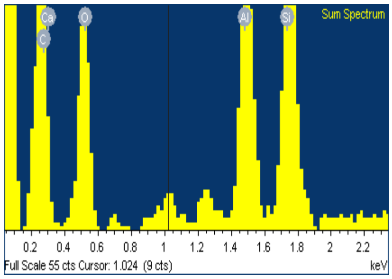

Figure 5. EDS spectra of ENC-3

The SEM photographs in Figure 4, 6 & 8 show that the uniform dispersion of ingredients in polymer matrix. Figures 5, 7 and 9 depict the EDS spectra which were taken on the scanned area of SEM to locate the dispersion of nano clay and its intensity. It has been found that as the dose of nano fillers in PNCs increases the intensity of nano clay in the EDS spectra also more. That shows that the nano fillers were distributed very well within the polymer matrix. In the above EDS spectra, (Figure 5, 7 & 9) it has been identified red colour nano particles are found to be nano clay in the EPDM matrix.

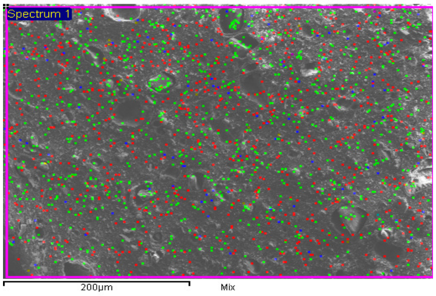

Figure 6. SEM of ENC-5

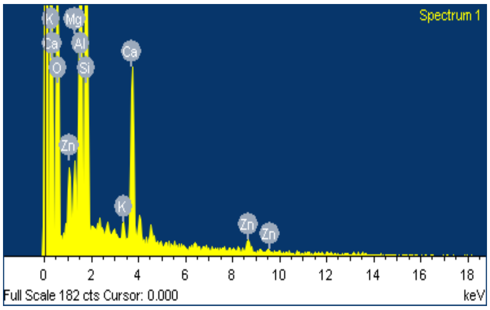

Figure 7. EDS spectra of ENC-5

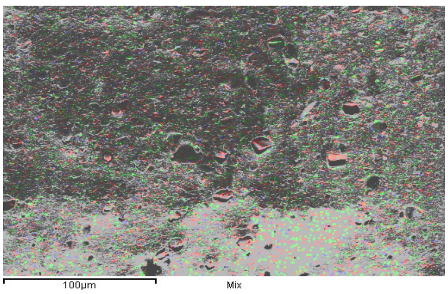

Figure 8. SEM of ENC - 7

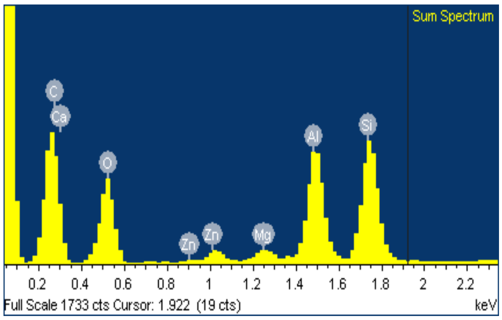

Figure 9. EDS spectra of ENC -7

Conclusion

Nano clay improves the physicomechanical properties of EPDM composites. From SEM - EDS it is understood that nano clay is uniformly dispersed in EPDM polymeric phase. TGA studies reveals that the thermal stability of polymer nano composites increases due to incorporation of nano clay.

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