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Processing of Nano Fillers in Nitrile Rubber – A Novel Technique.

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Abstract

Dispersion of various nano fillers like Nano silica, nano clay, Nano TiO_2, etc has been attempted in NBR rubbers using new technique of dispersion. Liquid NBR is taken as dispersion media for nano fillers in polymer matrix and polymer nano composites were characterized by Rubber Process Analyzer [RPA-2000, USA]. The dispersion of the nano fillers were investigated by XRD, SEM-EDS. The effect of increasing nano-fillers on mechanical properties like tensile strength, modulus and Elongation at break was studied. Hot air ageing of polymer nano composites was also studied.

Key Words : Nano-TiO_2, Nano Silica, NBR, Liquid NBR, Morphology, Mechanical properties, Microstructure characterization.

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Introduction

Elastomers are reinforced with fillers to improve their performance by incorporating materials conventional fillers such as carbon blacks, silica, clay, talc and calcium carbonate etc. In recent trends, Nanocomposites made out of nano fillers have been shown to afford remarkable property enhancements compared to conventional micro composites(1-3) which are made using conventional fillers. Polymer nanocomposites with layered silicates(4-9) and carbon nanotubes(10-12) have attracted major interest for the improvement of structural properties and the development of new materials having different functional properties. *Rajkumar et. al* studied that NBR-Nano graphite polymer nano composites were found to increase its thermal stability.(13) NBR-nano silica based Nanocomposite was prepared and mechanical and thermal properties were studied. The dispersion of the nano filler in the polymer matrix was studied using X-ray diffraction, scanning electron microscopy [SEM]-EDS. The effect of increase in nano-silica loadings on the performance characteristics like tensile strength, modulus and Elongation at break and its air ageing studies at 200°C for 24 hours were also reported.

Materials and Experimental Procedures

Materials

Acrylonitrile Butadiene Rubber (NBR JSR -230), Liquid NBR, Nano-silica powder obtained from Nano-shell USA, and other ingredients like curatives [S, MBTS], Activator [ZnO, Stearic Acid] & Antidegredants [TQD, 6PPD) were obtained from reputed manufacturers and used for studies.

Preparation of NBR-Nano-silica composites

Mixing of nanofillers in polymer was carried out in two stages. In the first stage, the nano-silica at different loading 1, 3 and 5 phr were mixed at ambient temperature in highly viscous liquid Nitrile Rubber [20 phr] and made into a paste like material which is known as “NBR-Nano-silica master batch”. In the second stage, the NBR-Nano-Silica master batch” was blended with NBR base polymer and then mixed with other rubber compounding chemicals, as per the formulation given in table 1 such as activators, curatives etc in a laboratory two roll. During mixing sulphur was added in the polymer at initial stage as per conventional mixing cycle followed for NBR. The rubber compound mixes were then passed several times in two roll mill to get uniform NBR Nano-silica based rubber compound.

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Table 1. Formulation for preparation of NBR – Nano-composites [Amounts in phr*]

Compounding Ingredients	NBS-0	NBS-1	NBS-3	NBS-5
NBR Rubber [JSR 230]	80	80	80	80
Liq. NBR	20	20	20	20
Sulphur	2	2	2	2
Zinc Oxide	4	4	4	4
Stearic Acid	1	1	1	1
Nano-silica	0	1	3	5
MBTS Accelerator	0.5	0.5	0.5	0.5
Antidegredants	2	2	2	2
Total Batch weight	109.5	110.5	112.5	114.5

*phr = Parts per hundred gram of rubber

Characterization

Characterization of Polymer Nano composites by RPA – 2000, USA

The rheological properties of polymer Nano composites were studied using Rubber Process Analyzer [RPA -2000] 150°C. The experiment was run for 60 minutes at 100 cpm frequency and 3° strain and minimum torque, maximum torque, scorch time Ts2, optimum cure time were recorded. The dynamic properties like minimum Tan delta and maximum Tan delta of polymer Nano composites were also studied in the RPA study at 100 cpm frequency and 3° strain.

Preparation of Specimens

Polymer Nano compounds was kept for maturation for 16 hours. Then the compounds were used for compression molding of sheets of 150 mm X 150 mm X 2mm thickness as per ASTM standard using hydraulic press at a temperature 150°C and the curing time as per the rheological data obtained from RPA 2000. The compression molded sheets were used for various physico-mechanical tests as per the ASTM standard.

Physico-mechanical properties

The test specimens i.e dumbbell specimens punched out from the compression molded sheet using Die C as per ASTM D 412 and used for determining physico-mechanical properties at the cross head rate of 500 mm per minute using universal testing machine (UTM, Zwick 1445). The ageing studies were carried out using hot air ageing oven at 100°C and 200°C for 24 hours as per ASTM D 573 and changes in physico-mechanical properties were calculated.

X- ray diffraction Study of Polymer Nano composites

X-ray diffraction study of the Nanocomposites were performed at room temperature using a Shimadzu X-ray diffractometer [Model- XRD-7000] in the angular range of 0° to 30° of 2θ (SAXD). The data was analyzed in the range of 2° to 10° of 2θ. The 2θ was calculated using Bragg's equation: - $2d \sin \theta = n\lambda$. Specimens for X-ray diffraction were taken from compression-molded sheets of 2mm thickness. The target was copper and (Cu Kα) radiation (λ= 1.540598°A) was obtained on applying 40 KV voltage to the generator and the current was 30 mA. The basal spacing of Nano Silica layers was estimated from the position of the plane peak in the SAXD intensity profile.

Scanning Electron Microscopy Studies (SEM-EDS) of Polymer Nano composites

Morphological characterization of the Nano-composites was carried out using a zeiss Digital Scanning Electron Microscope (SEM-EDS). Tensile fractured surfaces were examined under the SEM. The images were obtained at a tilt angle of 0° with an operating voltage of 20 kV. The SEM graphs further scanned through EDS attachment to study the distribution of elements in the polymer matrix.

Results and Discussion

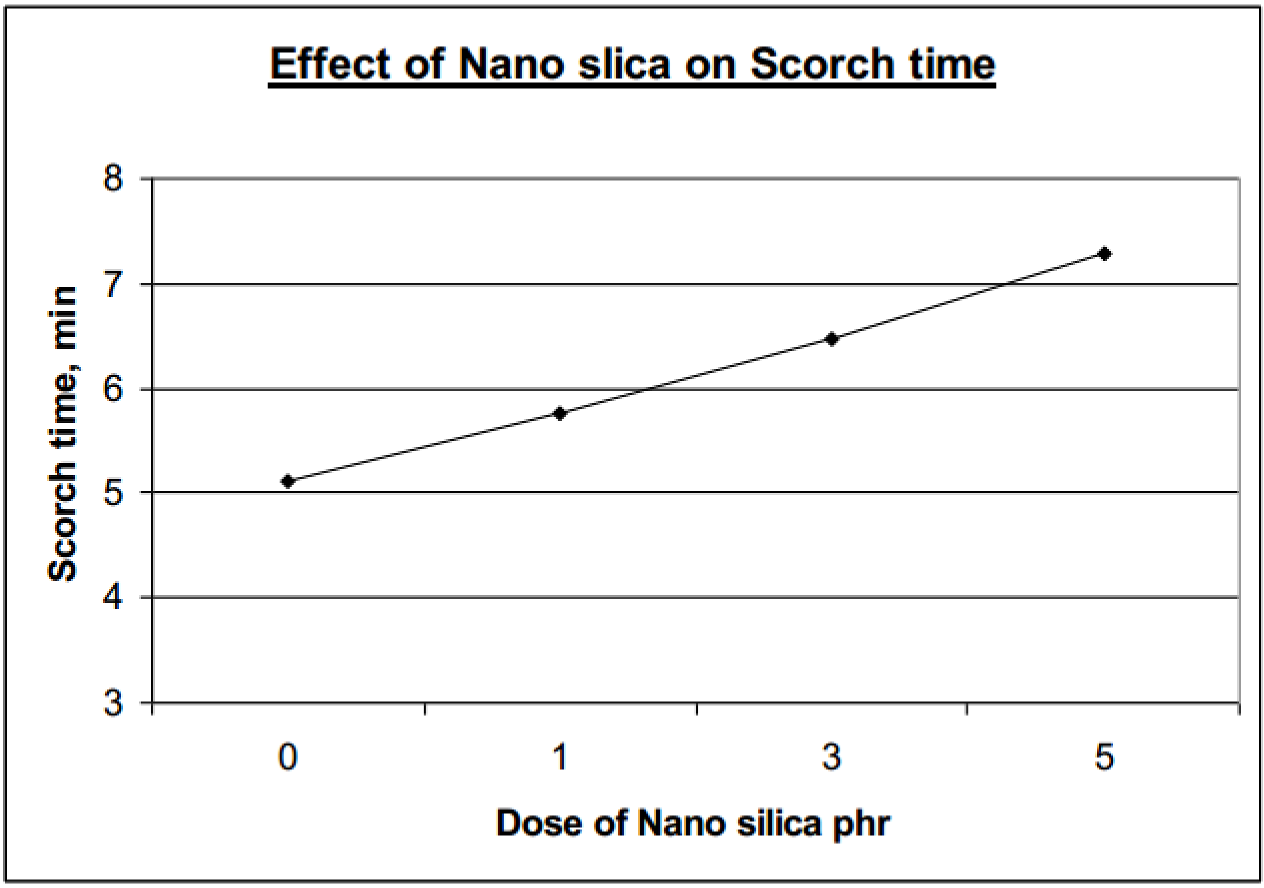


Figure 1. Rheological properties of NBR-Nano silica composites

The rheological study indicates that the presence of Nano silica improves the scorch properties. The figure 1 and 2 indicates the increase in scorch time and optimum cure time of polymer Nano-composites with increase in Nano silica dose. This may be due to the neutralization of active acid groups present in surface of Nano silica by the basic accelerators. Figure 3 gives tan delta curves of NBR Nano silica compounds. The tan delta increases as the dose of nano filler increases due to increase in stiffness. As the loading of Nano silica increases, the stiffness of vulcanizates increases resulting into increase in loss modulus of Nano composites due to higher filler – polymer network / interaction.

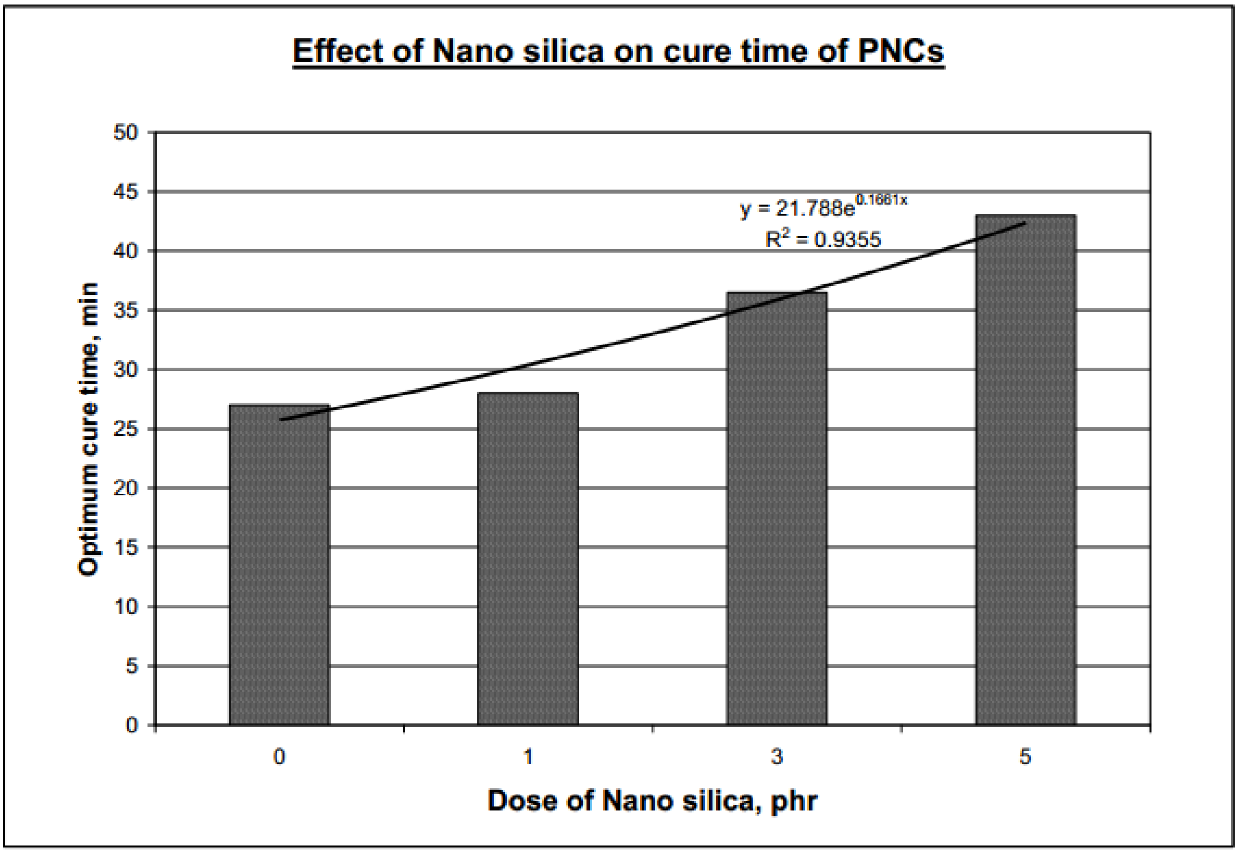


Figure 2. Rheological properties of NBR-Nano silica composites

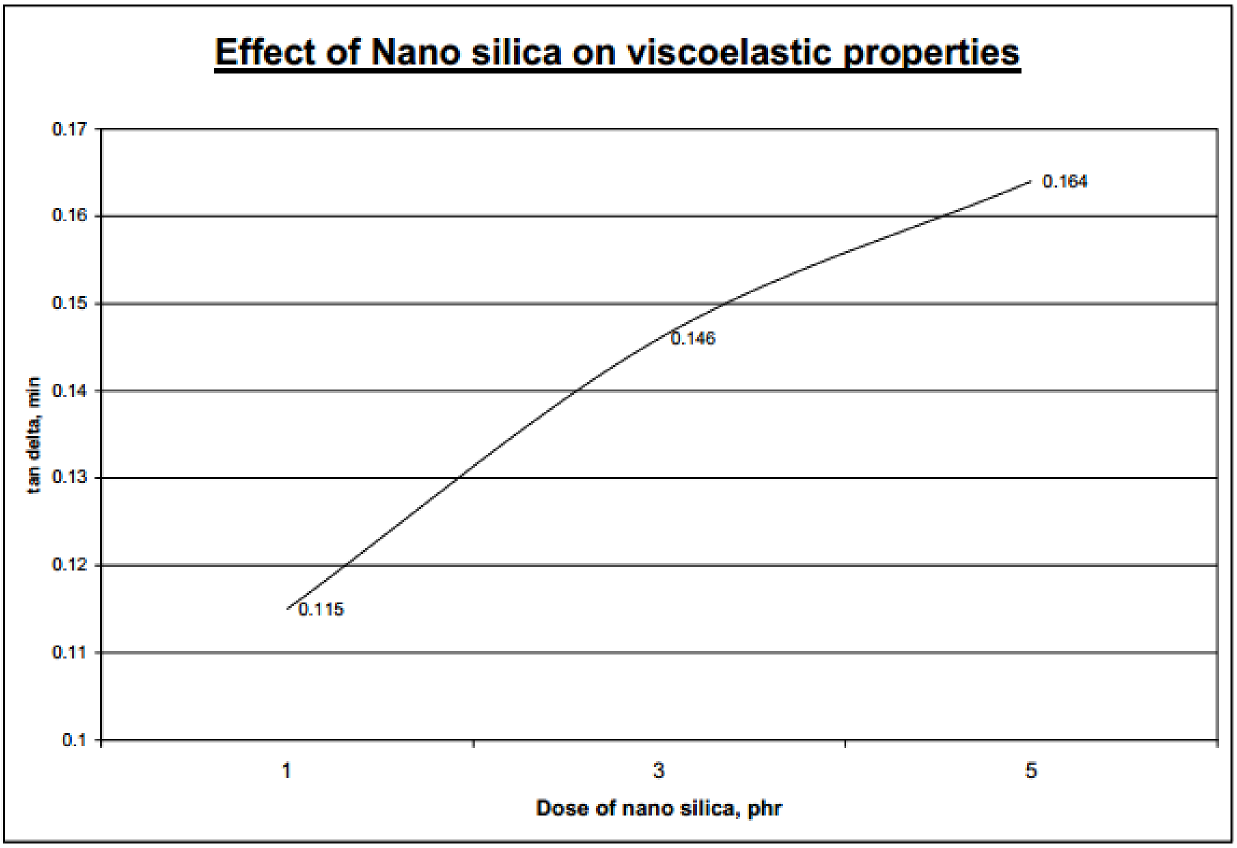


Figure 3. Rubber process analysis of NBR-Nano silica composites

Figure 4 shows values of tensile strength of the nanocomposite with different contents of nanosilica incorporated. In general, there was a positive correlation between tensile values and the quantity of nanosilica in the nanocomposite. The physical properties like tensile strength, modulus and hardness of NBR nanocomposites increase as loading of Nano silica increases.

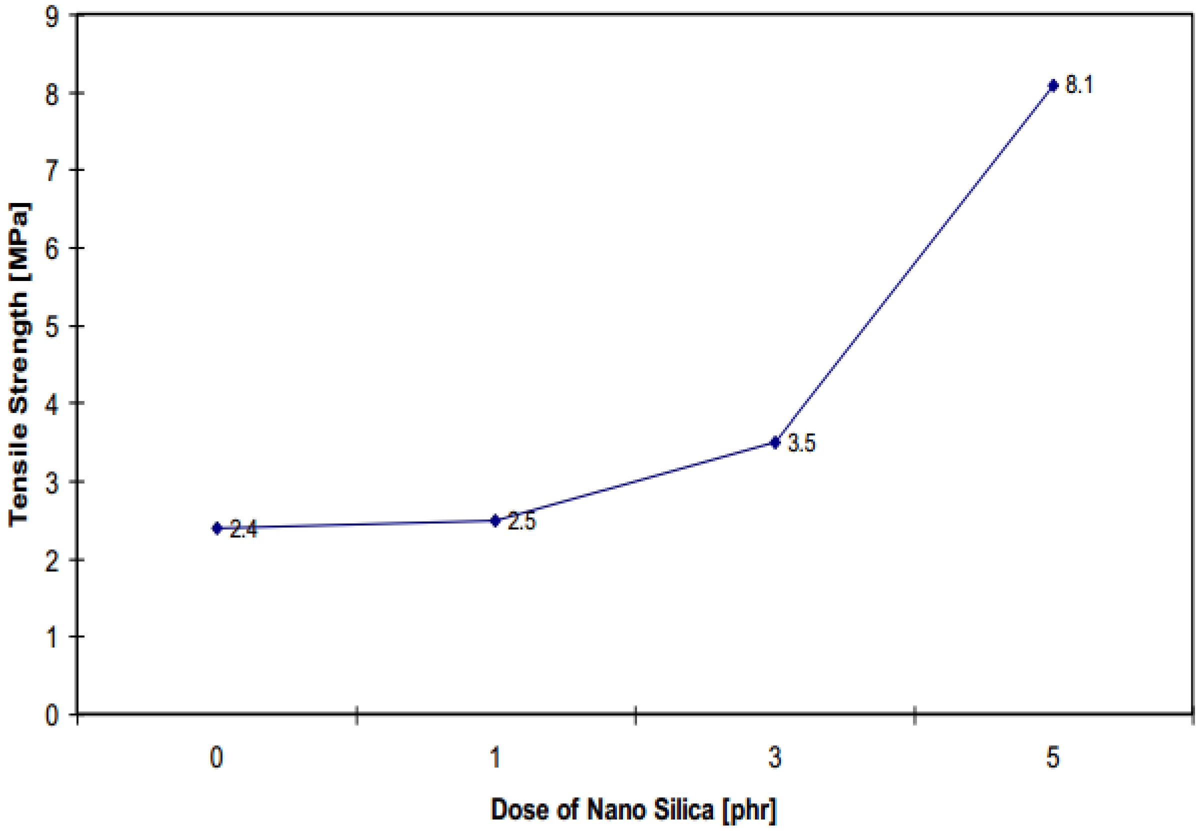


Figure 4. Effect of Nano silica on mechanical properties of NBR Nano silica composites

This shows that the Nano silica contributes in reinforcing of polymeric matrices. Tensile strength can be regarded as catastrophic tearing of cracks initiated by micro voids, from filler surface. If the elastomeric network is capable of dissipating the input energy into heat, then less elastic energy will be available to break this polymer network. Incorporation of fillers is the major source of energy dissipation. Increasing amounts of filler load to a large number of polymer chains to get adhered to the polymer. The increase in loading of Nano-silica showed increase in Tensile strength and modulus properties, due to reinforcement effect of filler-polymer interaction.

Figure 5 shows the Hardness of vulcanizates of NBR Nanosilicates containing different doses [0, 1, 3, 5 phr]. The increase in dose of Nano silica in NBR Nanocomposite increases the Hardness of vulcanizates. This corroborates the results of tensile properties which is due to increase in reinforcement of Nano filler in NBR polymer matrix

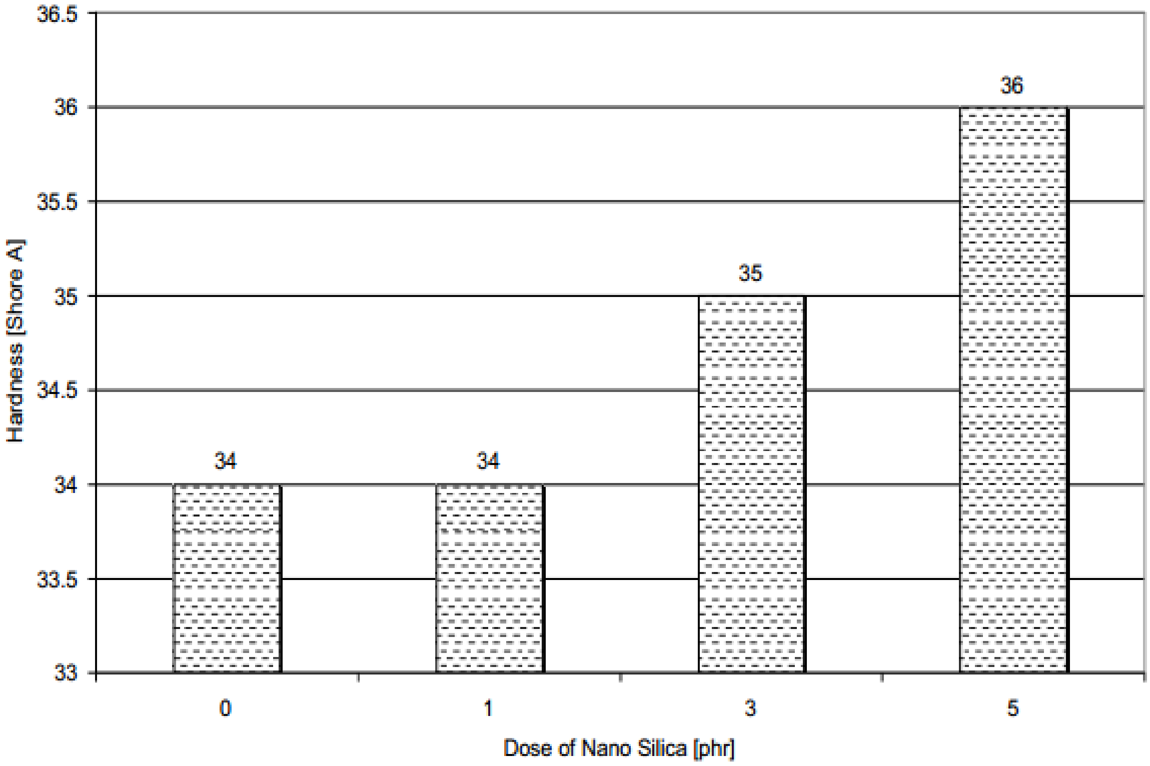


Figure 5. Mechanical properties of NBR Nanosilica composite – Hardness

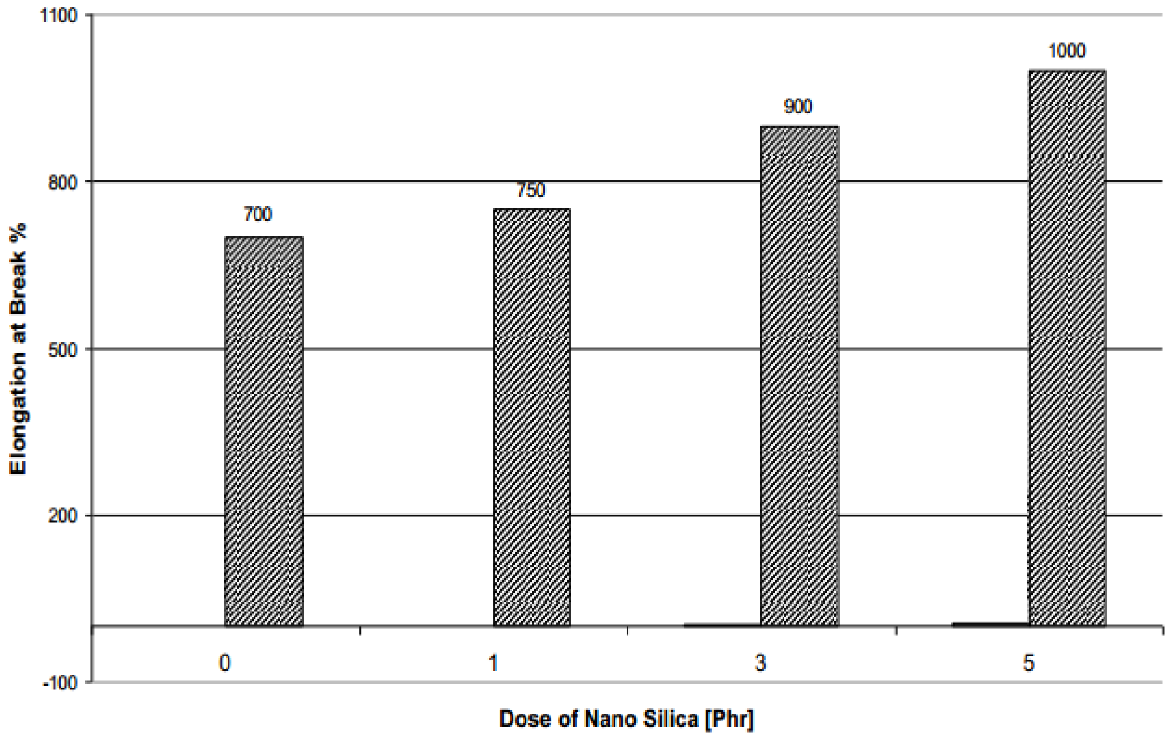


Figure 6. Mechanical properties of NBR nano silica composites

Figure 6 shows the percentage of Elongation at break which is unusually increases with increase in dose of nanofillers. This may be due to the lower amount of Nano fillers and hence the physical interaction between the rubber and filler becomes more homogenous and hence no much filler agglomeration takes place within the polymer networks. More than physical interaction, the Nano particles of filler has taken the place of micro phore spaces present in the polymer matrix. Elongation at break increases with loading unusually because of the layer of silicate structure restricts the tearing of polymer molecules under stretching during tensile test. The hardness of nanocomposites increases as the loading increases due to increase in loading of fillers. In general, NBR polymer is recommended up to 100°C.

Table 2 shows retention of physical properties of polymer Nanocomposites after hot air ageing at 100 deg C for 24 hours studies. As the loading increases initially improves the heat resistance properties and then it decreases. Changes in hardness after ageing is not significant where as the changes in elongation at break are quite significant after ageing.

Table 2. Mechanical Properties of NBR -nanocomposites with different concentration of nano-silica

Physical Properties	**NBS-0**	**NBS-1**	**NBS-3**	**NBG-5**
Air Oven Ageing study at 100°C for 24hrs				
Retention of Tensile Strength (%)	70	92.5	98	62.5
Retention of Elongation at break (%)	80	70	68	65
Changes in Hardness (Shore A), Points	+4	+ 3	+ 2	+2

Figure 7 shows the tear strength of polymer Nano composites. It was observed that the tear strength increases as the loading of Nano filler increases. This is due to strong network between the filler and polymer active surfaces. This further corroborates the increases in tensile strength which is also increases as the loading increases.

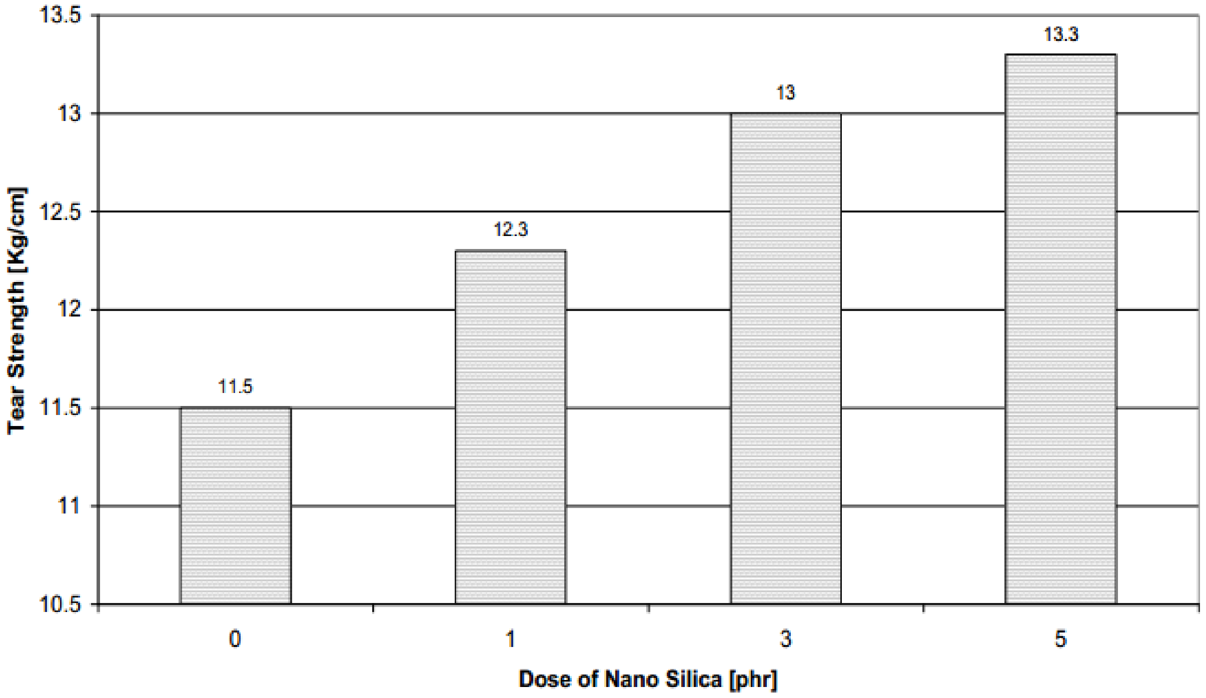


Figure 7. Mechanical properties of Polymer Nano composites – Tear Strength

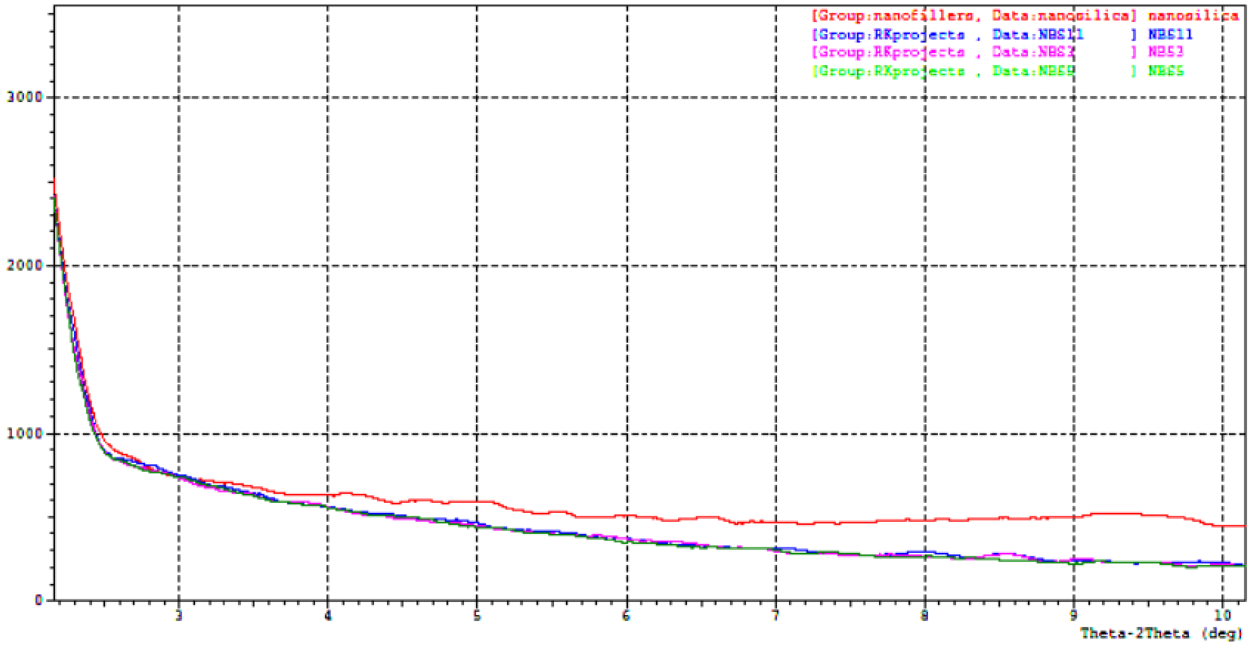
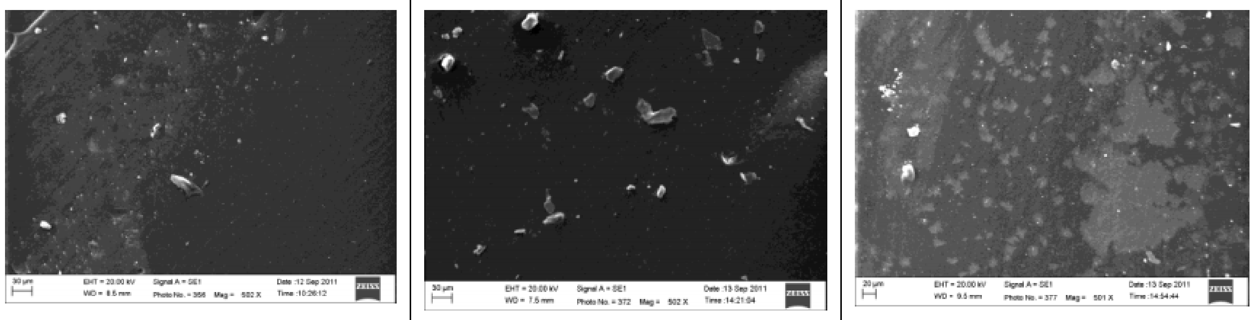


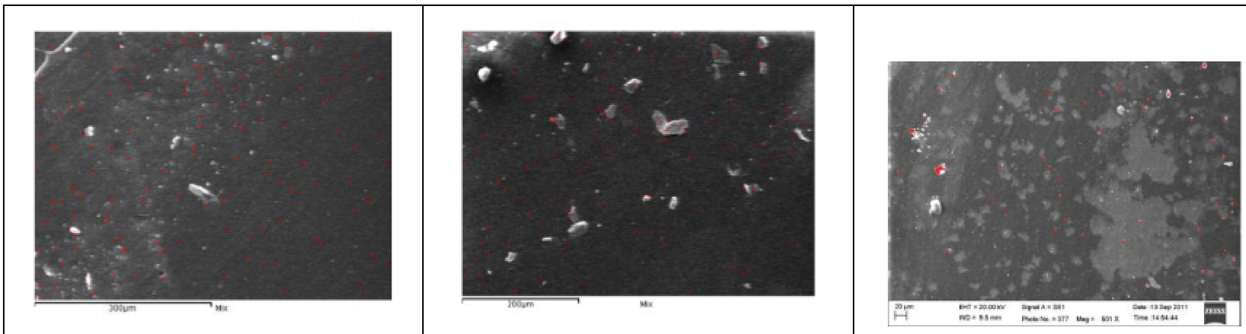
Figure 8. XRD study of NBR Nano-silica Nanocomposites

Figure 8 shows the X-ray diffraction studies of polymer Nano composites containing Nano silica. Figure 9 indicates the Morphology studies of the polymer nanocomposites micrographs of the nanocomposite with different dose of nanosilica incorporation. The dispersion of the Nano-silica was studied by XRD Figure 9 shows the X-Ray diffractograph of unfilled NBR compound vulcanizate and NBR-Nanocomposites. From the plots it can be observed that pure silica platelets and silica / NBR exhibit an intense peak at diffraction angle of 10.2. It was observed that with increase in Nano-silica loading lead to increase in intensity of the peaks (as shown in Figure 1), which can be attributed to presence of higher number of silicate layers.



SEM picture of NBS-01 SEM picture of NBS-03 SEM picture of NBS-05

Figure 9. Fracture surface morphology study of NBR Nanocomposites through SEM with different Nano-silica doses (1) 1 phr (2) 3 phr (3) 5 phr



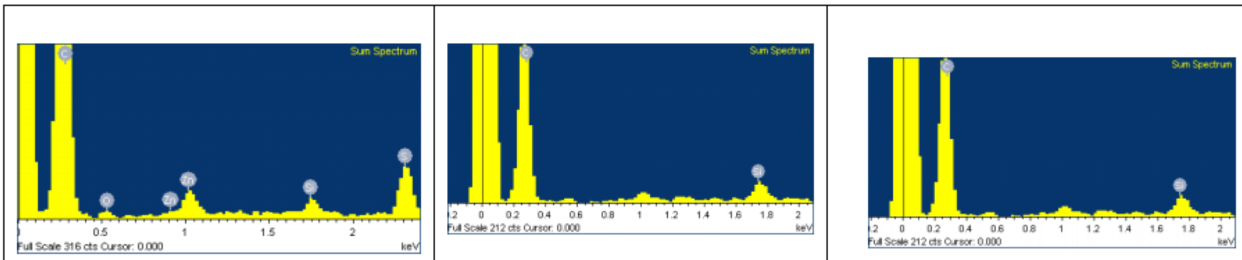
SEM picture of NBS-01

SEM picture of NBS-03

SEM picture of NBS-05

Figure 10. Fracture surface morphology study of NBR Nanocomposites through SEM with different Nano-silica doses (1) 1 phr (2) 3 phr (3) 5 phr

Figure 10 shows representative scanning electron micrographs [SEM] of tensile fracture surface of NBR Nanocomposites. The SEM of figure 10 showed that the distribution of particles of ZnO and Nano-silica fillers in NBR matrix. With increasing loading of fillers [1, 3 & 5 phr], particles are well dispersed in the polymer matrix and which was due to the two stage mixing using liquid NBR as a dispersion phase. Figure 11 EDS spectra of SEM photographs have been investigated for the distribution of Nano silica in the respective polymers. It is verified that the Nano fillers were distributed equally in polymer matrix.



EDS analysis - Nano Si : 0.57 %

EDS analysis : Nano Si : 2.07 %

EDS analysis : Nano Si : 2.09 %

Figure 11 : SEM – EDS spectra of NBR Nano silica composites with different Nano-silica doses (1) 1 phr (2) 3 phr (3) 5phr.

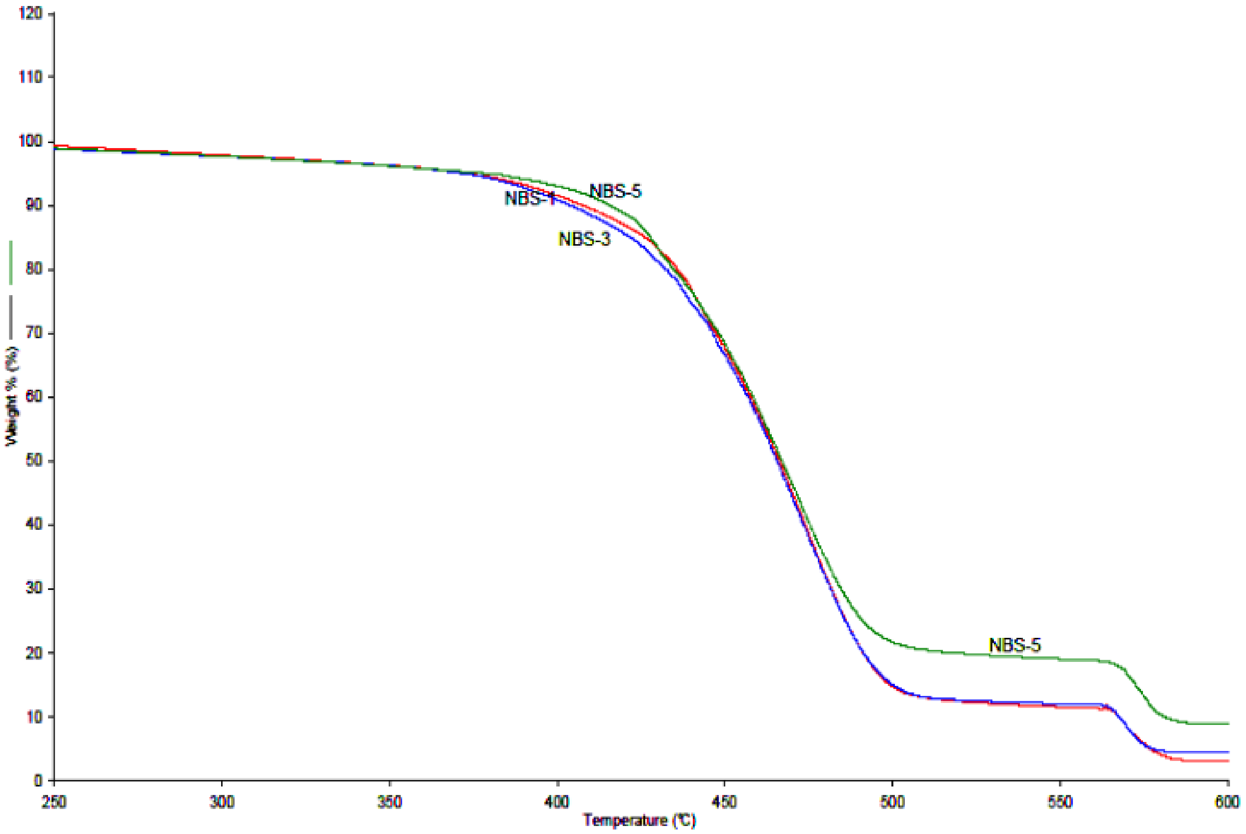


Figure 12. Thermogram of Nanosilica - NBR polymer nanocomposites

Figure 12 shows the thermogram of Nanosilica - NBR polymer nanocomposites. The increase in loading of Nano silica increases the thermal stability of the polymer nano composites. This is due to strong interfacial interaction between nano filler and polymer. This corroborates the hot air ageing resistance properties of nanocomposites.

Conclusions

The effect of addition of Nano-silica fillers in NBR Nanocomposites using liquid NBR as dispersion media was investigated. The addition of Nano-silica increases thermal resistance. Improvement in physical properties was found at higher loading of Nano fillers. The dispersion of nanofillers with increasing concentration of Nano silica was studied by XRD and SEM.

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