RASĀYAN *J. Chem.*
Vol. 6 | No.2 | 122-133 | April-June | 2013
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

DISPERSION STUDIES OF NANOSILICA IN NBR BASED POLYMER NANOCOMPOSITE

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ABSTRACT

Polymer-nanosilica composite was prepared using Silica nano particles as reinforcing fillers in Acrylonitrile Butadiene Rubber (NBR). The rheological behavior of the polymer nano composite was studied using Rubber Process Analyzer [RPA-2000, USA]. The dispersion of the silica nano particles based filler in the Nitrile Rubber was achieved using liquid NBR polymer matrix and was investigated by FTIR, SEM-EDS. The effect of increasing nano-silica loadings on mechanical properties of NBR nanocomposites was also studied. Mechanical tests demonstrate that the NBR/nano-silica based polymer nano composites possess greatly increased the elastic modulus and tensile strength, and desirably strong interfaces. The thermal resistance properties of NBR Nano-composites were studied through air ageing studies at 100°C and characterized through TGA studies.

Keywords: Nano-silica, Rubber**,** Morphology, Mechanical properties, microstructure characterization.

INTRODUCTION

In the last decade, polymer nano-composites have drawn significant interest from both industry & academia, because they often exhibit remarkable improvements in material properties at very fine level with very low nano filler loading when compared to pristine polymer or conventional composites. Polymer nano-composites are a special class of polymer composites, a type of reinforced polymer having a two phase material with the reinforcing phase having at least one dimension in the 10^{-9} m (nm) scale. It constitutes a new class of material having nano-scale dispersion, typically 1-100 nm, of the filler phase in a given matrix. The outstanding reinforcement of nano-composites is primarily attributed to the large interfacial area per unit volume or weight of the dispersed phase (e.g. 750 m^2/g). Silica is an abundant compound over the earth largely employed in industries to produce silica gels, colloidal silica, fumed silica and so on[1]. The nano-sized silica particles are interesting because they are applied in emerging areas like medicine and drug delivery etc. Silica nano-particles have been used in the industry to reinforce the elastomers as a rheological solute[2]. Silica nanocomposites have been attracting some scientific interest as well due to the advantage of low cost of production and in the high performance features. Studies on nanosilica dispersions in polymer matrices like poly(methyl methacrylate)[3,4], polyethylene[5] and poly(ethylene oxide- 600)[6] were reported. Studies were reported on polymer nanocomposites based on silica and polymers like poly (vinyl alcohol)[2,7], poly(vinyl pyrrolidone)[2] and chitosan[2]. The mechanical and thermal properties of polymer nanocomposites were found to be enhanced compared to the pristine polymers.

The nano fillers (especially SiO2 nano particles) have higher aspect ratio than typical microscopic aggregates. Nanosilica which can be dispersed as silicate nano layers of high aspect ratio is attractive for polymer reinforcement. Polymer clay nanocomposites had shown drastic enhancement in mechanical properties (modulus & tensile strength), thermal properties (heat resistance & flammability) and barrier properties. Similarly, the colloidal state & the surface chemistry of silicate layers in a polymer matrix play important roles in the synthesis of polymer silica nanocomposites. But, the greatest challenge in polymer nano technology is to uniformly disperse these nano dimensioned fillers which offer numerous advantages over conventional micron- sized fillers.

The interest in the area of polymer nanocomposites is many folds. Firstly, the present understanding of composite behavior does not fully satisfy or predict from a scientific standpoint why these systems are superior in many of its properties. Secondly, from an engineering standpoint, it is not fully explored that how these materials can achieve significant enhancement in properties with such a small amount of filler. Similarly, the field of nano materials has been extended to elastomeric matrices, particularly, for potential applications where barrier properties are required.

Acrylonitrile-Butadiene Rubber (NBR), is a synthetic Rubber, the most widely used rubber in automobiles components such as fuel hoses, gaskets, rollers, and other products in which oil resistance is required along with heat resistance properties. Rubbers are reinforced with fillers to improve their performance by incorporating materials of conventional fillers such as carbon blacks, silica, clay, talc and calcium carbonate etc. In recent trends, Rubber Nanocomposites made out of nano fillers were found to exhibit remarkable property enhancements compared to conventional micro composites[8-10] which are made using conventional fillers. Polymer nanocomposites with layered silicates[11-16] and carbon nanotubes[17-19] had attracted major interest for the improvement of structural properties and the development of new materials having different functional properties.

The effect of acrylo-nitrile content on the mechanical, dynamic mechanical and rheological properties of the nano composite was reported by Sadhu and Bhowmick[20-21]. The Role of Organic modifier used with montmorrilite on the formation of nanocomposite in melt compounding process has been studied by Kim and White[22]. Rajkumar et al studied the effect of liquid NBR as dispersion media for dispersing nanographite in NBR matrix and consequently, polymer nano- composites were found to improve its thermal stability[22]. To incorporate layered silicates into rubbers, the routes like: solution blending (solvent-assisted techniques)[23-25], latex compounding (water assisted techniques)[26-27], melt mixing (direct methods)[28] were followed. The drawbacks of a solution intercalation method were found the requirement of a suitable monomer/solvent or polymer/solvent pairs and the high costs associated with the solvents, their disposal as well as their impact on the environment. Melt intercalation does not require the use of any solvent. The melt-intercalation process involves annealing a mixture of the polymer and organically modified nano clays above the softening point of the polymers under shear. While annealing, the polymer chains diffuse from the bulk polymer melt into the galleries between the silicate layers i.e intercalation, leading to the formation of nanocomposites. Phenomenon of interaction between polymer and nanosilca[29] was explained.

In the current studies, Liquid NBR was used as dispersion media to disperse the nanosilica in NBR matrix using conventional mixing techniques. NBR-Nanosilica based Nanocomposites were prepared using liquid NBR as dispersion media and conventional mixing processes. The effect of Nanosilica on mechanical and thermal properties of polymer nanocomposites were studied. The dispersion of the silica nano particle in the polymer matrix was studied using scanning electron microscopy [SEM] combined with EDS and also by FTIR. The effect of increase in nano-silica loadings on the physical properties like tensile strength, modulus and Elongation at break, retention properties after air ageing were studied and significant changes were found in the properties of NBR polymer nanocomposite.

EXPERIMENTAL

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 [TDQ, 6PPD) were obtained from reputed manufacturers and used for studies.

Preparation of NBR-Nano-silica composites

The formulation used for mixing NBR rubber and compounding ingredients are tabulated in Table-1.

Method

Mixing of nanofillers in NBR polymer was carried out in two steps. In the first step, the silica nano particles 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".

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

Compounding Ingredients	NBS-0	NBS-1	NBS-3	NBS-5
(a.) Master Batch				
Liq. NBR	20	20	20	20
Nano-silica	0	1	3	5
(b.) Main Formulation				
NBR Rubber [JSR 230]	80	80	80	80
Sulphur	2	2	2	2
Zinc Oxide	4	4	4	4
Stearic Acid	1	1	1	1
MBTS Accelerator	0.5	0.5	0.5	0.5
Anti-degredents	2	2	2	2
Total Batch weight	109.5	110.5	112.5	114.5

*phr = Parts per hundred gram of rubber

In the second step, the raw NBR rubber [balance 80 phr] is milled in two roll mill and then NBR-Nano-Silica master batch" was added to it to get uniform blending of liquid NBR and NBR rubber. Then other rubber compounding chemicals, as per the formulation given in table 1 such as activators, curatives etc were added and mixed. During mixing sulphur was added in the polymer at initial stage to ensure proper dispersion of sulphur in polymer matrix. Mixing was carried out in a controlled manner in two roll mixing mill with maintaining speed ratio 1 : 1.2 and temperature was maintained by passing water. The same procedure was followed for all the mixes. The mixing cycle time was maintained constant at 25 min for all the mixes. The polymer nanocomposite mixes were then passed several times in two roll mill to get uniform mixes of polymer nanocomposites.

Characterization of Polymer Nano compound by RPA – 2000, USA

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

Preparation of Specimens

Polymer Nano composite mixes were kept for maturation for 16 hrs. Then the composites were moulded by compression molding techniques to prepare the sheets of 150 mm X 150 mm X 2mm thickness as per ASTM standard using hydraulic press at a temperature 150°C. The curing time was taken 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 after 16 hrs of interval between mixing and vulcanization.

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 for 24 hrs as per ASTM D 573 and retention of physico-mechanical properties from its original properties were determined.

Thermo gravimetric Analysis of polymer nano composites

Thermal decomposition studies of the polymer nano composites were carried out by using a thermo gravimetric analyzer (TGA) of TA instruments (model: Q 50) in nitrogen atmosphere. All these analysis were carried out at heating rate of 20^o C/ min from 70^o C to 900^o C. The degradation pattern of nanocomposites was studied.

Scanning Electron Microscopy Studies (SEM-EDS)

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

FTIR Spectroscopy studies

The FTIR spectra of Nanosilica, Raw NBR and NBR – Nanosilica Polymer nano composites were recorded in the range of 600 – 3000 cm^{-1} using Model- Nicolet 6700 under ATR mode, in order to study the chemical interaction of Nanosilica in NBR polymer matrix.

RESULTS AND DISCUSSION

Rheological study and curing behavior

The fig.-2 and 3 shows the rheological data of polymer nanocomposites. The study reveals that the presence of Nanosilica delays the curing and scorch properties and increase in scorch time and optimum cure time of polymer Nano- composites were observed with increase in Nanosilica doses. This may be due to the neutralization of active acid groups present in surface of Nanosilica by the basic accelerators present in the system. Increase in curing time was observed in the conventional composites filled with silica nano-particles and they tend to increase with increasing Nanosilica loading up to 5 phr. This may be because the silanol groups on the silica surface react with the activator as well as accelerator and, consequently, reduce the number of active sulfurating agents which are necessary for sulfur vulcanization[34], and finally leading to increase in cure time as it was seen in case of 5 phr loading of nanosilica in Fig.-3 in which there was sudden increase in the curing time. This increase in curing time may also be attributes to the formation of agglomerates due to increased silica loading, which has been proved to be a natural tendency of nanoparticles, and create a barrier in vulcanization process.

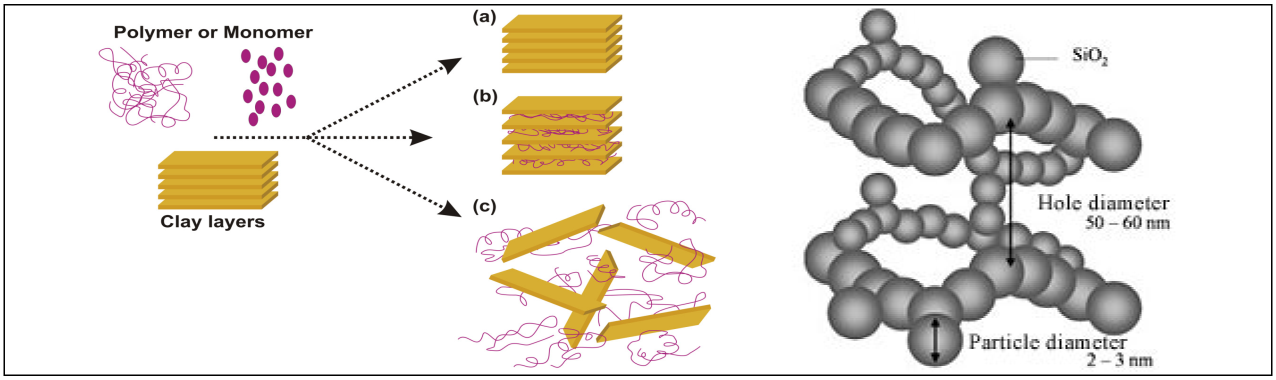


Fig.-1: Microstructures of polymer-layered silicate and structure of Nanosilica.
(a) Un-intercalated composites, (b) Intercalated Nanocomposite, (c) Exfoliated composites

Table-2: Mechanical Properties of NBR -nanocomposites after air ageing

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

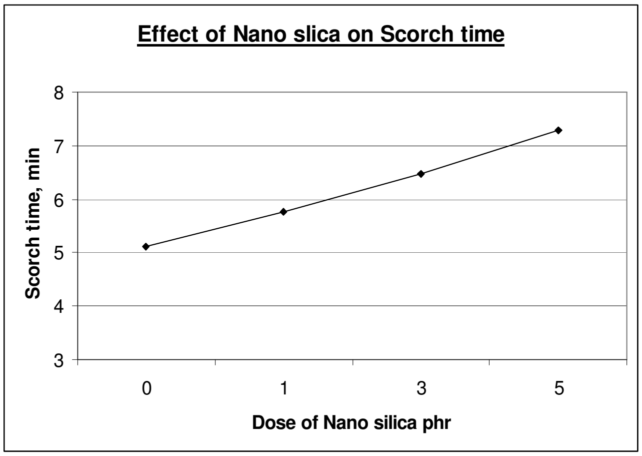


Fig.-2: Rheological properties of NBR-Nanosilica composites

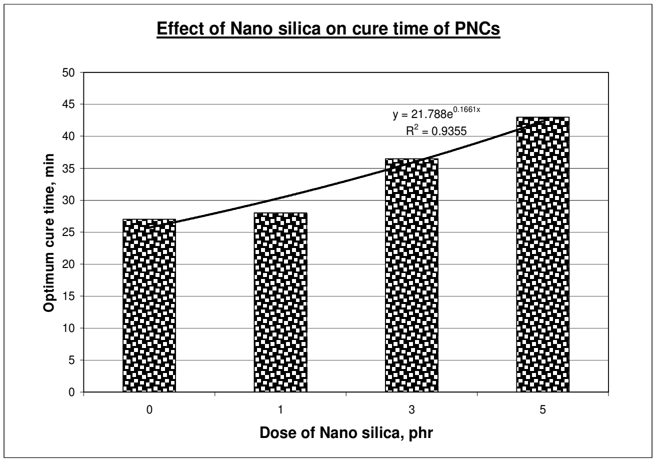


Fig.-3: Rheological properties of NBR-Nanosilica composites

Visco-elastic Properties

Fig.-4 gives minimum tan δ curves of NBR Nanosilica composites due to increase in stiffness. As the loading of Nanosilica increases, the stiffness of composites increases resulting into increase in loss modulus as seen from the increasing values of tan δ of Nano composites. This is because the mobility of polymer segments is more restricted by the increase in content of silica nanoparticles, and by the increase in crosslink density and attributing to greater polymer–filler interaction Nanosilica which has very high surface area. This may also be attributed to the enhancement in degree of filler dispersion within the polymer matrix. Again in case of fig.-5, there was increase in maximum tan δ and then sudden decrease in the same was observed may be because of increase in the agglomerates due to increase amount of silica nanoparticles leading to dispersion in to the matrix.

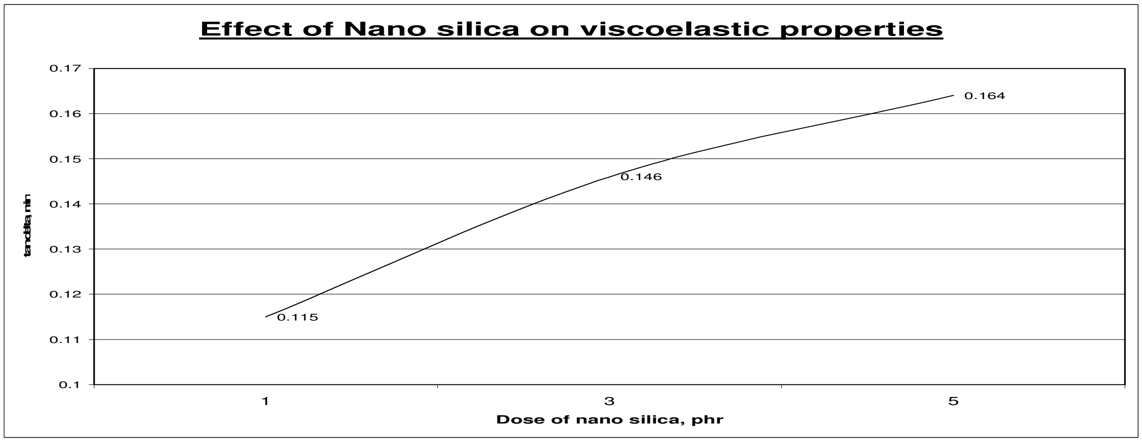


Fig.-4: Rheological studies NBR-Nanosilica composite by RPA 2000

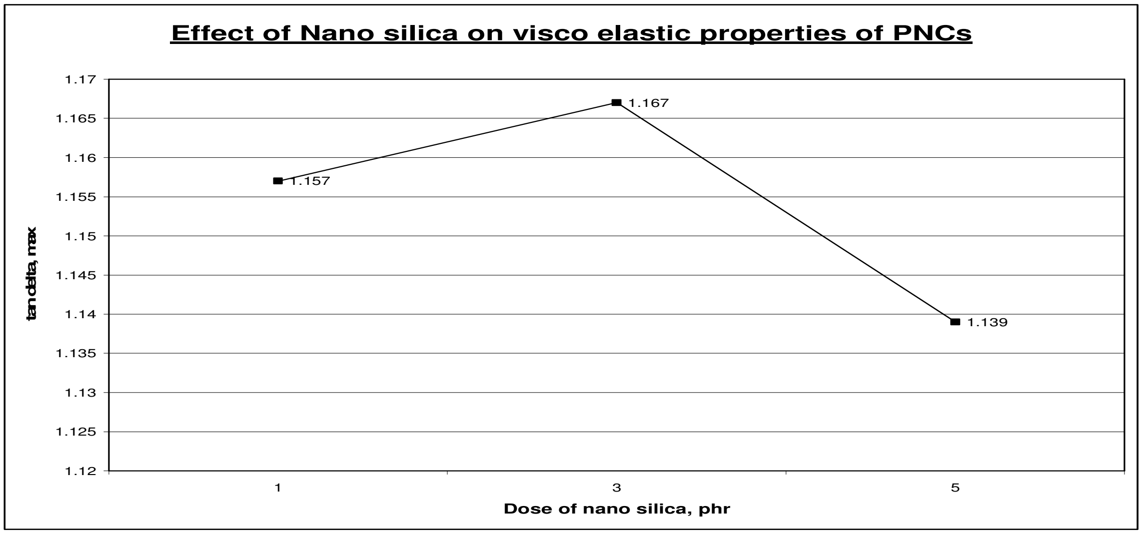


Fig.-5: Visco-elastic properties of NBR-Nanosilica composites by RPA

Physico-Mechanical properties

Fig.-6 shows values of tensile strength of the polymer nanocomposite with different contents of Nanosilica incorporated within the polymer matrix. The physical properties like tensile strength, modulus and hardness of NBR nanocomposites found to increase with increase of loading of Nanosilica. This showed that the Nanosilica contributes to the reinforcement of polymeric matrices. In general, there was a positive correlation between tensile values and the quantity of silica nanoparticles present in the nanocomposite. Incorporation of 1 phr Nanosilica increases the tensile strength by 4% from that of the composite without any other filler. Further addition of 2 phr showed 10 times of enhancement of Tensile strength reaching as high as 40 %. The incorporation of 5 phr Nanosilica in the polymer nano composite showed i.e 237 % enhancement of tensile strength of the composites than that of the composites without nano filler. The increase in loading of Silica nano particles showed increase in Tensile strength and modulus properties, due to reinforcement effect of filler-polymer interaction. Tensile strength can be regarded as catastrophic tearing of cracks initiated by micro voids, from filler surface. When 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. Fig-7 shows the Shore A Hardness of composites of NBR Nanosilicates containing different doses [0, 1, 3, 5 phr]. As the loading of filler increases the hardness (shore A) increases due to increase in stiffness of the polymer nanocomposites. Increasing amounts of filler loading to a large number of polymer chains to get adhered to the polymer. In general, increase in reinforcement is associated with a decrease in ultimate elongation. However, this is not always the case with nanosilica. Fig.-8 shows the percentage of Elongation at break which is unusually increases with increase in dose of silica nanoparticles. Karger-Kocsis et al.[20]

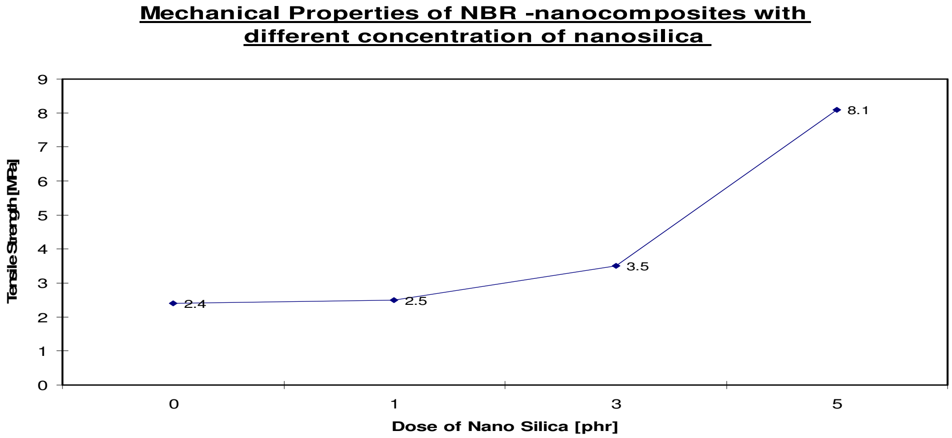


Fig.-6: Mechanical properties of NBR Nanosilica composite – Tensile strength

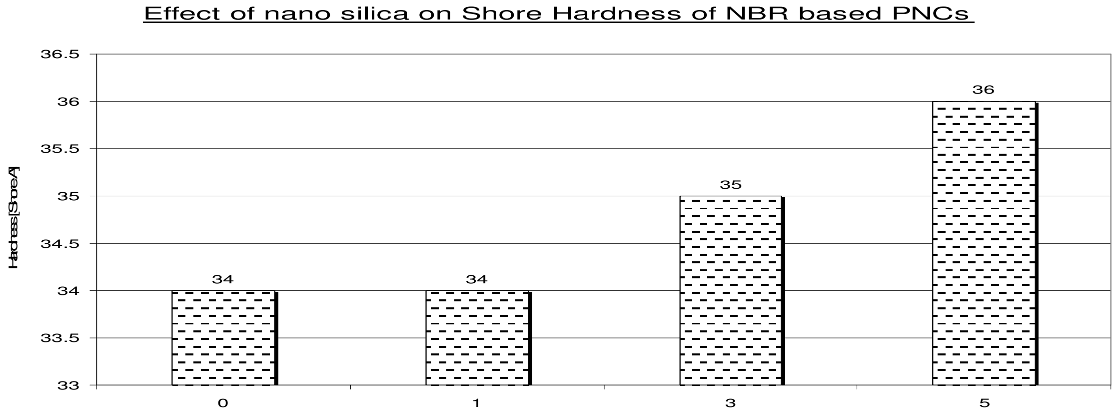


Fig.-7: Mechanical properties of NBR Nanosilica composite – Hardness

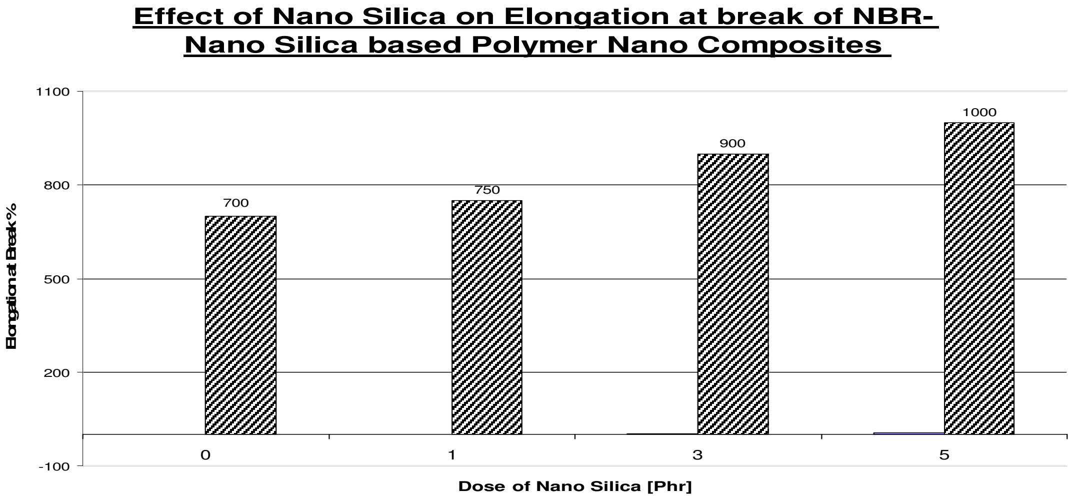


Fig.-8:Mechanical properties of NBR Nanosilica composites speculated that the unexpected high elongation in polymer nanocomposites was likely due to the encapsulation of individual Nanosilica layers and tactoids in a more cross linked polymer fraction than the bulk itself. As a consequence, the less cross linked portion of polymer contributes more towards the deformation of the polymer matrix resulting in higher percentage in elongation at break. This may also be due to the lower amount of Nano fillers and hence the physical interaction between the polymer 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 microphore 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.

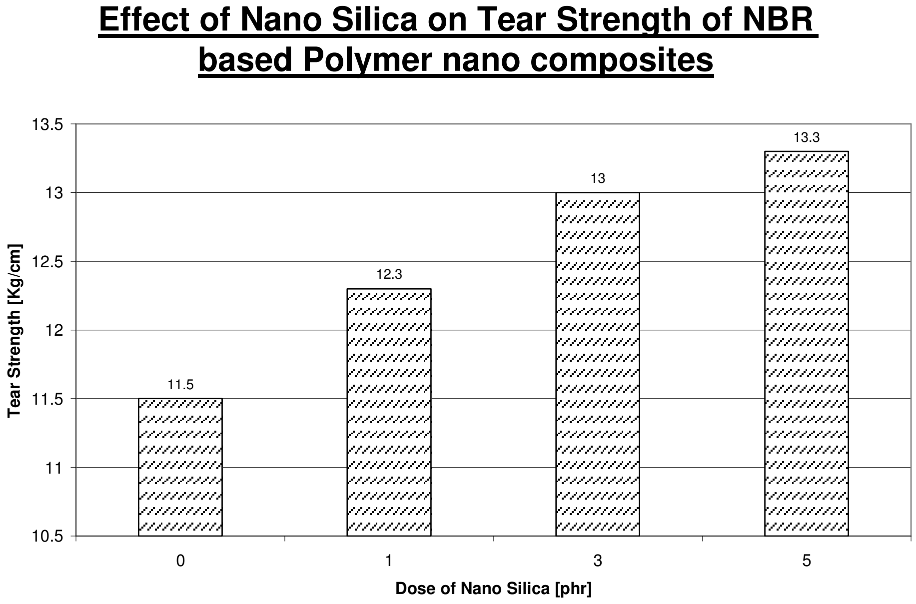


Fig.-9: Mechanical properties of Polymer Nano composites – Tear Strength

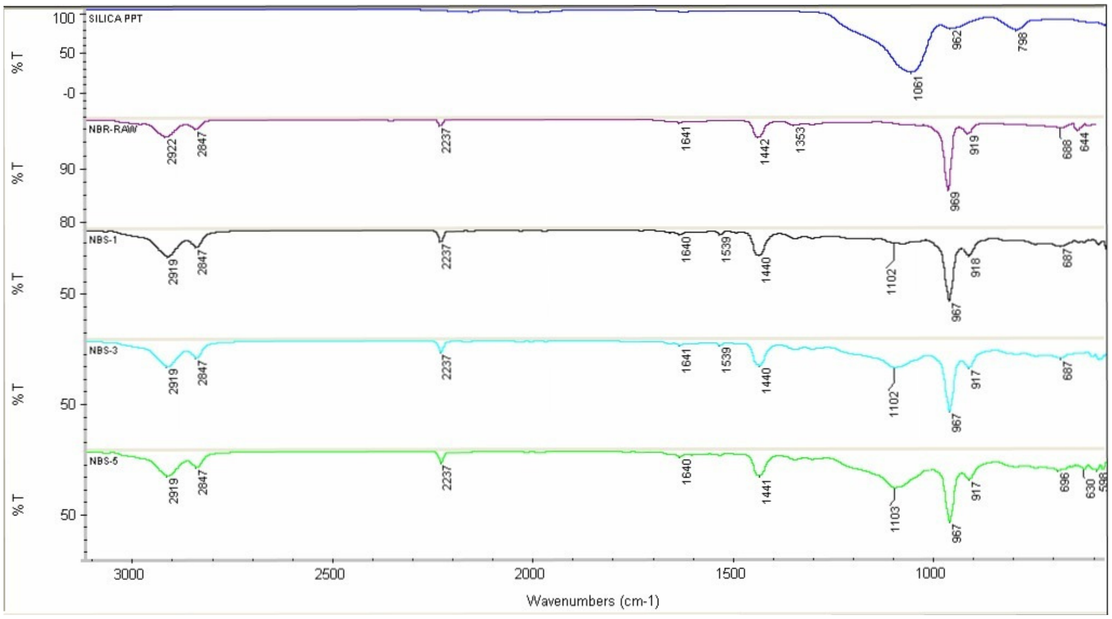
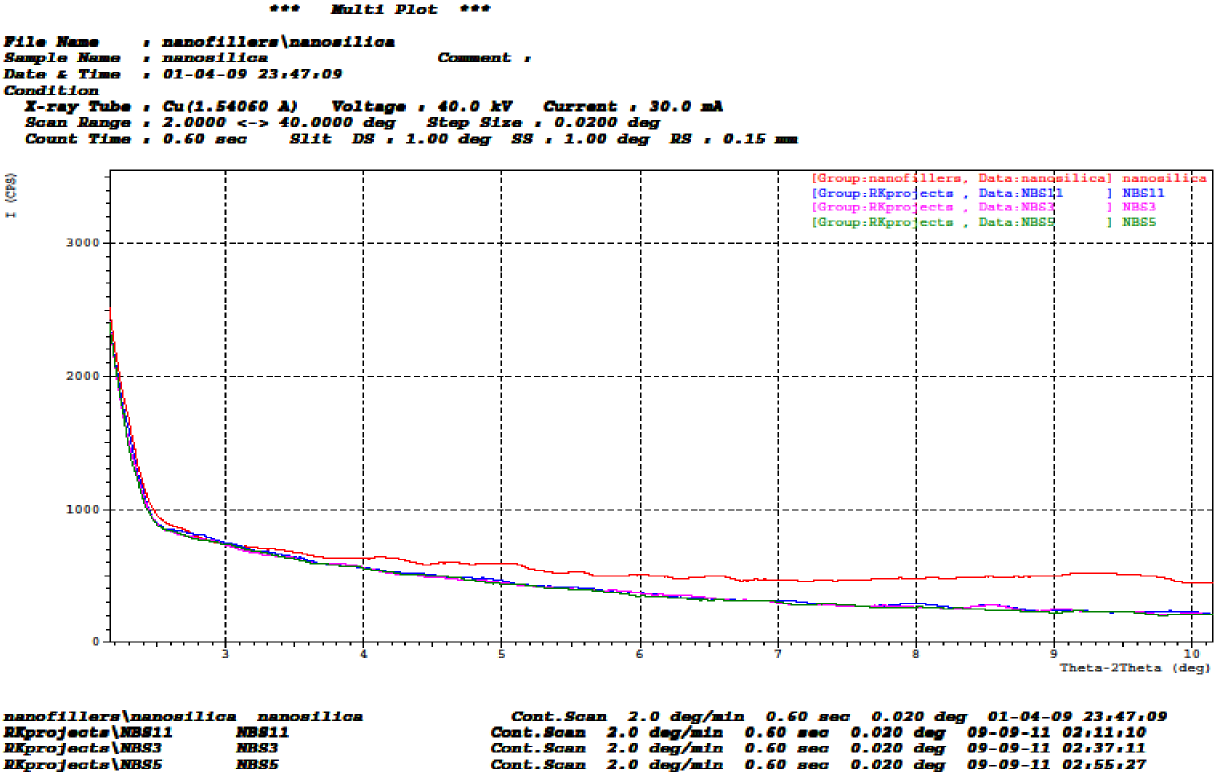


Fig.-10: FTIR spectra of Silica and NBR based Nanosilica Composites



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                    ***   Multi Plot   ***

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  Scan Range : 2.0000 <-> 40.0000 deg   Step Size : 0.0200 deg
  Count Time : 0.60 sec    Slit  DS : 1.00 deg  SS : 1.00 deg  RS : 0.15 mm
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RKprojects\NBS3         NBS3               Cont.Scan  2.0 deg/min  0.60 sec  0.020 deg  09-09-11 02:37:11
RKprojects\NBS5         NBS5               Cont.Scan  2.0 deg/min  0.60 sec  0.020 deg  09-09-11 02:55:27
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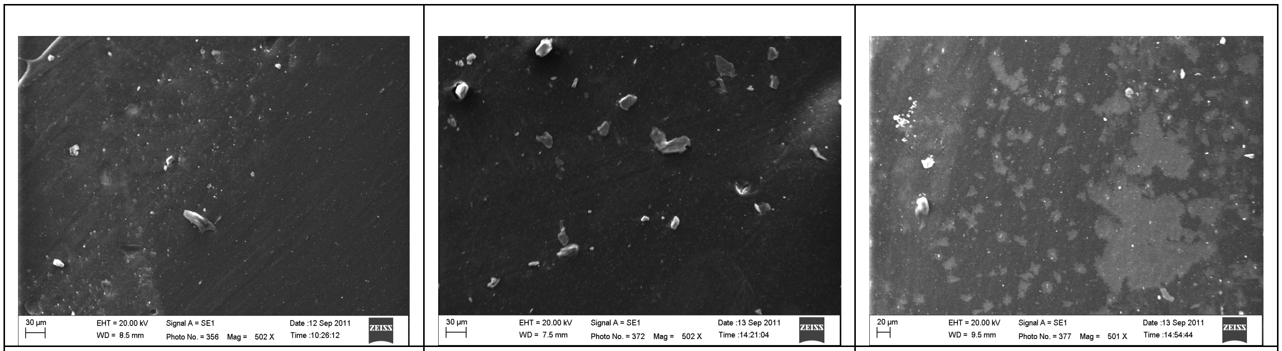
Fig.-11: XRD study of NBR Nano-silica Nanocomposites



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

Fig.-12 : Fracture surface morphology study of NBR Nanocomposites through SEM with different Nano-silica doses (1) 1 phr (2) 3 phr (3) 5 phr

After Ageing studies

Table-2 shows retention of physical properties of polymer Nano composites after hot air ageing at 100° C for 24 hrs. As the loading of Nanosilica increases from 0 to 5 phr the retention of tensile strength after ageing found to improve initially [from 70 % to 98 %] and then it decreases drastically. This shows that 3 phr is an optimum dose for enhancement of heat resistance properties of NBR nano composites. This trend show that the silica nanoparticles increases the thermal stability of the polymer nanocomposites which was corroborated by the thermal analysis studies discussed in later part of this paper. The retention of tensile strength increases as the Nanosilica reacts with the base polymer and forms new C-Si-O bond between two polymeric chains which has been characterized by FTIR spectroscopy also. The retention of tensile strength enhanced due to restriction of bond cleavage of C-Si-O bond in nano composites which is stronger than that of C-C or C-H bonds in polymeric chains having no Nanosilica fillers. As the dose increases, inter molecular distance between the polymer chains increases as the nano fillers gets physically absorbed between the chains leading to separation of polymer chains and hence the polymer chains breaks down faster than that of C-Si-O bonds formed due to presence of Nanosilica filler in the polymer network. From table-2, we observe that changes in hardness after ageing is not significant where as the changes in elongation at break are quite significant after ageing.

Tear strength

Fig.-9 shows the effect of Nanosilica on 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 the strong polymer filler network developed between the Nanosilica and NBR polymer. The energy required for tearing the specimen at the nick where in Nanosilica has stronger bond with the polymer net work which elongates more than the expected values and hence the tear strength also increases. This corroborates the increases in tensile strength as the loading of silica nanoparticles increases.

FTIR spectra

Fig-10, FTIR spectra of Nanosilica, Raw NBR and NBR based Nanosilica polymer nano composites indicate that Nanosilica interacted with NBR polymer structure. Transmittance peak at 1061 cm^{-1} was corresponding to Si-O bond stretching. This peak was found at NBR based Nanosilica composites with a shift at 1102 cm^{-1}. The peak intensity at 1102 cm^{-1} also increases with the increase of dose of Nanosilica in the polymer nano composites. This peak was completely absent in NBR raw polymer which contain no silica. This corroborates that the Nanosilica dispersed very well within the polymer matrix of NBR nano composites.

X- ray diffraction studies

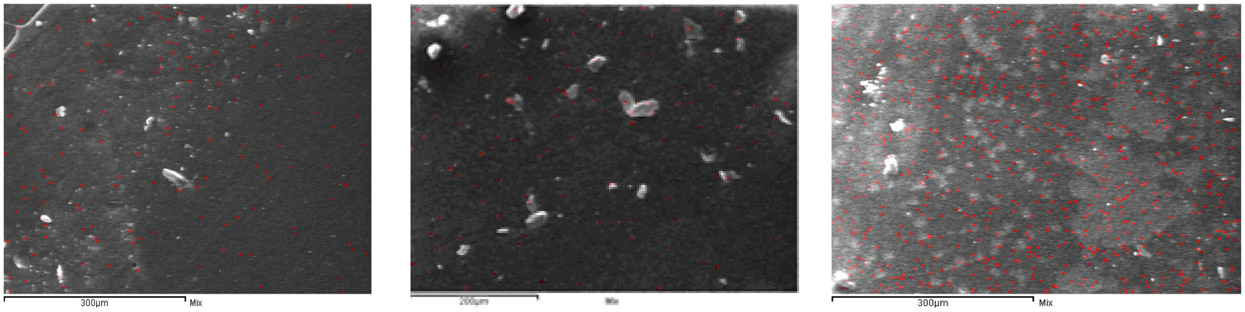
Fig.-11 shows the X- ray diffraction studies of polymer Nano composites containing Nanosilica. The dispersion of the Nano-silica was studied by XRD Fig.-10 shows the X-Ray diffractograph of unfilled NBR compound vulcanizate and NBR-Nanocomposites. From the plots it can be observed that pure silica platelets and silica / NBR exhibit an intense peak at diffraction angle of 10. It was observed that with increase in Nano-silica loading lead to increase in intensity of the peaks (as shown in Fig.-1), which can be attributed to presence of higher number of silicate layers.

SEM-EDS studies

Fig.-12 depicts the SEM of the polymer nanocomposites with different doses of nanosilica incorporation. The SEM of fig.-13 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. Fig.-13 depicts the EDS spectra of SEM photographs have been investigated for the distribution of Nanosilica in the respective polymers. From these EDS spectra, it is verified that the Nano fillers were distributed equally in polymer matrix and the concentration of Nanosilica presence increases from NBS 1 to NBS 5.

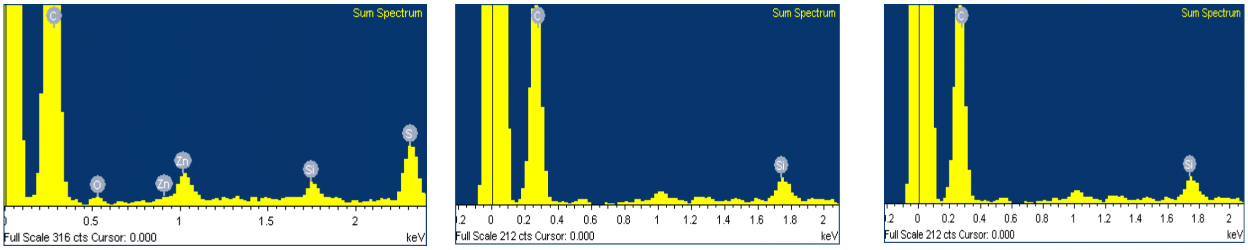
TGA Analysis

Fig.-15 depicts the thermogram of Nanosilica based NBR polymer nanocomposites. The TGA technique was useful to study complex systems like polymer blends[30-31], nanocomposites[32-33], etc. The thermal decomposition of the nanohybrids was studied in a wide range of composition by systematically changing the nature of both the polymer and the nano-filler. This corroborates the hot air ageing resistance properties of nanocomposites. From the Fig.-15 it is clearly visible that on incorporation of 5 phr nanosilica (NBS-5) has made significant reduction of initial degradation temperature as well as the final degradation temperature. These characteristic can be attributed to the fact the intercalation of polymeric chains in to silicate layers act as barrier against temperature and shows more stability than pristine polymer or lower loading of Nanosilica particles.



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

Fig.-13 : Mapping of Nanosilica distribution in NBR Nanocomposites through SEM – EDS with different Nano-silica doses (1) 1 phr (2) 3 phr (3) 5 phr [In the Pictures red colour particles are Nanosilica]



EDS analysis – Nano Si : 0.57 % EDS analysis : Nano Si : 2.07 % EDS analysis : Nano Si : 2.09 %

Fig.-14 : SEM – EDS spectra of NBR Nanosilica composites with different Nano-silica doses (1) 1 phr (2) 3 phr (3) 5phr.

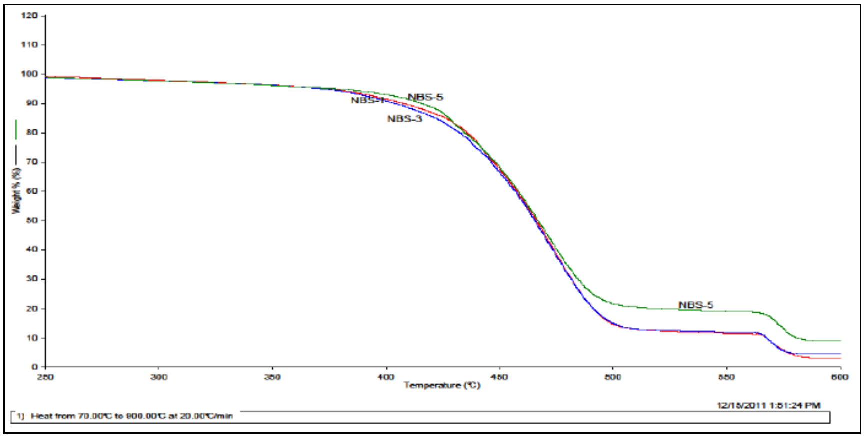


Fig.-15: Thermogram of Nanosilica – NBR polymer nanocomposites

CONCLUSIONS

The effect of addition of Nano-silica fillers in NBR Nanocomposites using liquid NBR as dispersion media using conventional mixing techniques was investigated. The addition of Nano-silica increases thermal resistance of polymer nanocomposites. Improvement in physical properties was found at higher loading of Nano fillers. The dispersion of nanofillers with increasing concentration of Nanosilica was studied by using X-Ray Diffraction and Scanning Electron Microscope and FTIR spectroscopy.

ACKNOWLEDGEMENTS

Authors are thankful to the management of IRMRA for providing support for carrying out this research work and permitting for publication.

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[RJC-1035/2013]