

High Temperature Resistance Properties of NBR Based Polymer Nanocomposites

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Abstract: The high temperature resistant Polymer-nanographite composite was prepared using Nanographite as reinforcing fillers in Acrylonitrile Butadiene Rubber (NBR) and investigated. The effect of increasing nanographite loadings on mechanical properties like tensile strength, modulus and Elongation at break was studied. Mechanical tests demonstrate that the NBR/graphite nanocomposites possess greatly increased elastic modulus and tensile strength, and desirably strong interfaces. The NBR nanocomposites showed higher thermal stability in comparison unfilled rubber vulcanizate. Physico-mechanical properties of the polymer nanocomposites after air ageing studies at 200°C showed improved thermal resistance and increases with loading of nanographite. The dispersion of the nanographite filler in the Nitrile Rubber was achieved using liquid NBR polymer matrix and was investigated by SAXD, SEM and Mechanical properties. SAXD study indicated that the composites did not change the inter-gallery distance (d-spacing) of the graphite platelets and as the loading of nano filler increases the dispersion of nanoparticles improved due to filling effect.

Keywords: Nanographite, Rubber, Morphology, Mechanical properties, TGA.

Introduction

For all applications, elastomers are reinforced with fillers to improve their performance by incorporating materials such as carbon blacks, silica, clay, talc and calcium carbonate etc. These composites which are made with the above mentioned fillers are called micro composites. 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. Graphite is a layered material with high aspect ratio in

its exfoliated state; it 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) compared to layered silicates [13]. In addition, nano graphite is cheap in comparison with carbon nanotubes. Recently, polymer/graphite nanosheet composites have made a great impact in nanocomposite research [14–27]. Improved mechanical and functional properties of elastomer/graphite nanocomposites prepared by NBR latex compounding were reported by Li-Qun Zhang [28].

NBR-based Nanocomposite was prepared and mechanical and thermal properties were studied. The dispersion of the filler in the polymer matrix was studied using the modern instrumentation techniques

like X-ray diffraction, scanning electron microscopy (SEM). The effect of increase in graphite loadings on the performance characteristics like tensile strength, modulus and Elongation at break and its air ageing studies at 200°C for 24 hrs were also reported. The thermal degradation properties of the composites were studied using Thermo-Gravimetric Analyzer.

Experimental

Materials

Acrylonitrile Butadiene Rubber (NBR), Liquid NBR, Nanographite powder and other ingredients [like curatives (S, MBTS), Activator (ZnO, Stearic Acid) and Antidegradants (TQD, 6PPD)] were obtained from reputed manufacturers and used for studies.

Preparation of NBR-Nanographite composites

Mixing of nanofillers in polymer were carried out in two stages. In the first stage, the nanographite at different loading 3, 6 and 9 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-Nanographite masterbatch”. In the second stage, the “NBR-Nanographite masterbatch” 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 nanographite based rubber compound. The compounded rubber sheet was kept for maturation for 16 hrs and then taken for moulding of various test specimens as per ASTM standard using hydraulic press at a temperature 150°C. The curing time was obtained from rheological studies carried out using Mansanto Rheometer.

Physico-mechanical properties

The test specimens i.e dumbell specimens punched out from the compression molded sheet and used for determining physico-mechanical properties as per ASTM D 412 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 hrs as per ASTM D 573 and change in physico-mechanical properties were also measured.

Characterization

Small angle X-ray diffraction (XRD) study of the Nanocomposites were performed at room temperature using a Philips PW 1710 diffractometer in the angular range of 0° to 10° 2θ (SAXD). The target was copper and the (Cu Kα) radiation ($\lambda = 1.540598 \text{ \AA}$) was obtained on applying 50 KV voltage to the generator and the current was 40 mA. The basal spacing of nano graphite layers was estimated from the position of the plane peak in the SAXD intensity profile. Specimens for X-ray diffraction were taken from compression-molded sheets of 2mm thickness.

Morphological characterization of the nanocomposites was carried out using a JEOL JSM 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° with an operating voltage of 20 kV at 0°C. Then the cut specimens were suspended in a copper grid.

Thermo gravimetric analysis

Small cut sample of moulded polymer composites were used for Thermal characterization of Nanocomposites under N₂ atmosphere using Q50 TA instrument, USA. The samples were heated from 30°C to 900°C at a heating rate of 10°C/min.

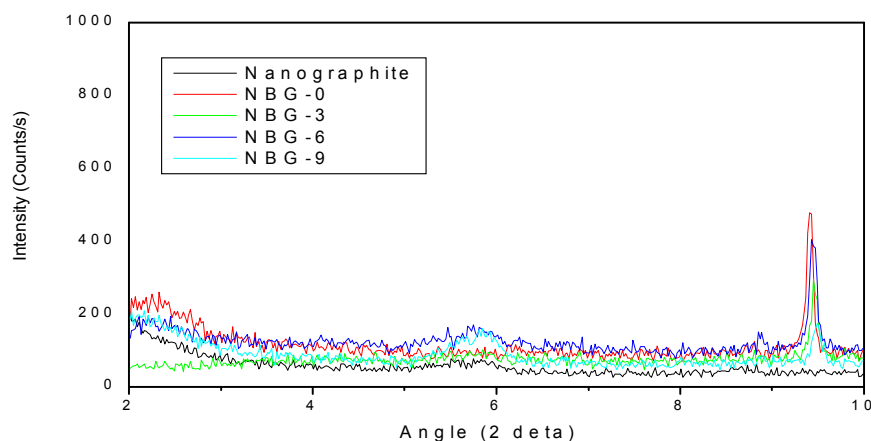


Figure 1 . SAXD of NBR Nanocomposites using Nanographite

Table1. Formulation for preparation of NBR – Nanocomposites (Amounts in phr*)

Ingredients	NBG-0	NBG-3	NBG-6	NBG-9
NBR rubber	80	80	80	80
Liq. NBR	20	20	20	20
sulphur	2	2	2	2
ZnO	4	4	4	4
Stearic Acid	1	1	1	1
Nanographite	0	3	6	9
MBTS	0.5	0.5	0.5	0.5
Antidegredents	2	2	2	2
Total Batch weight	109.5	112.5	115.5	118.5

*phr: Parts per hundred gram of rubber

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

Physical Properties	NBG-0	NBG-3	NBG-6	NBG-9
Tensile Strength (MPa)	2.4	3.5	5.2	6.3
Elongation at break (%)	700	800	850	910
Hardness (Shore A)	40	41	42	44
100% modulus (MPa)	1.0	1.1	1.2	1.4
300% Modulus (MPa)	1.4	1.6	1.9	2.1
Air Oven Ageing study at 100°C for 24hrs				
Retention of Tensile Strength (%)	70	75	78	81
Elongation at break (%)	650	680	700	710
Hardness (Shore A)	44	47	47	48
Air Oven Ageing study at 200°C for 24hrs				
Retention of Tensile Strength (%)	23	24	37	59
Elongation at break (%)	<10	<10	<10	<10
Hardness (Shore A)	83	81	78	70

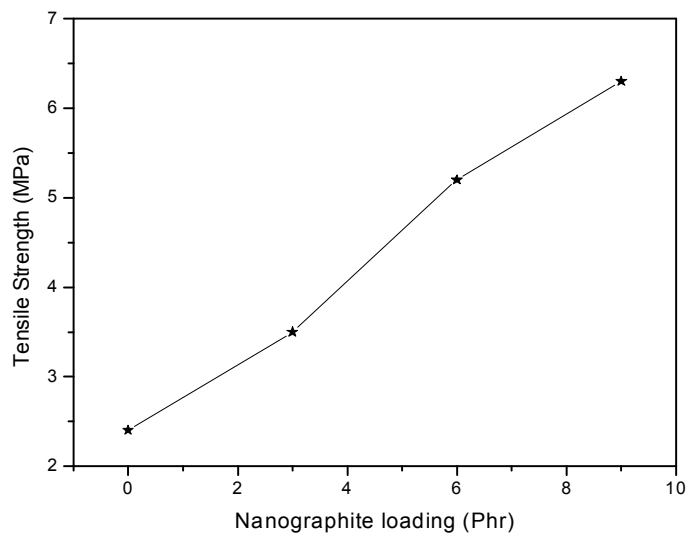


Figure 2. Tensile strength Vs nanographite loading in NBR Nanocomposites

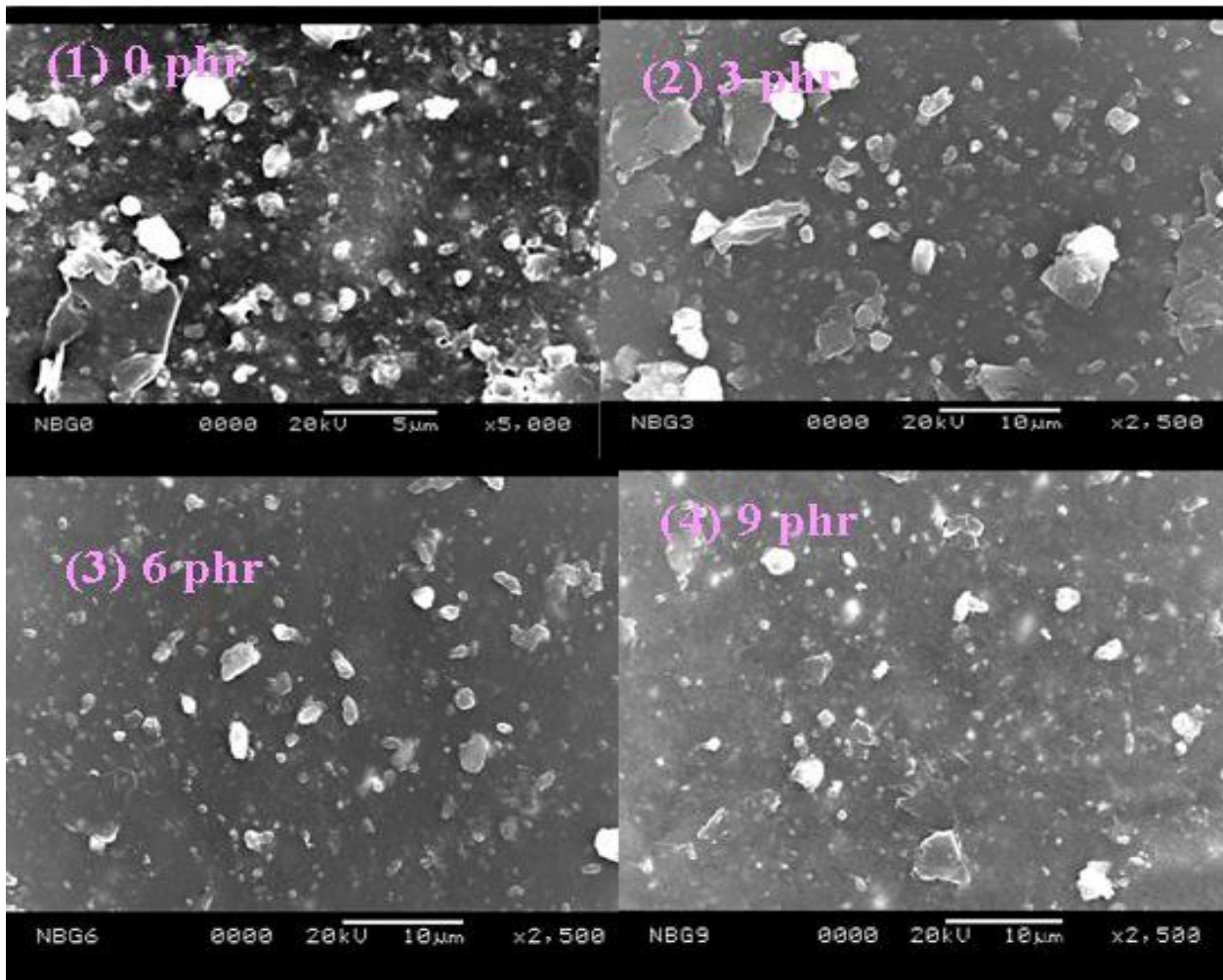


Figure 3. Fracture surface morphology of NBR Nanocomposites through SEM with different Nanographites doses (1) 0 phr (2) 3 phr (3) 6 phr (4) 9 phr

Table 3. Thermal characteristics of NBR rubber with nanographite based nanocomposites

Sample Code	Initial Temp. (Ti°C)	Maximum Temp. (Tmax°C)	Residual weight (%)
NBG-0	338	454	4.7
NBG-3	340	459	6.6
NBG-6	343	460	9.1
NBG-9	346	463	11.2

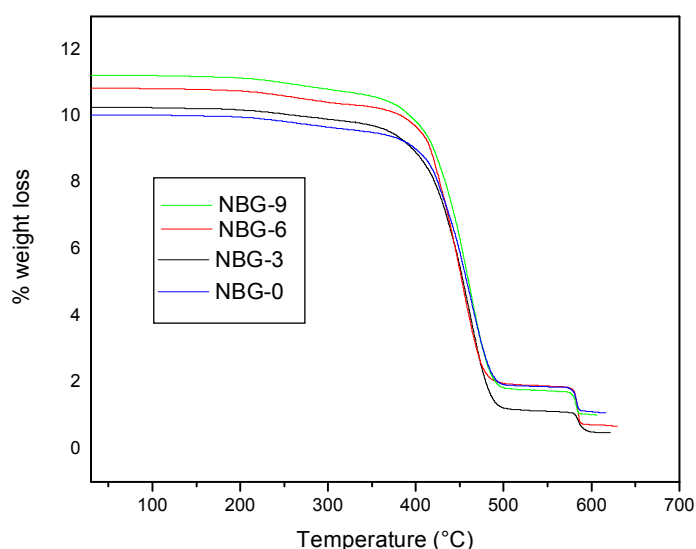


Figure 4. Thermogram of NBR Nanocomposites

Results and Discussion

The dispersion of the nano graphite platelets was studied by SAXD Figure -1 shows the X-Ray diffractograph of unfilled NBR compound vulcanizate and NBR-Nanocomposites. From the plots it can be observed that both pure graphite platelets and graphite/NBR exhibit an intense peak at diffraction angle of 10.2° . It was observed that with increase in nano-graphite loading lead to increase in intensity of the peaks (Figure 1), which can be attributed to presence of higher number of graphite layers.

The physical properties like tensile strength, modulus and hardness of NBR nanocomposites having increasing nano graphite loadings (0 to 9 phr) is shown in Table-2 respectively. From the Figure-2 it can be observed that there is a steady increase in tensile strength with filler loadings of Nanographite. 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 nanographite showed increase in Tensile strength and modulus properties (Table 2), due to reinforcement effect of filler-polymer interaction. Elongation at break (Table 2) increases with loading unusually because of the layer of graphite 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 where as in our study the heat resistance was also carried out at 200°C for 24 hrs and the results were tabulated in Table-2. The results showed that retention of its tensile strength of polymer nanocomposites were much higher than that of unfilled NBR vulcanizate due to effective polymer filler interaction. This could be explained that polymer molecules were protected by the nanographite filler layer with reaction of Nitrile group of NBR and with graphite structure [28]. Hence the degradation of polymer molecules was considerably reduced. The changes in hardness (Table 2) after ageing at 200°C for unfilled polymer (NBG-0) from 40 to 83 was found to be much higher than that of nano filled polymer (NBG-9) from 44 to 70. This corroborates other finding of protection of polymer layers by the nano graphite. Elongation at break for all composites was found to be less than 10 % after ageing due to conventional thermal ageing effect of polymers.

Figure 3 shows representative scanning electron micrographs of tensile fracture surface of NBR Nanocomposites. The SEM image Figure 3(1) to 3 (4) showed that the distribution of particles of ZnO and nanographite Graphite fillers. With increasing loading of fillers [0, 3, 6 & 9 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.

The thermal stability of NBR Nanocomposites was measured using Thermo-Gravimetric Analyzer in nitrogen atmosphere and the Thermogram of composites with different filler loadings is shown in

Figure-4. The onset and end set of thermal degradation temperature were calculated from TGA(Table 4). The results indicated that with increasing in nanographite loadings a continuous increase in onset, end set, degradation temperatures and weight loss, which indicate the trend of increasing the thermal stability of the nanocomposites. The residual weight increases with increase in nano filler loading.

Conclusion

The effect of addition of nano graphite fillers in NBR Nanocomposites using liquid NBR as dispersion media

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was investigated. The addition of nanographite increases thermal resistance after ageing at 200° C and improvement in physical properties were found at higher loading of nano fillers. The dispersion of nanofillers with increasing concentration of nano graphite was studied by XRD and SEM.

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