

**ELASTOMERIC COMPOSITE: MECHANICAL AND
THERMAL PROPERTIES OF STYRENE BUTADIENE
RUBBER (SBR) BASED ON CARBON BLACK AND
NANOCLAY**

¹ROHIT SINGH, ²M.D.SHAH, ³S. K. JAIN, ⁴S.C. SHIT, AND ⁵RADHASHYAM GIRI

^{1, 2, 3, 4, 5} Plastic Engineering Department, High Learning Centre,
Central Institute of Plastic Engineering and Technology (CIPET),
Ahmedabad – 382445, Gujarat, INDIA.

*rohitsingh4258@gmail.com, sandesh_cipet@hotmail.com, Subhasch.shit@yahoo.com,
shh_mynk@yahoo.co.in, giripolymer@gmail.com,*

ABSTRACT: Styrene butadiene Rubber (SBR) based hybrid nanocomposites containing carbon black (CB) and Organo-modified nanoclay (MMT Cloisite-20A) were prepared. The mixing and compounding at different proportion was done on two-roll-mill and composite sheets were prepared in compression molding. Mechanical properties such as (tensile strength, elongation at break), hardness, Compression set measurement, and ageing properties were studied. The effect of carbon black and organo-modified nanoclay on these rubber hybrid nanocomposites were investigated by Thermal gravimetric analysis (TGA). Morphological properties of composites were evaluated by SEM analysis. The mechanical and thermal properties were found to improve at 5 phr organo-modified nanoclay and further increase in loading of organically modified nanoclay the respective properties found to be decreases due to agglomeration of the organo-modified nanoclay on SBR nanocomposites.

KEY WORDS: Styrene butadiene rubber (SBR), Carbon Black (CB), Organo-modified Nanoclay, Mechanical properties, Thermal properties.

1. Introduction

Carbon black (CB) is the most important reinforcing filler used in the rubber industry. About 90% of the worldwide production of CB is used in the tire industry in which the CB serves as reinforcing fillers for improving tear strength, modulus, and wear characteristics of the tires. As the source of CB is petroleum, the preparation and processing of CB is hazardous. Moreover, CB imparts black colour to rubber. In the past two decades, research was aimed to develop other reinforcing agents to replace CB in rubber compounds such as sepiolite, kaolin, and precipitated silica [1-3]. These fillers are inorganic in nature and incompatible with organic polymer matrices. Thus, the reinforcing effect of these fillers was much lower than that of CB. However, the layered silicate nano-fillers have already been developed. In those nano-fillers, the silicate layer surfaces have been effectively modified to render them organophilic so that the organically modified nano-fillers can significantly enhance the critical performance properties of polymer-clay composites [4-7]. The unique properties, imparted by nanoclay (NC) to rubber composites, have opened up a new prospect in developing CB-NC-hybrid nanocomposites via facilitating the possible partial replacement of CB with NC in rubber products

without affecting the critical performance properties. The aim of this work, the unique properties, imparted by nanoclay to rubber composites, have opened up a new prospect in developing carbon black-nanoclay-hybrid composite via facilitating the possible partial replacement of carbon black with nanoclay in rubber products without affecting the critical performance properties.

2. Experimental

2.1 Materials

SBR 1502 (Styrene content 23%, ML (1+4) at 1000 C = 60) was supplied by Sinopec Qilu Company, Malaysia. Cloisite 20A (Cation exchange capacity = 95 miliequivalent / 100 g of clay,) was purchased from southern clay products, USA. N330 grade carbon black (nitrogen adsorption surface area 80 m²/gm) was procured from Philips carbon Ltd. Calcutta, India. Other compounding (Paraffin oil) and curing additives (Zno, stearic acid, sulphur, CBS, TMTD), including antioxidant (TQ) were purchased from local suppliers (analytical grade).

2.2 Preparation of SBR nanocomposites

All the rubber nanocomposites were prepared on a two roll mill of 300 mm length, 170 mm diameter

with speed of slow roll (18 revolution/min) and friction ratio (1.4). In case of CB filled nanocomposites, NC was added to the SBR prior to the addition of CB. After the addition of NC, the compound was passed 3–4 times through the rollers having a tight nip gap of <1 mm. The compounding ingredients were added as per procedure given in ASTM D 3184–89 and ASTM D 3182–89 in the following order: activator, filler, accelerator and curing agents. After mixing, the rubber compounds were left for 24 hrs and then moulded in the form of sheets in an electrically heated hydraulic press at 150°C. The details of formulation and sample identification used in this study are listed in Table 1.

2.3 Tensile Strength and Elongation at break

These tests were carried out according to ASTM D 412–1998, using dumbbell specimens. Test specimens were punched out from the molded sheets using the C- type die, along the mill grain direction. The measurements were carried out at a cross head speed of 500 mm/min on an Instron Universal Testing Machine according to ASTM standards, D 412–68 and D 624–54 respectively.

2.4 Tear Strength

Tear resistance of the samples was tested as per ASTM D 624–1998, using un-nicked 90° angle test specimens that were punched out from the moulded sheets, along the mill grain direction. The measurements were carried out a crosshead speed of 500 mm per minute on a on an Instron Universal Testing Machine according to ASTM standards, D 412–68 and D 624–54 respectively. The tear strength was reported in KN/m.

2.5 Hardness

The testing was done as per ASTM D 2240–1997 using Shore A type Durometer. Readings were taken after 15 seconds of the indentation when firm contact has been established with the specimens.

2.6 Compression Test Measurement

Compression set test (ASTM D395) was performed on standard test specimen of cylindrical shape of 25 ± 0.1 mm diameter and 12 ± 0.5 mm thickness vulcanized by compression molding method. The test specimen shall be placed between the plates of the compression device with the spacers on each side of it, allowing sufficient clearance for bulging of the rubber when compressed. The bolts shall be tightened so that the plates are drawn together uniformly until they are in contact with the spacers. The percentage of the compression employed shall be 25% of the original thickness. Then the

assembled compression device shall be placed in oven at 70°C for 22 h. After completion of the assembly and remain in dry air circulated oven for heating period at the test temperature, the device shall be taken from the oven and the test specimen removed immediately and allowed to cool for 30 min, after this rest time the final thickness shall be measured by an electronic digital caliber with 0.01 mm accuracy. The compression set is defined as:

$$C\% = \frac{t_0 - t_1}{t_0 - t_s} * 100$$

where t_0 = Original thickness of the sample
 t_1 = thickness of the sample after removed from the clamp, and t_s = thickness of the spacer bar.

2.7 Thermogravimetric Analysis

The thermograms of SBR-CB-NC hybrid composites are recorded with a thermogravimetric analyzer TGA (Perkin Elmer, Pyris 1 TGA). It is computer controlled instrument that permits the measurement of the weight changes in the sample material as a function of temperature. The sample placed in a temperature programmed furnace is subjected to temperatures in the ranges 30°C to 800°C with a heating rate of 10°C/minute and the corresponding weight changes were noted with the help of an ultra sensitive microbalance. Air and nitrogen were used as purge gases.

2.8 Thermal Ageing Studies

Tests were carried out as per ASTM D 573–1999. Test specimens were exposed to oxygen atmosphere at specified elevated temperature in an air oven, for known periods of time, after which their physical properties were determined and were compared with the properties of the samples. Air oven (Techno Laboratory Instrument Ltd, Chennai) was used to carry out the aging test. Aging temperatures were 70°C in 48 hrs for SBR composites

2.9 Scanning electron microscopy

The fracture surface of the vulcanizate was studied with JEOL (JSM-5610LV) scanning electron microscope.

Table 1: Sample designations for neat SBR, SBR/CB without NC and with NC composites.

Sample code	SBR	Zno	Stearic Acid	Carbon Black	Oil	TDQ	Sulphur	CBS	TMTD	Nano Clay
SBRN ₀ C ₀	100	5.0	2.0	–	2.0	1.0	2.5	1.5	0.2	–
SBRN ₀ C ₁₀	100	5.0	2.0	10	2.0	1.0	2.5	1.5	0.2	–
SBRN ₀ C ₁₅	100	5.0	2.0	15	2.0	1.0	2.5	1.5	0.2	–
SBRN ₀ C ₂₀	100	5.0	2.0	20	2.0	1.0	2.5	1.5	0.2	–
SBRN ₀ C ₂₅	100	5.0	2.0	25	2.0	1.0	2.5	1.5	0.2	–
SBRN ₀ C ₃₀	100	5.0	2.0	30	2.0	1.0	2.5	1.5	0.2	–
SBRN ₃ C ₂₀	100	5.0	2.0	20	2.0	1.0	2.5	1.5	0.2	3.0
SBRN ₅ C ₂₀	100	5.0	2.0	20	2.0	1.0	2.5	1.5	0.2	5.0
SBRN ₇ C ₂₀	100	5.0	2.0	20	2.0	1.0	2.5	1.5	0.2	7.0
SBRN ₁₀ C ₂₀	100	5.0	2.0	20	2.0	1.0	2.5	1.5	0.2	10.0
SBRN ₁₂ C ₂₀	100	5.0	2.0	20	2.0	1.0	2.5	1.5	0.2	12.0

3. Results and discussion

3.1 Mechanical properties

The effect of nanoclay on tensile properties, elongation at break and hardness of the SBR- carbon Black-clay hybrid nanocomposites at room temperature was investigated the values summarized in Table 2. Sample containing without nanoclay with increase in CB content in SBR rubber, the tensile strength, elongation at break, tear strength and hardness improves 19.89 mpa, 655 %, 32 KN/m and 61 Shore A up to 20 phr CB were shown in Table 2. Beyond 20 phr of CB there is high amount agglomerates in high filler dosage composites, these agglomerate played the role of an obstacle to molecular chain movement of the SBR rubber, thereby initiating failure under stress. Similarly Sample containing increase in nanoclay proportion with fixed 20 phr CB content in SBR rubber, the tensile strength, elongation at break, tear strength and hardness of 26.54 mpa, 780 %, 35.0 KN/m and 62.0 Shore A up to 5 phr NC were shown in Table1. Beyond 5 phr NC, the high amount agglomerates in high filler concentration played the role of obstacle to molecular chain movement of the SBR nanocomposites and finally failure under stress.

3.2 Phase Morphology

The SEM photomicrographs fractured surfaces of SBR/Carbon Black/nanoclay composites of samples SBRN5C20 and SBRN12C20 are shown in figure 1. Even though there appeared to be no significant difference in the morphology between SBRN5C20 and SBRN12C20. The SEM photomicrographs shown in fig. there is however agglomeration of the organoclay at 12 phr due to poor dispersion. This also explains why there occurred a reduction in the mechanical properties after 5 phr of carbon black with organoclay loading.

Table 2: Mechanical properties of neat SBR, SBR/CB without NC and with NC composites with and without air ageing

Sample code	Tensile strength (mpa)	Elongation at break (%)	Hardness	Tear strength (KN/m)
SBRN ₀ C ₀	2.0±0.8	510±4	48	9.0±0.6
SBRN ₀ C ₁₀	8.42±0.5	556±6	56	15.0±0.5
SBRN ₀ C ₁₅	12.80±0.5	583±4	58	18.0±0.6
SBRN ₀ C ₂₀	19.89±0.8	655±7	61	32.0±0.5
SBRN ₀ C ₂₅	18.86±1.0	640±8	59	31.5±1.2
SBRN ₀ C ₃₀	18.24±0.6	636±5	59	29.0±1.4
SBRN ₃ C ₂₀	20.28±1.2	705±2	61	34.0±0.6
SBRN ₅ C ₂₀	26.54±0.8	780±5	62	35.0±0.8
SBRN ₇ C ₂₀	24.20±0.5	745±3	60	33.4±0.5
SBRN ₁₀ C ₂₀	23.38±1.2	722±5	60	32.0±1.2
SBRN ₁₂ C ₂₀	22.25±0.6	714±2	59	32.0±0.5

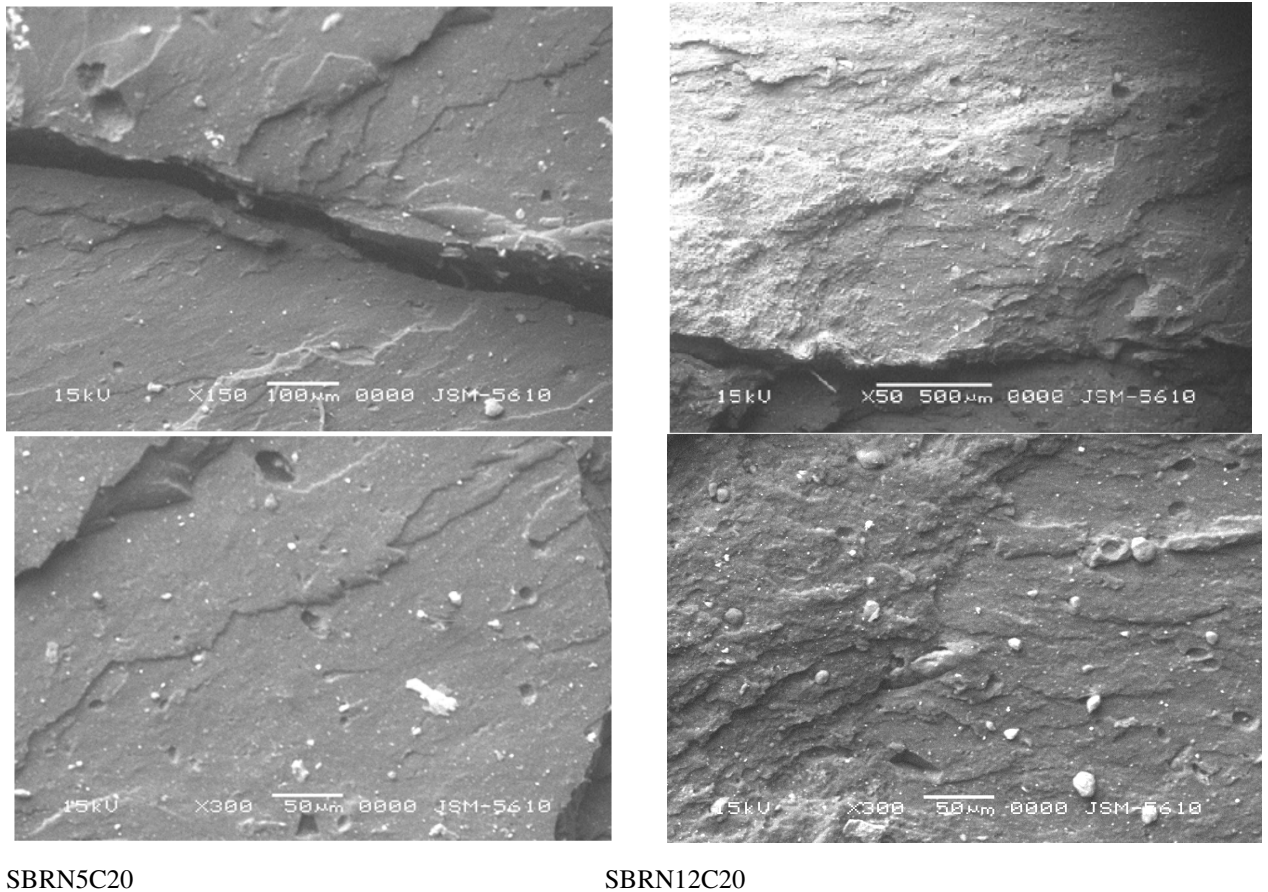


Fig.1 SEM micrographs of SBRN5C20 and SBRN12C20

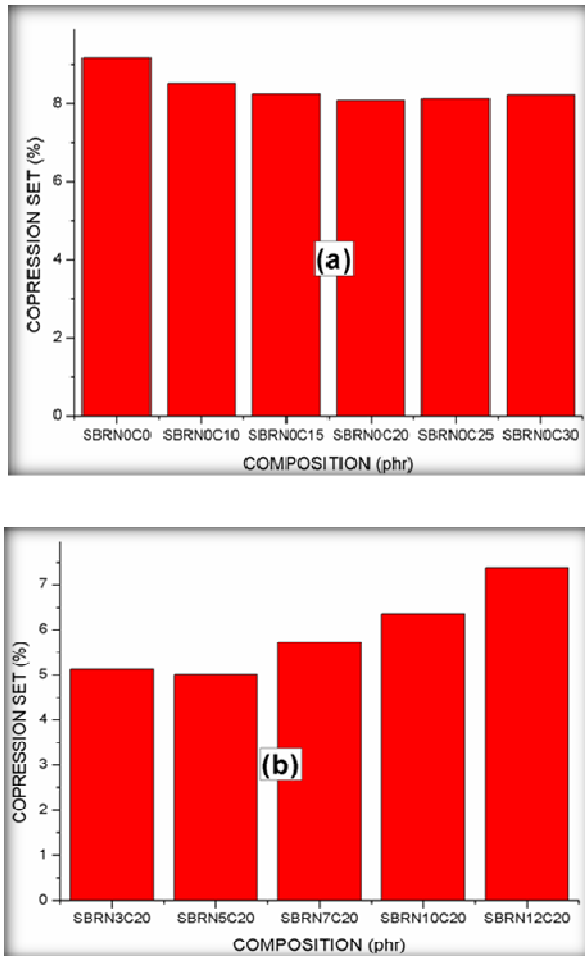


Fig: 2 (a & b) - Effect of carbon black (N330) and Carbon black with Nanoclay on Compression set of SBR nanocomposites

Compression set testing measures the ability of the rubber to return to its original thickness after prolonged compressive stresses at a given temperature and deflection. As a rubber material is compressed over time, it loses its ability to return to its original thickness. This loss of resiliency may reduce the capability of a rubber seal to perform over a long period of time. The resulting permanent set that a seal may take over time may cause a leak. Compression Set results for a material are expressed as percentage. The lower the percentage, the better the material resists permanent deformation under a given deflection and temperature range. The results of the compression set for the samples of carbon black (N330) and Carbon black with Nanoclay SBR composites shown in Fig.3.1(a & b). Comparison of the samples results indicates that unfilled SBR reinforced by 20 phr carbon black and 5 phr nanoclay hybrid composites has the lowest percentage of compression, which means that it permanent deformation better than the other samples. Compression set is a measure of the ability of the rubber to retain their elastic properties after prolonged compression at a constant strain under

specific set of conditions, and its permanent set of rubber compounds. The poor performance of materials in terms of compression set is attributed to uncross-linked chains and to network defects such as long dangling chains, which do not contribute to the permanent network and are able to relax during the compression stage, then providing no elastic contribution to the recovery stage. In the case of SBR/CB/NC hybrid nanocomposites samples the nanoclay results in restriction in polymer chain movements and lower compression set.

3.2 Thermogravitric Analysis

The thermogravitograms of neat SBR and different SBR-Carbon black-organically modified nanoclay compound are shown in Table 3. The thermal analysis data (T_i , T_{50} , T_f and % residue at 800°C) are presented in Table 2. It is evident from the Table 2 that, the initial decomposition temperatures (T_i), and temperature were corresponding to 50% degradation (T_{50}) of the neat polymers and SBR-carbon black-Organically modified nanoclay compound shift towards a higher temperature indicating higher thermal stability of the composites. The initial decomposition temperature (T_i) and temperature corresponding to 50% degradation (T_{50}) of the neat SBR are 350.6°C and 471.6°C respectively and with increasing the organically modified nanoclay content the thermal stability maximum at SBRN5C20 compound (366.0°C and 490.0°C respectively). Thermal stability of carbon black and organo-modified nanoclay may increases due to proper adhesion and crosslinking of matrix and filler and other reason already explain in mechanical properties.

3.3 Thermal Ageing Analysis

The variations of aging properties on tensile strength and tear strength at 70°C in 48 hrs are shown in Table 4. The rate of change in tensile strength and tear strength of SBR/clay nano- composites were less than that of SBR/CB composites. That is to say, the aging resistance of SBR/clay nanocomposites is significantly better than that of SBR/CB composites. The reason is that during the aging period, the rubber chain will be deteriorated or cross- linked by the action of heat, oxygen and ozone, resulting in the change of molecular structure. By analyzing the reason of aging, it is supposed that the heat and air barrier of nanodispersed silicate layers would endure the SBR/clay nanocomposites with excellent aging resistance. Specifically, the gas barrier property of silicate layers could decrease the diffusion rate of gas molecules passing through the rubber and lower the concentration of oxygen and ozone in the SBR matrix, and then reduce the chance of weak bonds in the rubber chain being attacked. SBR nanocomposites shows excellent aging

resistance due to the heat and air barrier of nano dispersed organically silicate layer as compared to neat SBR.

Table 3: Thermogravimetric analysis of neat SBR and SBR/CB/NC nanocomposites.

Sample code	T _i (°C)	T ₅₀ (°C)	T _f (°C)	% Residue at 800 °C
SBRN ₀ C ₀	350.6	471.6	791.6	6.7
SBRN ₃ C ₂₀	361.5	485.6	800.0	21.39
SBRN ₅ C ₂₀	366.0	490.0	800.0	23.6
SBRN ₇ C ₂₀	362.0	489.5	800.0	23.4
SBRN ₁₀ C ₂₀	361.5	485.2	800.0	24.2
SBRN ₁₂ C ₂₀	357.5	481.2	800.0	24.5

Table 4: Mechanical properties of neat SBR, SBR/CB without NC and with NC composites with and without air ageing

Sample code	Tensile strength (mpa) at room temp	Tensile strength (mpa) after 48 hrs at 70 ⁰ c	Tear strength (KN/m) at room temp	Tear strength (KN/m) after 48 hrs at 70 ⁰ c
SBRN ₀ C ₀	2.0±0.8	1.86±0.4	9.0±0.6	6.8±0.5
SBRN ₀ C ₁₀	8.42±0.5	8.12±0.6	15.0±0.5	12.8±0.6
SBRN ₀ C ₁₅	12.80±0.5	12.28±1.4	18.0±0.6	15.5±1.2
SBRN ₀ C ₂₀	19.89±0.8	19.06±0.7	32.0±0.5	31.5±0.6
SBRN ₀ C ₂₅	18.86±1.0	17.85±0.8	31.5±1.2	30.6±1.2
SBRN ₀ C ₃₀	18.24±0.6	17.73±0.5	29.0±1.4	26.4±0.5
SBRN ₃ C ₂₀	20.28±1.2	20.02±1.2	34.0±0.6	31.8±1.2
SBRN ₅ C ₂₀	26.54±0.8	25.86±0.5	35.0±0.8	31.5±0.6
SBRN ₇ C ₂₀	24.20±0.5	23.92±1.3	33.4±0.5	30.4±0.5
SBRN ₁₀ C ₂₀	23.38±1.2	23.0±0.5	32.0±1.2	29.5±0.4
SBRN ₁₂ C ₂₀	22.25±0.6	21.91±1.2	32.0±0.5	28.5±1.3

4. CONCLUSION:

SBR hybrid nanocomposites have been studied by different proportion of CB and NC. The optimum loading of carbon black was found to be 20 phr. SBR-carbon black-clay hybrid composites with 20 phr HAF and 5 phr Nanoclay were shown in excellent mechanical properties, thermal stability and further loading of organo-modified nanoclay the respective properties found to be decreases due to agglomeration of the organo-modified nanoclay on SBR nanocomposites. Since, there is high amount agglomerate in high filler dosage composites; these agglomerates played the role of an obstacle to

molecular chain movement of the SBR, thereby initiating failure under stress.

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