CHAPTER 4

DEVELOPMENT AND CHARACTERIZATION OF NANOCOMPOSITES FOR PASSENGER CAR RADIAL (PCR) TIRE TREAD APPLICATION

Passenger car radial (PCR) tire tread compounds are almost always prepared from blends of SBR/BR. One objective of this study was to develop low hysteresis passenger car radial tread compound with SBR/BR – organoclay nanocomposite. To achieve these goals two different types of high performance SBR/BR based nanocomposites were developed and characterized. In this Chapter the effect of organoclay and dual fillers on mechanical and viscoelastic properties of these nanocomposites are elaborated and the results obtained are discussed in detail.

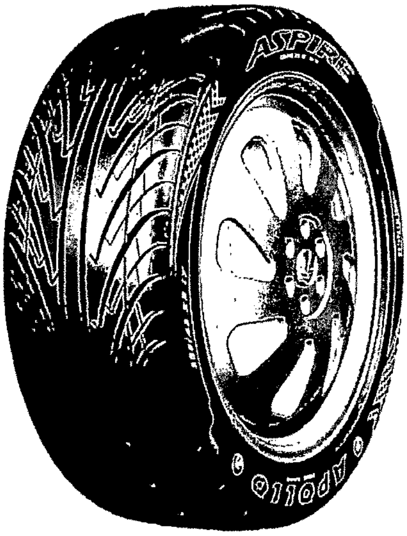


Fig. 4.1- PCR Tire

4.1 PREPARATION AND CHARACTERIZATION OF NANOCOMPOSITES BASED ON ORGANOCLAY AND BLENDS OF DIFFERENT TYPES OF SBR WITH BR

4.1.1 Introduction

Polymer/clay nanocomposites are being extensively investigated because these nanocomposites have enormous potential for commercial utilization in diversified areas such as coating, flame-retarding, barrier materials, electronic materials and composite. Rubbers are generally organophilic; unmodified nanoclay (Na-Montmorilonite) disperses in rubbers with great difficulty. However, through clay surface modification, nanoclay can be made organophilic called organoclay and, therefore, compatible with conventional organic rubbers. Modified organoclay disperse readily in rubbers. Cloisite®15A organically modified nanoclay (Na-MMT) used in this investigation is referred as organoclay (OC) in the subsequent Chapters.

In this investigation, nanocomposites based on 70/30, SBR/BR and organoclay using XNBR as compatibilizer were prepared and characterized aiming for PCR tire tread applications. The performance of nanocomposites depends on several parameters such as nature of rubber, dosage of organoclay and most importantly exfoliation of the organoclay. Similarly organoclay dispersion also depends on a number of parameters such as;

a) Polarity of compatibilizer (Carboxyl group % in XNBR)
b) Mixing techniques
c) Types of SBR rubbers
d) Dosages of organoclay and XNBR

To achieve the best performance properties in the nanocomposite, the effects of all these parameters were studied independently and sequentially and finally the nanocomposite that gave the best performance was selected and used in the preparation of high performance tread compounds. The raw materials, compound formulations, synthesis of nanocomposite, testing and characterization methods are detailed in Chapter 3 in Materials and methods; however compounds codes and brief descriptions are presented in Table 4.1. The results and discussion incorporating the influence of each parameter on mechanical and dynamic mechanical properties of nanocomposites are elaborated in the subsequent sections.

4.1.2 Rheometric properties

The importance of rheometric properties is undisputed since it provides valuable information on compound processing and curing characteristics. The time required to cure any rubber compound at a particular temperature is known as optimum cure time (Tc90) and it is obtained from rheometric data. It also provides additional information like minimum torque (ML) representing the compound viscosity, maximum torque (MH) representing compound modulus and scorch time (Ts2) representing process safety. Table 4.2 presents rheometric properties of gum compounds and various other nanocomposite formulations. Gum compound has minimum viscosity as well as minimum modulus since it does not have any filler. Gum compound (G1) shows highest scorch safety and slowest curing rate among all the compounds. With addition of organoclay, cure became faster and scorch time gets reduced substantially as observed in C-0.

Table 4.1-Compound codes and brief descriptions

	Code	Rubber (Phr)	XNBR (phr)	Organoclay (phr)	Mixing Method
% Carboxyl group in XNBR	C-0	FSSBR/BR (70/30)	XNBR-0 (10)	6.0	Internal mixer
	C-1		XNBR-1 (10)		
	C-4		XNBR-4 (10)		
	C-7		XNBR-7 (10)		
Mixing Methods	M-1	FSSBR/BR (70/30)	XNBR-7 (10)	6.0	2 roll Mill
	M-2				Solution
	M-3				Internal mixer
Type of SBR	G1	FSSBR/BR (70/30)	XNBR-7 (10)	0.0	Internal mixer
	R1			6.0	
	G2	SSBR/BR (70/30)	XNBR-7 (10)	0.0	Internal mixer
	R1			6.0	
	G3	ESBR/BR (70/30)	XNBR-7 (10)	0.0	Internal mixer
	R1			6.0	
Dosage variation of XNBR and organoclay	D0	ESBR/BR (70/30)	0.0	0.0	Internal mixer
	D1		XNBR-7 (6.3)	3.8	
	D2		XNBR-7 (10.0)	6.0	
	D3		XNBR-7 (13.8)	8.3	
	D4		XNBR-7 (5.6)	4.4	
	D5		XNBR-7 (8.9)	7.1	
	D6		XNBR-7 (12.2)	9.8	

In nanocomposite, with the increase of carboxyllation of compatibilizer, compound viscosity as well as compound modulus increases which are attributed to higher filler-rubber interaction at higher % of carboxyl groups. However; with the increase of % carboxyl group, the scorch times were higher and cure became slower. Carboxyl groups being acidic in nature retards the curing reaction as a results cure rate becomes slower.

Table 4.2-Rheometric properties (MDR; 160°C/ 20 min)

	G1	**C-0**	**C-1**	**C-4**	**C-7**
Min. Torque (ML) dN-m	0.23	0.43	0.47	0.48	0.53
Max. Torque (MH) dN-m	6.58	7.41	7.99	8.14	8.34
Δ Torque (MH – ML), dN-m	6.35	6.94	7.56	7.66	7.81
Scorch Time (Ts2) min	**2.68**	**1.57**	**1.63**	**1.72**	**1.83**
50% Cure Time (Tc50) min	3.09	1.85	2.02	2.08	2.17
Optimum Cure Time (Tc90) min	**6.21**	**3.36**	**4.40**	**4.60**	**5.78**

4.1.3 Mechanical Properties

4.1.3.1 Effect of carboxyl content of compatibilizer in nanocomposite.

Organoclay is a polar material and has layer silicate structure. SBR is non polar rubber and it has bulky styrene group in its side chain. To achieve good clay dispersion, there should be good interaction between organoclay and rubber. Further rubber molecules also penetrate easily into the gap among the silicate layers and expand the layer structure. SBR shows less interaction with organoclay due to its non polar nature and bulky styrene group which is evident from poor mechanical property of SBR nanocomposite (Bhowmick *et al.* 2003). However, use of polar rubber as compatibilizer (Das *et al.* 2008) has improved the mechanical properties of SBR nanocomposite remarkably due to fine dispersion of clay.

The polarity of the carrier polymer (compatibilizer) has an immense influence on the mechanical properties of the SBR/BR nanocomposites. Natural rubber (NR) undergoes strain induced crystallization and hence shows very high strength without any filler at higher strain, on the other hand SBR is a non-crystallize rubber, therefore 40-50 phr reinforcing filler such as carbon black is necessary to get comparable strength to NR. The role of filler in SBR is not only to improve modulus, hardness and tear strength but also to improve tensile strength.

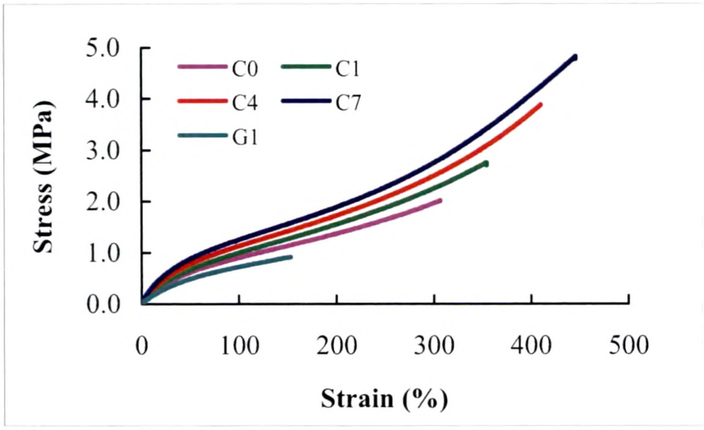


Fig. 4.2-Effect of carboxyllation on stress-strain properties

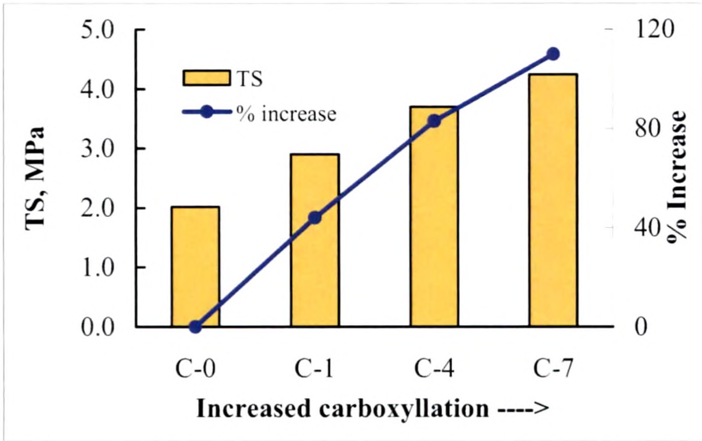


Fig. 4.3-Effect of % carboxyl group on T.S properties of nanocomposite

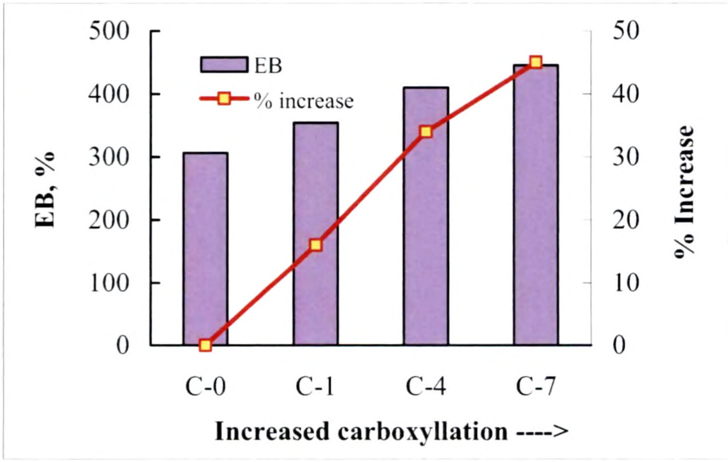


Fig. 4.4-Effect of % carboxyl group on E.B properties of nanocomposite

The stress-strain properties of the nanocomposites with varying percentage of carboxyl group are presented in Fig. 4.2. Substantial improvement in stress strain properties was observed in nanocomposite (C0) compared to gum compound (G1). As % carboxyl group in XNBR increases, the polarity of the polymer also increases. It was observed that all the mechanical properties like modulus, tensile strength, elongation at break and breaking energy increase with the increase of carboxyl group percentage in XNBR. This behavior is attributed to higher interfacial interaction between organoclay and XNBR which increases with the increasing polarity of XNBR due to higher carboxyl content. Higher interfacial interaction between the filler and the rubber leads to better intercalation and exfoliation of organoclay within the rubber matrix, which leads to enhanced mechanical and dynamic mechanical properties. In elastomeric nanocomposite, interfacial interactions between filler particles and rubber matrix affect;

a) Dispersibility of the nano-fillers in the rubber
b) Adhesion properties of fillers and rubber
c) Filler flocculation (re-agglomeration) within rubber matrix.

XNBR has the highest polarity among all the rubbers used and organoclay is highly polar filler in comparison with other fillers, hence combination of XNBR with organoclay show the highest free energy compared to any other rubber-filler combination; this in turn indicates that the dispersion of organoclay in XNBR rubber is likely to be very good.

Effect carboxyl percentage on tensile strength (TS), elongation at break (EB) and breaking energy (BE) are presented in Fig. 4.3, 4.4 and 4.5 respectively. It is observed from Fig. 4.2 that tensile stress increases from 2.0 MPa to 4.2 MPa when carboxyl content in XNBR increases from 0 to 7%. Improvement of TS, EB and BE are 110, 45 and 154 % respectively when carboxyl % changed from 0 to 7%.

4.1.3.2 Effect of mixing techniques

It is known that mixing technique has a great influence on the mechanical property of nanocomposites hence three different mixing techniques viz. 2 roll mill, solution method and internal mixer were used to prepare the nanocomposite. It was noticed that mixing of organoclay was extremely difficult in 2 roll mill, while solution method required a large quantity of solvent which had to be removed after mixing.

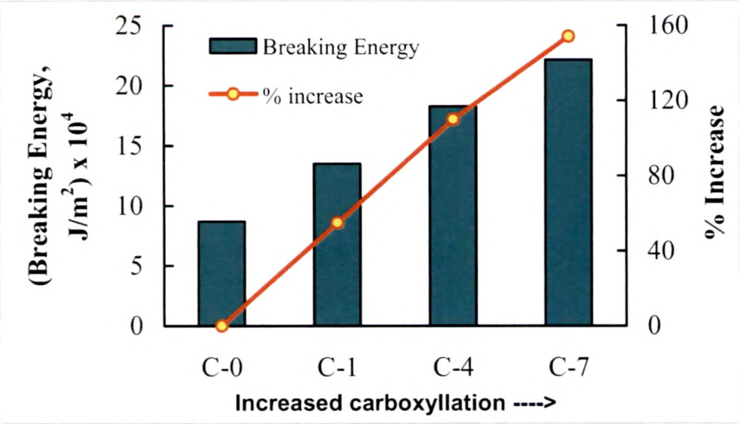


Fig. 4.5-Effect of % carboxyl group on breaking energy properties of nanocomposite

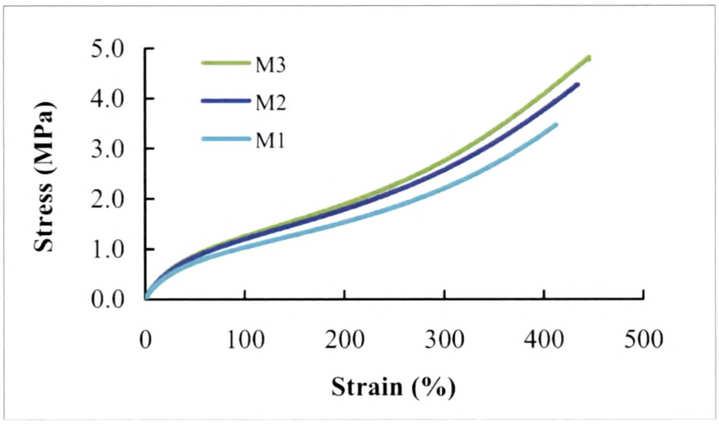


Fig. 4.6-Effect of different mixing techniques on stress-strain properties of nanocomposites

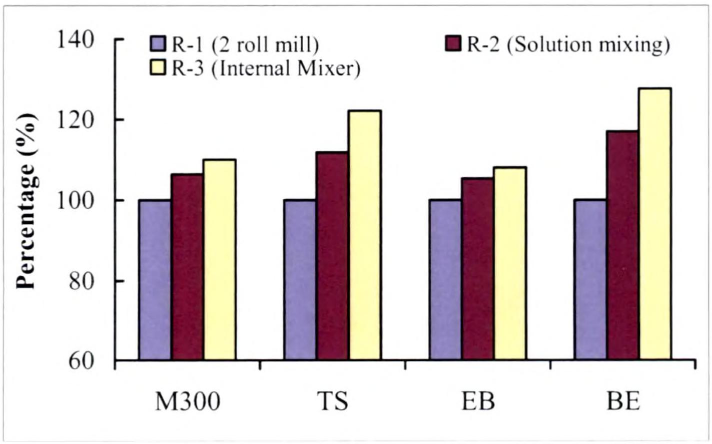


Fig. 4.7-Comparative properties of different mixing techniques taking 2 roll mill as 100

In comparison to these techniques the internal mixer provides very easy and convenient mixing. The stress-strain properties of nanocomposites are shown in Fig. 4.6. Internal mixer exhibited the best mechanical properties like modulus, tensile strength, elongation at break and breaking energy followed by solution mixing and 2 roll mill mixing, hence internal mixing was adopted here for further investigation. Comparative properties of different mixing techniques are shown in Fig. 4.7 considering the properties obtained using 2 roll mill as reference.

4.1.3.3 Compatibilizer (XNBR) and filler(organoclay) dosage optimization

The dosages of organoclay and compatibiliser have immense influence on mechanical properties. The combined effect of organoclay and XNBR dosages on mechanical properties was studied and is presented in Fig. 4.8 and Table 4.3. Nanocomposites with 10 phr XNBR and 6 phr organoclay exhibited the best properties such as tensile strength, elongation at break and breaking energy.

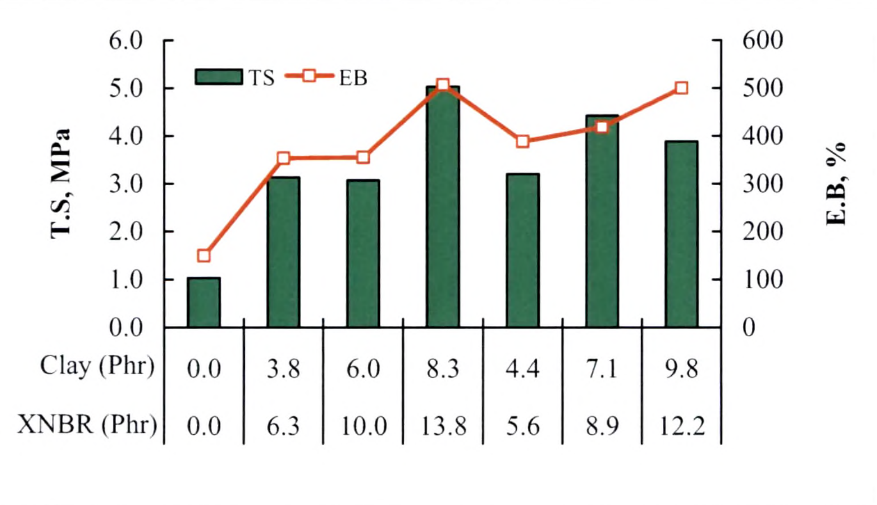


Fig. 4.8- Optimization of Clay and XNBR dosages in nanocomposite

4.1.3.4 Effect of type of SBR

The properties of nanocomposites with different type of SBR were also studied in this work. The mechanical properties of three styrene butadiene rubbers functionalized solution styrene butadiene rubber (FSSBR), solution styrene butadiene rubber (SSBR) and emulsion styrene butadiene rubber (ESBR) were very close, however ESBR showed better mechanical properties than SSBR and FSSBR (Table 4.4). ESBR has higher polarity than SSBR and hence better interfacial interaction with organoclay is expected which resulted in better mechanical properties.

Table 4.3-organoclay and XNBR dosages optimization- formulations, rheometric and mechanical properties

Compound code	D0	D1	D2	D3	D4	D5	D6
MH-ML (dN-m)	7.6	7.3	7.0	6.8	7.5	7.2	7.0
Scorch time, Ts2 (min)	3.85	1.95	1.76	1.90	1.92	1.87	1.85
Optimum cure time, Tc90 (min)	6.43	4.93	5.68	5.45	4.67	5.18	5.80
300% Modulus, M300 (MPa)	-	2.62	2.68	2.63	2.54	2.44	2.41
Tensile Strength, T.S (MPa)	1.04	3.13	5.03	4.42	3.07	3.20	3.89
Elongation at Break, E.B (%)	150	353	507	419	355	388	500
Breaking Energy, BE (J/m^2) x 10^4	2.44	14.30	30.21	25.44	14.26	16.26	26.84

Table 4.4-Mechanical properties of gum compounds and SBR/BR-organoclay nanocomposites

Properties	FSSBR/BR		SSBR/BR		ESBR/BR	
	G1	R-1	G2	R-2	G3	R-3
	Gum	filled	Gum	filled	Gum	filled
Hardness, Shore A	49	54	50	55	51	56
100% Modulus, MPa	0.73	1.26	0.76	1.22	0.84	1.27
300% Modulus, MPa	-	2.77	-	2.65	-	2.75
Tensile Strength, MPa	0.93	4.76	1.10	4.90	1.10	5.36
Elongation at Break,%	154	445	169	470	155	507
Breaking Energy, J/m^2 x 10^4	2.27	22.13	2.76	24.2	2.63	32.20

4.1.4 Viscoelastic Properties

The viscoelastic properties of nanocomposites were measured by dynamic mechanical testing. The dynamic mechanical properties of nanocomposites of all three types of SBR gum compounds (G1, G2 and G3) and corresponding nanocomposites (R1, R2 and R3) were studied by temperature sweeps from –110°C to +70°C (Table 4.5 and Fig. 4.9 and 4.10). ESBR showed the highest storage modulus, loss modulus and Tan δ followed by SSBR and FSSBR as reported in Table 4.5.

Table 4.5-dynamic mechanical properties of gum compounds and SBR/BR-organoclay nanocomposites

Properties	**FSSBR**		**SSBR**		**ESBR**	
	G1	**R-1**	**G2**	**R-2**	**G3**	**R-3**
Tg (°C)	***-29.0***	***-30.5***	***-26.2***	***-28.5***	***-50.0***	***-53.5***
Tan δ at Tg	1.001	0.821	0.928	0.679	0.981	0.572
Storage Modulus, E' at 25°C, MPa	2.90	4.43	2.66	4.58	2.87	6.74
Loss Modulus, E" at 25°C, MPa	0.209	0.412	0.226	0.531	0.196	0.995
Tan δ at 25°C	0.072	0.093	0.085	0.116	0.068	0.148

Both SSBR and FSSBR compounds and their nanocomposites have glass transition temperatures (Tg) in the range –26°C to –30°C. However, Tg of ESBR gum compound was at –50°C and its nanocomposite was at –53.5°C. Due to high vinyl content in SSBR and FSSBR, Tg gets shifted towards ambient temperature. All the nanocomposites exhibited lower Tan δ at Tg compared to the corresponding unfilled gum compounds as shown in Fig. 4.9 and 4.10. At glass transition temperature (Tg), nanocomposites show higher dynamic modulus in comparison with gum compounds and this pattern is attributed to the enhancement of stiffness in the matrix by organoclay. The Tan δ maximum decreased with the addition of organoclay, indicating good polymer-filler interaction which affected the relaxation mechanisms. However at higher temperature Tan δ values of nanocomposites were higher than corresponding gum vulcanizates and these are attributed to filler-filler interaction of organoclay which increases the loss modulus and hence returns higher Tan δ.

Fig. 4.9- Tan δ versus temperature of SSBR - Gum compounds and nanocomposites

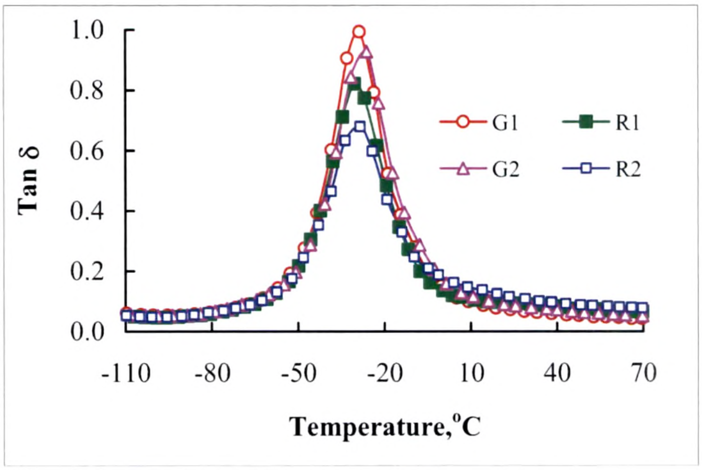


Fig. 4.10- Tan δ versus temperature of ESBR - Gum compounds and nanocomposites

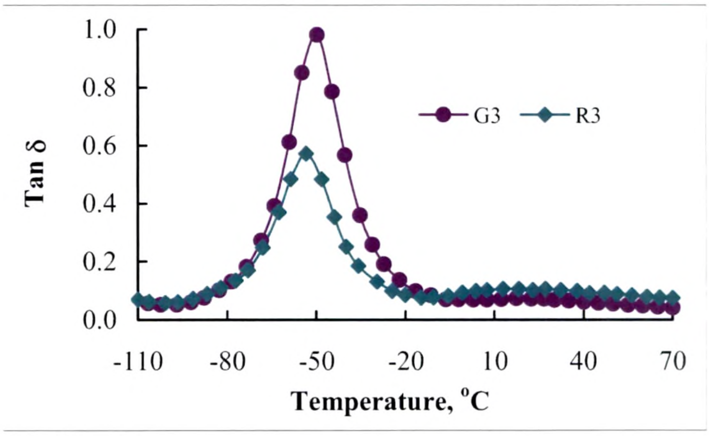
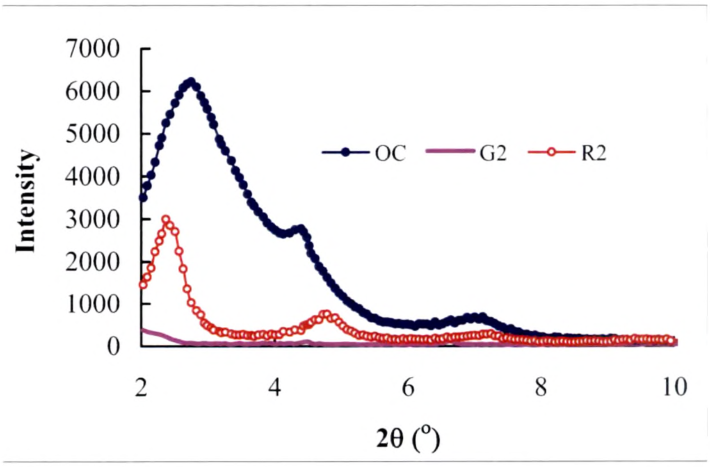


Fig. 4.11-XRD graph of Clay (OC), SSBR/BR gum (G2) and SSBR/BR nanocomposite (R2)



4.1.5 X-Ray Diffraction Study

High-resolution Wide-Angle XRD at lower angular range was used to identify intercalated and aggregated clay structures in rubber matrices. In such nanocomposites, the repetitive multilayer structure is well preserved, allowing the interlayer spacing to be determined. The intercalation of the polymer chains usually increases the interlayer spacing, in comparison with the spacing of the organoclay used, leading to a shift of the diffraction peak toward lower angle values. The diffraction angle or glancing angle (θ) and layer spacing values being related through the Bragg's relation, $n\lambda=2d\sin\theta$, where ''λ'' corresponds to the wave length of the X-ray radiation used in the diffraction experiment, ''d'' is the spacing between diffractional lattice planes and n is the order of diffraction (Alexandre, 2000).

The XRD patterns were obtained for organoclay (OC), gum rubber compound (G2) and nanocomposite (R2). XRD studies of organoclay showed the diffraction peaks at around 2.8°, 4.4 °, 7.1 ° and 9.5°, corresponding to d-spacing 3.1, 2.0, 1.3 and 0.93 nm respectively. The nanocomposite (R2) had shown the diffraction peaks at around 2.39°, 4.79 °, and 7.25 ° corresponding to d-spacing 3.7, 1.8 and 1.2 nm respectively (Fig. 4.11). Diffraction peaks at lower degree and reduction of peaks at higher degree in the nanocomposite indicated that d-spacing between silicates layers had increased. The increase of d_{001}-spacing and reduction of peaks intensity revealed that silicate layers were expanded which resulted in the intercalated/exfoliated structure of nanocomposite.

4.1.6 Transmission Electron Microscopy

The filler dispersion in the nanocomposites was studied by transmission electron microscopy (TEM). TEM images of ultrathin sections of FSSBR/BR nanocomposites mixed by three different methods 2 roll mill mixing, solution methods and internal mixer containing 10 phr XNBR and 6 phr organoclay were studied in this investigation. Fig. 4.12 shows the TEM images of samples prepared by 2 roll mill mixing method (M1). The dark regions are the hard layered silicates while the light region is the soft rubber matrix. TEM reveals mostly intercalated and partially exfoliated structure of the organoclay and it is seen that the ordered structure of layer silicate is also partially retained in 2 roll mill mixing.

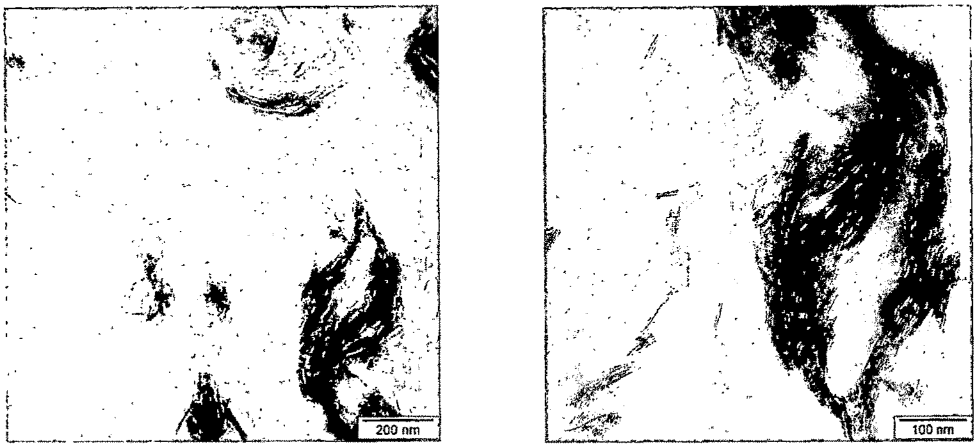


Fig. 4.12- TEM image of nanocomposite (M1) prepared in 2 roll mill.

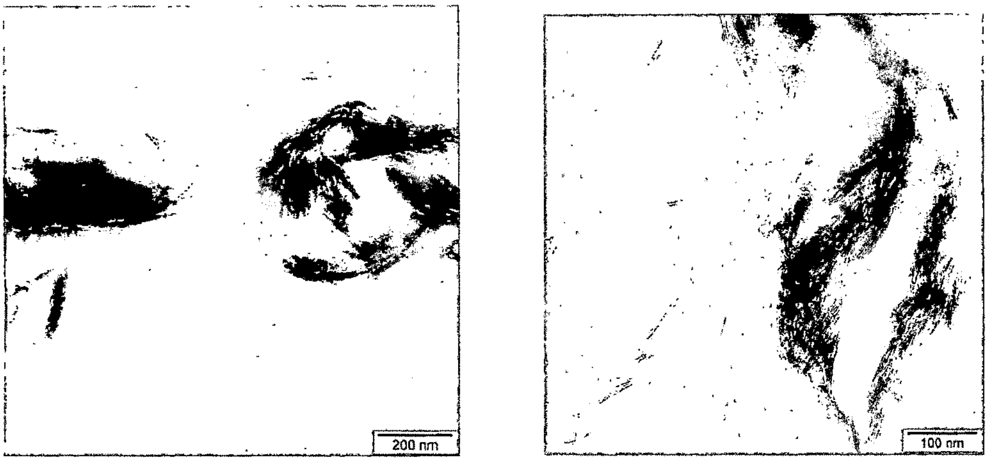


Fig. 4.13- TEM image of nanocomposite (M2) prepared by solution mixing method

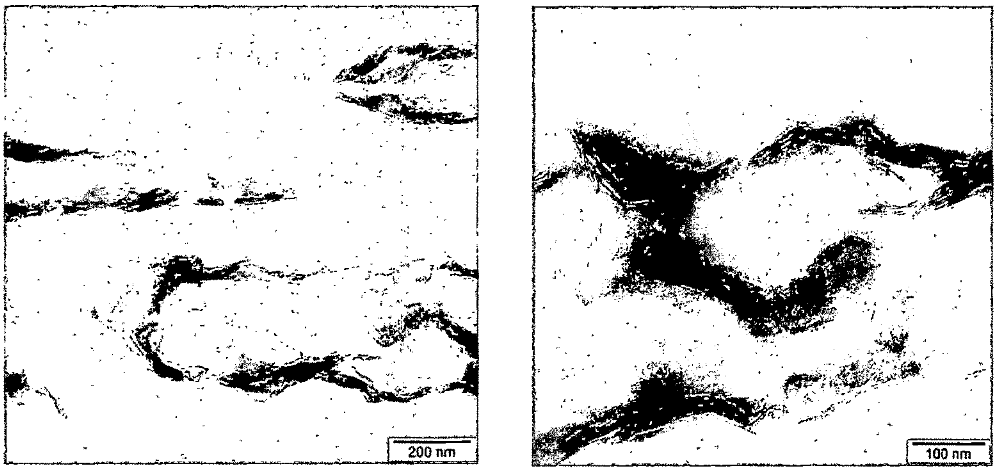


Fig. 4.14- TEM image of nanocomposite (M3) prepared by internal mixer

In solution mixing (M2) mixed intercalated and exfoliated structure was evident from TEM images (Fig. 4.13). In internal mixer, mostly exfoliated and partially intercalated morphology was noticed in TEM images (Fig. 4.14). In internal mixer silicate layer were expanded and randomly oriented. Internal mixer showed the best clay dispersion among all three mixing methods.

4.1.7 Conclusions

a) The mechanical and dynamic mechanical properties of the investigated rubber nanocomposites improved as the carboxyl content in XNBR increased.
b) Among the three mixing techniques used in this investigation internal mixing resulted in the best properties. Moreover, this method is very convenient for industrial applications. The solution method provided better properties than 2 roll mill mixing but removal of solvent was difficult, time consuming and therefore not feasible for industrial applications where as, mixing of clay in 2 roll mill was quite difficult.
c) For SBR/BR=70/30 blends, the optimum dosages of organoclay and XNBR were found to be 6 and 10 phr respectively.
d) Among three types of SBR investigated, ESBR showed the best mechanical properties followed by SSBR and FSSBR.
e) All SBR nanocomposites showed slightly lower glass transition temperature and lower Tan δ values at Tg compared to their corresponding gum counter parts in dynamic mechanical testing.
f) TEM images of SBR nanocomposites prepared by all three mixing technique exhibited mixed intercalated and exfoliated structure of layer silicate in the matrix; however internal mixer showed the best exfoliated morphology.
g) XRD investigations also supported the intercalated and exfoliated morphology of nanocomposite which was evidenced by the increase of d-spacing of layer silicate and reduction of peaks intensity.
h) Although organoclay nanocomposite showed excellent mechanical properties but hardness, modulus and other performance properties such as abrasion resistance, tear strength were not sufficient for tire tread application. Further research is required in this field to improve these properties.

4.2 DEVELOPMENT AND CHARACTERIZATION OF HIGH PERFORMANCE NANOCOMPOSITES BASED ON DUAL FILLER SYSTEM AND BLENDS OF DIFFERENT TYPES OF SBR WITH BR

4.2.1 Introduction

The main objective of this work was to develop nanocomposites which can be used for passenger car radial tire tread to reduce hysteresis loss i.e. rolling resistance of the tire. Besides mechanical properties, nanocomposites used as tread compounds also have to meet the performance requirement of tire treads such as wet and dry traction, handling, rolling resistance and tire wear.

SBR/BR-organoclay nanocomposite showed remarkable improvement of high strain modulus, tensile strength, elongation at break, tear strength and tear energy but could not meet the requirements of hardness, low strain modulus, wear properties and dynamic modulus of tire tread compounds. Tread hardness, low strain modulus and dynamic modulus are important for handling, cornering, braking and tire noise; wear resistance is important for tire durability and hysteresis property is important for wet traction and rolling resistance. Higher hysteresis loss at 0°C or below provides higher wet traction and lower value at 60-70°C gives lower rolling resistance.

In order to overcome these deficiencies the concept of dual filler was adopted so as to attain the required compound properties without increasing the hysteresis losses too much. In this section, preparation and characterization of 70/30 SBR/BR dual filler high performance nanocomposites is discussed. The mechanical, viscoelastic and other critical properties of nanocomposites and its comparison with commercial tread compounds with carbon black (Control-1) and silica (Control-2) are elaborated.

The detailed compound formulations are described in Chapter 3, Materials and methods, however compounds codes and their brief descriptions are also given in Table 4.6 for ready reference.

Table 4.6-Compounds code and descriptions

	ESBR	SSBR	FSSBR	PBR	XNBR	MMT	CB	Silica	TDESP
EG	70.0			30.0					
EOC-6	70.0			30.0	10.0	6.0			
SG		70.0		30.0					
SOC-6		70.0		30.0	10.0	6.0			
EC-25	70.0			30.0	10.0	4.0	25.0		
SC-25		70.0		30.0	10.0	4.0	25.0		
FC-25			70.0	30.0	10.0	4.0	25.0		
ES-25	70.0			30.0	10.0	4.0		25.0	2.0
SS-25		70.0		30.0	10.0	4.0		25.0	2.0
FS-25			70.0	30.0	10.0	4.0		25.0	2.0

4.2.2 Filler Characterization

In this investigation, three different fillers like Carbon Black (N220), highly dispersible silica and organoclay are used. The filler particle size and the size distribution of all the fillers are shown in Fig. 4.15. Carbon black (N220) showed bimodal distribution; one in the range of 1 to 50 μm and another is in the range of 50 to 400 μm. Silica showed unimodal distribution in the range of 2 to 40 μm with maximum frequency at around 10 μm. Nanoclay showed broader distribution compared to silica and ranges from 0.4 to 40 μm with maxima at 10 μm.

Surface area of carbon black and silica fillers measured by BET method were 120.5 and 160.2 m^2/g respectively. The secondary structures of agglomerates measured by DBP adsorption number were 116.0 and 198 respectively. The organoclay has layer silica structure with one dimension in nanometer level. It was not possible to separate the layered silicate structure by ultra sonic vibration used during the measurement of particle size and particle size distribution; as a result the particle size of nanoclay measured by particle size analyzer is not in the nano scale. Ahmed (2009) measured the particle size distribution of nanoclay using image analysis software from the TEM image of Nanocomposite and reported particle size in the range 10 to 60 nm.

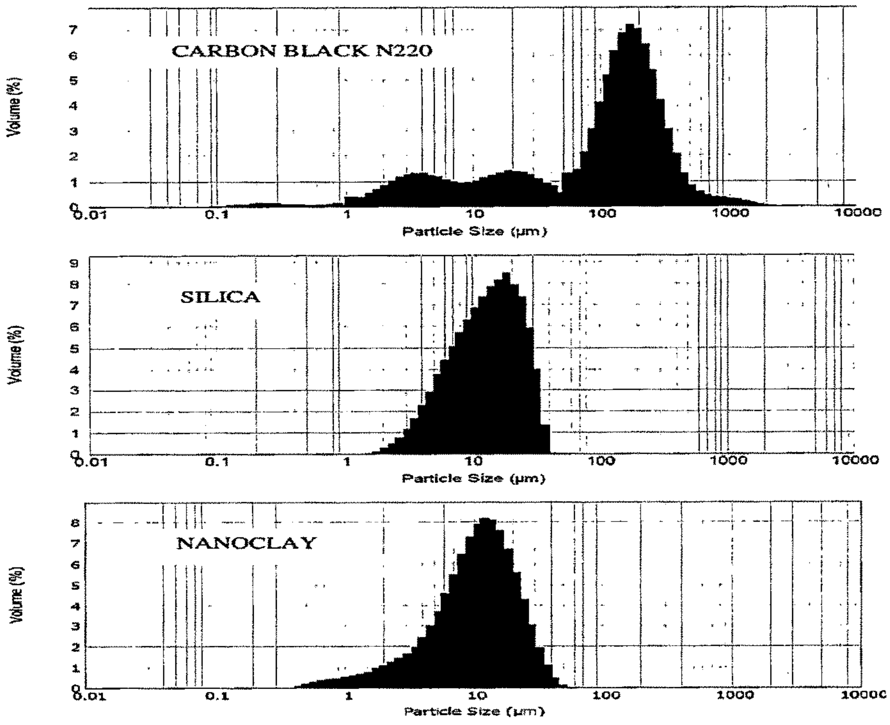


Fig. 4.15- Particle size distribution of carbon black, silica and nanoclay.

4.2.3 Rheometric Properties

The rheometric properties of dual filler nanocomposite were studied at 160°C for 30 minutes and are shown in Table 4.7.

Table 4.7-Rheometric properties of dual filler nanocomposites

	EOC-6	EC-5	EC-15	EC-25	ES-5	ES-15	ES-25	SC-25
ML, dN-m	0.53	0.78	0.94	1.16	0.81	1.00	1.25	1.16
MH, dN-m	8.34	8.35	9.9	11.4	8.30	9.89	11.54	11.4
MH-ML, dN-m	7.81	7.57	8.96	10.24	7.49	8.89	10.29	10.24
Ts2, min	**1.83**	**1.72**	**1.53**	**1.38**	**1.82**	**1.73**	**1.62**	**1.38**
Tc50, min	2.17	2.05	1.9	1.8	2.10	2.07	2.00	1.8
Tc90, min	**5.78**	**5.00**	**4.88**	**4.72**	**4.63**	**4.13**	**3.90**	**4.72**

Incorporation of carbon black in the nanocomposites makes the curing faster and reduces the scorch safety and the effect is more when carbon black dosages are increased. Addition of silica also shows the similar behaviour like carbon black. Replacement of 2 phr organoclay by 5 phr carbon black or silica reduces the reinforcement in comparison with 7 phr organoclay as evident from the lowering of rheometric modulus in EC-5 and ES-5. Combination of 25 phr carbon black or silica and 4 phr organoclay shows much improvement of rheometric modulus in nanocomposite EC-25 and ES-25 indicating high extent of reinforcement.

4.2.4 Mechanical properties

The nanocomposite EOC-6 and SOC-6 showed excellent improvement in mechanical properties when compared with their corresponding gum vulcanizates EG and SG respectively as shown in Figure 4.16 and 4.17. In this investigation, as reported in section 4.1 it was found that for 70/30 SBR/BR blend 6 phr is optimum loading of organoclay and offered the best properties. To incorporate second filler in the SBR/BR-organoclay nanocomposite, reduction of organoclay dosage is essential otherwise filler dosages will be more than optimum that leads to higher filler-filler interaction and increases the hysteresis loss and reduce mechanical properties. 5-6 phr organoclay gives reinforcement equivalent to 50-60 phr carbon black or silica in SBR/BR system, hence 2 phr organoclay was replaced by 15 – 20 phr carbon black or silica and investigated in this section

To develop the dual filler system, 15 and 25 phr of carbon black or silica were added along with 4 phr of organoclay in 70/30 ESBR/BR blends. It was observed that with an increased dosage of the second filler (carbon black or silica) mechanical properties of the nanocomposite improved. The properties of nanocomposite developed with 4 phr organoclay and 25 phr carbon black or silica are close to commercial carbon black and silica tread compounds as evidenced by Stress strain curves shown in Fig. 4.16 and 4.17. In a similar way, nanocomposites based on other SBR rubbers, such as SSBR and functional SSBR (FSSBR), with dual filler systems were developed.

The properties of nanocomposite treads are within typical performance parameters range of passenger car radial tire tread compounds that was noted for PCR tires published in Smithers ***Tire analysis*** report (2004, 2008) and also analyzing commercial tread compounds (Table 4.8).

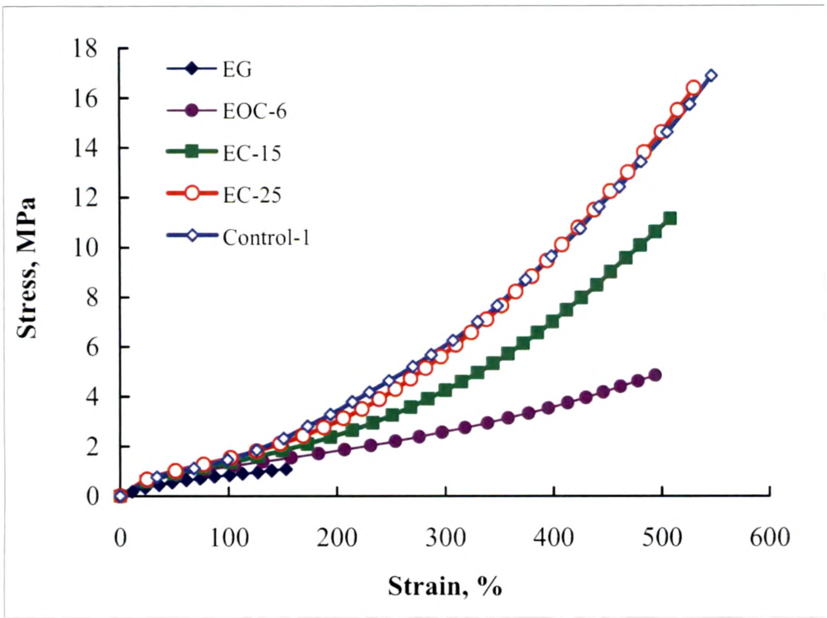


Fig. 4.16- Stress-strain properties of nanocomposites based on ESBR/BR blend and organoclay-carbon black dual filler

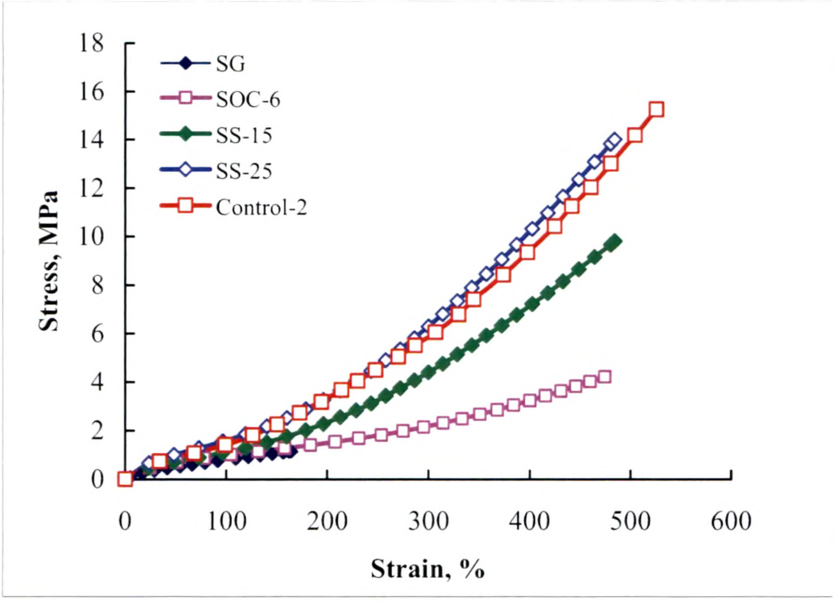


Fig. 4.17- Stress-strain properties of nanocomposites based on SSBR/BR blend with organoclay-silica dual filler

Table 4.8-Mechanical properties of dual filler nanocomposites

	Typical Performance value[b]	organoclay-carbon black			organoclay-silica		
		EC-25	SC-25	FC-25	ES-25	SS-25	FS-25
100% Modulus, MPa	1.6 – 2.5	1.62	1.77	1.80	1.51	1.61	1.60
300% Modulus, MPa	5.0 - 9.0	6.03	6.60	6.94	5.07	6.29	6.46
Tensile Strength, MPa	12.5 min	17.7	14.5	14.8	17.5	14.0	13.0
Elongation at Break,%	350 min	544	483	460	597	484	452
Hardness, Shore A	60-70	64	62	62	63	62	61
Tear Strength, N/mm	30 - 50	43.0	45.9	40.7	47.3	41.9	38.3
Abrasion Loss, mm^3	90 - 150	93	129	134	94	127	125
Heat Build Up, ΔT, °C	25- 40	25.6	25.6	23.9	25.6	22.8	20.6

[b] Typical performance parameters range of passenger car radial tire tread compounds.

4.2.5 Viscoelastic Properties

Viscoelastic properties of nanocomposites were determined by dynamic mechanical measurement and are presented in Fig. 4.18 to 4.20. Different dynamic properties such as storage modulus (E'), loss modulus (E''), Tan δ, Loss compliance (J'') have great influence on viscoelastic behaviors of the compounds and their performance during applications. Tan δ is the ratio of loss modulus to storage modulus of the compound and it represents the hysteresis loss of the compound. In a tire tread compound, Tan δ values at different temperatures correlate, as a rule of thumb, with different performance properties of tires, e.g. –25 °C represents ice or snow traction, 0°C represents wet traction and 10-25 °C represents dry traction. The higher the Tan δ values at these temperatures, the higher will be the corresponding tire tractions.

Tan δ value at 60°C represents tire rolling resistance, lower this value lower will be the rolling resistance. All nanocomposite based tread compounds show much lower Tan δ values at 60°C when compared with the typical range of Tan δ values of commercial tread compounds as shown in Table 4.9.

Further, tread compounds based on SSBR/BR and FSSBR dual filler nanocomposite also meet the traction requirements of tire tread as observed from their Tan δ values at temperatures of -25°C, 0°C and 25°C (Table 4.9). The ESBR/BR nanocomposite shows lower rolling resistance but poor ice and wet traction as evidenced by lower Tan δ values at -25°C and 0°C. This can be attributed to the much lower glass transition temperature of ESBR (Tg:-55°C) compared to SSBR (Tg: - 26°C) and FSSBR (Tg: -28°C).

Lower Tan δ values of nanocomposites at 60°C are attributed to lower loading of fillers in these compounds in comparison with the commercial tread compounds. The SSBR/BR and FSSBR/BR dual filler nanocomposites offer much lower rolling resistance when used as tread compound in tires without sacrificing performance and traction properties. ***ESBR/BR dual filler nanocomposites offer lower rolling resistance comparable to other nanocomposites developed but because of poor ice and wet tractions, it not suitable for low rolling resistance high traction tread compound.***

Table 4.9-Viscoelastic properties (Tan δ) at different temperatures of dual filler nanocomposites

Compound as specified in Chapter 3	Tan δ			
	Temperature			
	- 25°C	0°C	25°C	60°C
	Ice/snow Traction	Wet Traction	Dry Traction	Rolling Resistance
Typical Value [c] *of conventional tread*	0.30 -0.6	0.20 – 0.4	0.15 – 0.25	0.15 – 0.20
FC-25	0.615	0.202	0.154	0.104
FS-25	0.740	0.223	0.128	0.095
SC-25	0.522	0.226	0.184	0.117
SS-25	0.683	0.271	0.145	0.104
EC-25	0.183	0.144	0.168	0.113
ES-25	0.198	0.135	0.142	0.106

[c] Typical performance parameters range of high performance passenger car radial tread compounds

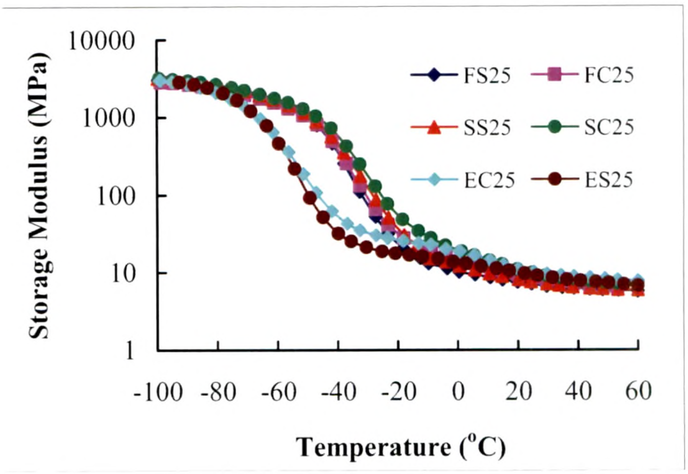


Fig. 4.18- Storage modulus versus temperature

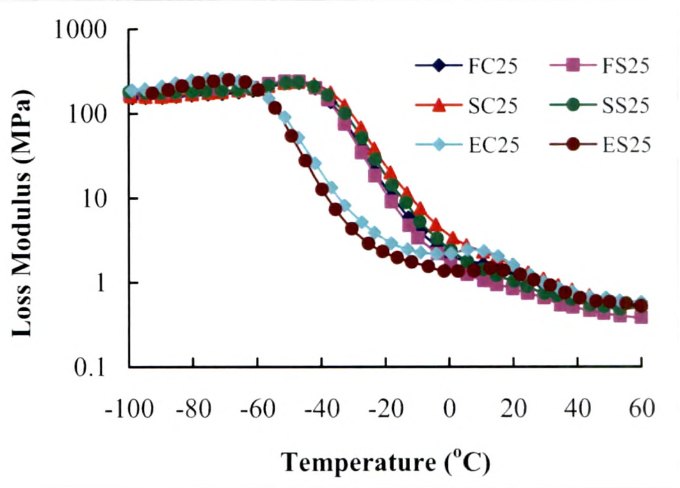


Fig. 4.19- SBR/BR dual filler nanocomposite: Loss modulus versus temperature

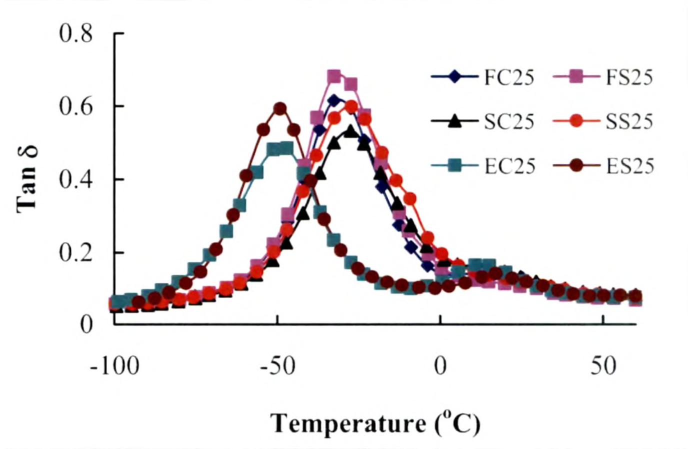


Fig 4.20- Tan δ versus temperature

The hysteresis loss in rubber originates predominantly due to filler-filler interaction in the rubber matrix. Filler-filler interaction is accounted by measuring the difference in shear modulus (ΔG) at very low strain (G_0 ~ 0.1%) and very high strain ($G\infty$ ~ 100%) i.e. $\Delta G = G_0 - G\infty$. At low strain strong filler aggregates gives very high modulus and modulus starts decreasing as the filler aggregates break down when strain level increases. This behavior was first investigated by Payne (1965) and is known as Payne's effect. Strong filler network originated from high filler-filler interaction results in big difference in modulus measured at low strain and high strain i.e. drop in modulus is very high indicating high Payne's effect. For the reduction of rolling resistance of tread compounds, magnitude of Payne's effect at 60°C has to be brought down as higher Payne's effect is associated with higher Tan $\delta_{max.}$

Dual filler nanocomposites shows much lower Payne's effect in comparison with commercial tread compounds (Control-1 and Control-2) as shown in the Table-4.10. ***Lower Payne's effect in nanocomposites are due to lower volume fraction (dosages) of filler and better filler-polymer interaction compared Control compounds as observed in and Fig. 4.21 and Fig.4.22.***

Table 4.10-Payne's effect of Control compounds and nanocomposites

	Control-1	Control-2	EC-25	SC-25	FC-25	ES-25	SS-25
Go	7.70	6.93	2.68	1.73	1.60	2.15	1.46
G∞	1.31	1.49	1.38	0.94	0.91	1.17	0.88
ΔG (G∞- Go)	***6.40***	***5.44***	***1.30***	***0.79***	***0.69***	***0.98***	***0.58***

It is observed from Fig. 4.23 and 4.24 that tan δ become maximum when filler aggregates break during strain sweep of dynamic mechanical test. Tan δ_{max} represents the hysteresis loss arising from break down of fillers network that highly influence the tire rolling resistance and it was found that higher the Tan δ_{max} higher is the tire rolling resistance. ***Organoclay-silica based nanocomposites (SS-25 and FS-25) have lower Tan δ values than the organoclay-carbon black based nanocomposite (SC-25 and FC-25) as observed during viscoelastic test (Fig. 4.23 and Fig. 4.24).*** In organoclay-silica nanocomposite, silane coupling agent was used to modify the silica filler surfaces which reduce the filler-filler interaction in strong silica filler network due to hydrogen bonding. Silane coupling agent makes chemical bond between inorganic silica filler and organic rubber hydrocarbon.

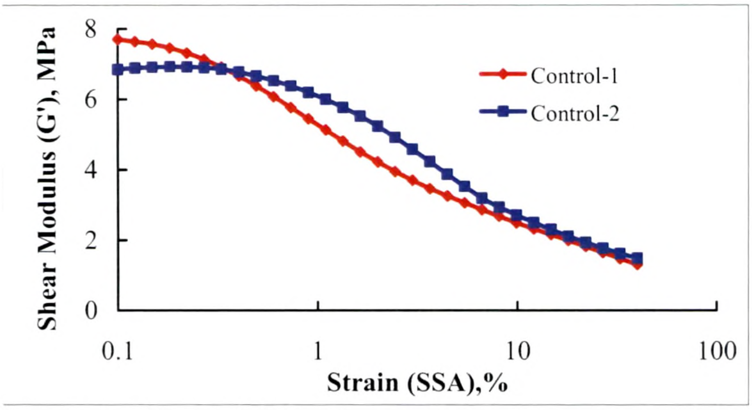


Fig. 4.21- Strain sweep at 10 Hz and 60°C: Shear modulus versus strain of Control compounds

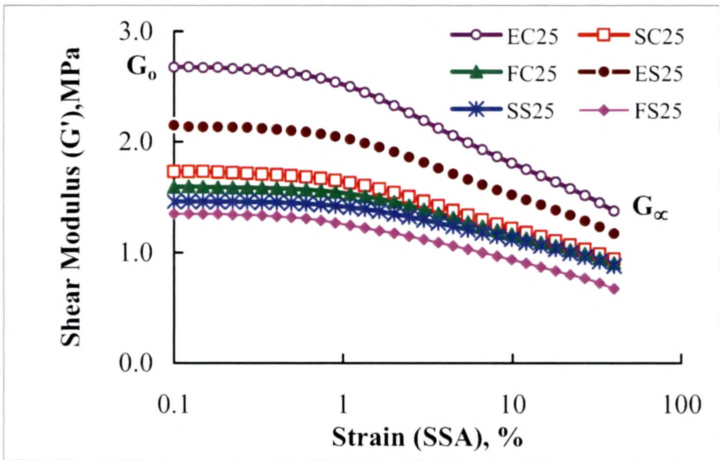


Fig. 4.22- Strain sweep at 10 Hz and 60°C: Shear modulus versus strain of nanocomposites

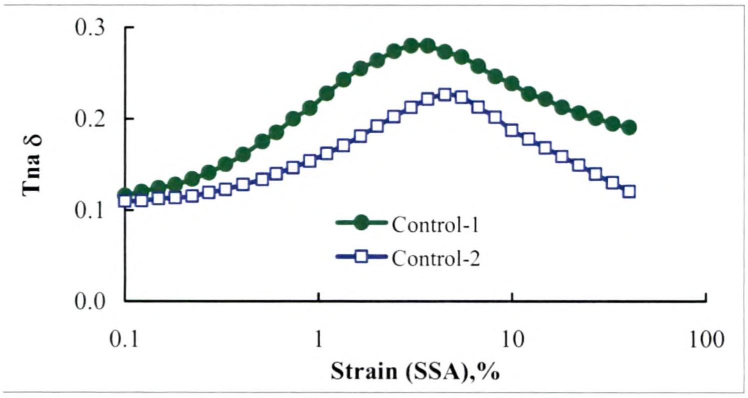


Fig. 4.23- Strain sweep at 10 Hz and 60°C: Tan δ versus strain of Control compounds

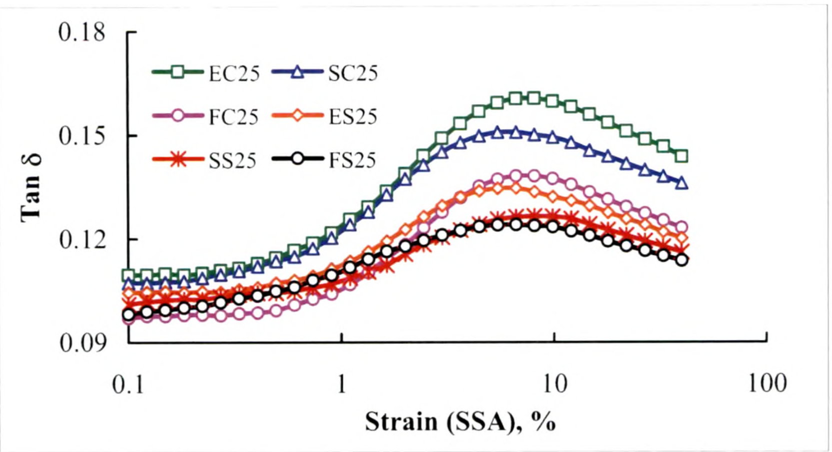


Fig. 4.24- Strain sweep at 10 Hz and 60°C: Tan δ versus strain of Control compounds

The silane coupling agent also reduces filler-filler interaction in organoclay and improves the filler-polymer interaction as observed by Ganter *et al.* (2001). The may be attributed to the reaction of hydroxyl group present in the organoclay with silane coupling agent.

4.2.6 X-Ray Diffraction Study

The X-ray diffraction patterns of organoclay, gum rubber vulcanizate and Organoclay nanocomposites, organoclay-carbon black and organoclay-silica dual filler system are shown in Fig.4.25.

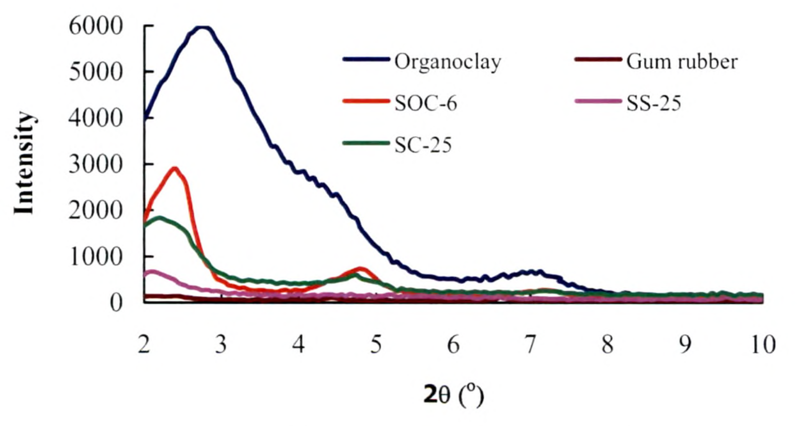


Fig. 4.25- XRD graph-Organoclay, Gum rubber and Nanocomposites

The organoclay showed X-ray diffraction peaks at 2θ angles of 2.8°, 4.4°, 7.1 ° and 9.5°, corresponding to d-spacing 3.1, 2.0, 1.3 and 0.93 nm respectively. For gum rubber vulcanizate no peak was identified since gum rubber is amorphous in nature.

The nanocomposite SOC-6 based on 6 phr organoclay and SSBR/BR blend showed diffraction peaks at 2θ angles of 2.39°, 4.79° and 7.25° corresponding to d-spacing of 3.69, 1.85 and 1.22 nm respectively. Diffraction peaks at lower degree and reduction of peaks at higher degree in the nanocomposite revealed that d-spacing between silicate layers were increased. The increase of d_{001}-spacing revealed that silicate layers were expanded which leads to the intercalated/ exfoliated structure of nanocomposite.

The nanocomposite SC-25 based on SSBR/BR and organoclay-carbon black dual filler had diffraction peaks at 2θ angles of 2.2°, 4.7 °, and 7.13° corresponding to d-spacing 4.02, 1.88 and 1.24 nm respectively. Incorporation of carbon black in the nanocomposite improved the dispersion as well as distribution of organoclay and resulted in better exfoliated structure and excellent mechanical properties of nanocomposite.

The nanocomposite SS-25 based on SSBR/BR and organoclay-silica dual filler showed the diffraction peak at 2θ angle of 2.1° corresponding to d-spacing 4.21 nm. No other peak was observed at higher angle. Like carbon black, incorporation of silica filler also improved the dispersion as well as distribution of organoclay and resulted in better exfoliated structure than carbon black which was evident from much higher d_{001}-spacing and absence of peaks at higher angle.

Organoclay has crystalline structure whereas rubber is amorphous in nature thus incorporation of organoclay in rubber imparts an element of crystallinity in the nanocomposites. The crystallinity in the nanocomposite decreases as intercalation and exfoliation of organoclay increases. Hence, with completely exfoliated structure of the organoclay in the nanocomposite, the matrix will be close to amorphous. Highly exfoliated structure of organoclay in dual filler system reduces the crystallinity compared to organoclay alone and this was observed in XRD..

4.2.7 Transmission Electron Microscopy

Transmission electron microscopy (TEM) was used to image the filler dispersion in the nanocomposites. These images were observed at different magnifications ranging from 0.5 microns to 100 nm.

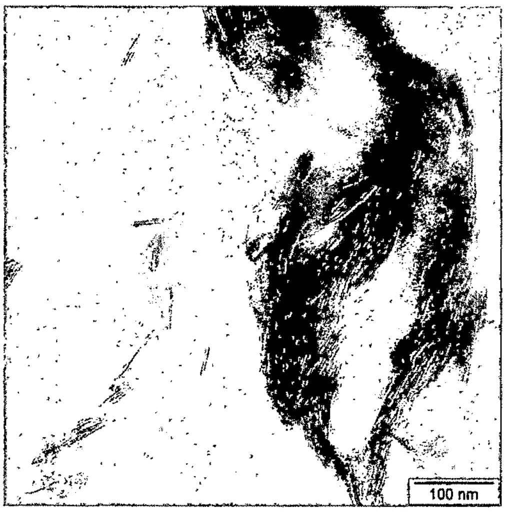


Fig 4.26- TEM image of SSBR/BR-organoclay nanocomposite (SOC-6)

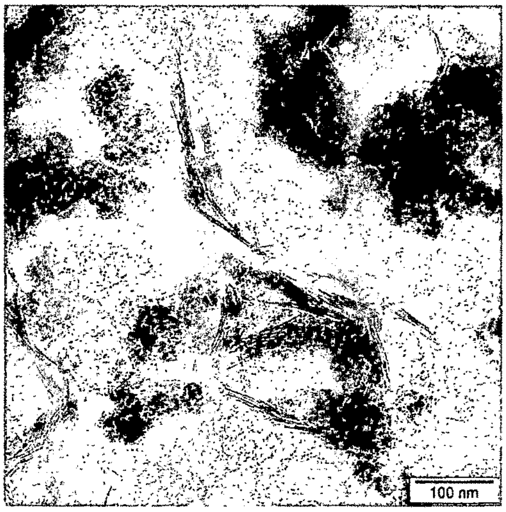


Fig. 4.27- TEM image of ESBR/BR and organoclay-carbon black dual filler system nanocomposite (EC-25)

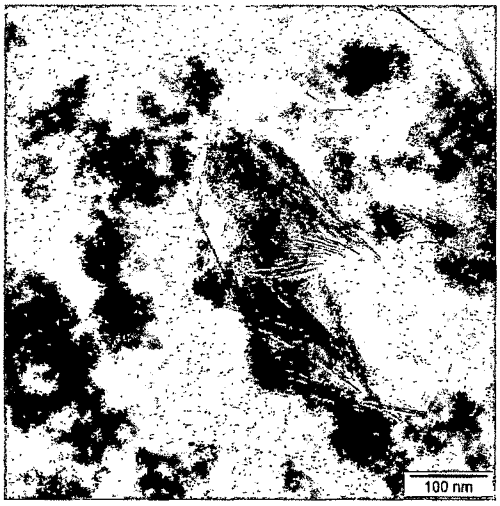


Fig. 4.28- TEM image of ESBR/BR and organoclay-silica dual filler nanocomposite (ES-25)

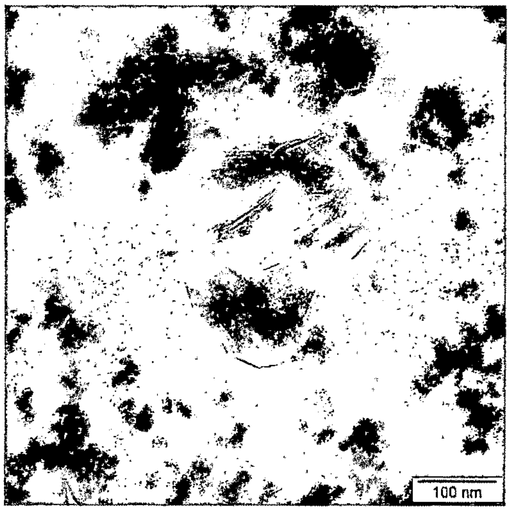


Fig. 4.29- TEM image of SSBR/BR and organoclay-silica dual filler nanocomposite (SS-25)

The exfoliated morphology of organoclay in the nanocomposite (SOC-6) was evident from images as shown in Fig. 4.26.

In organoclay-carbon black dual filler system the TEM images showed a large extent of exfoliation of the organoclay, which appeared to have a fiber like structure in the image whereas carbon black particles have a spherical shape and are deeper in color. The dispersion of both organoclay and carbon black is very fine in the nanocomposite (EC-25) as shown in Fig. 4.27. Similar patterns were also observed in organoclay-silica dual filler system nanocomposites (ES-25 and SS-25) which are shown in Fig. 4.28 and 4.29.

Much superior exfoliation of the organoclay was observed in both the dual filler systems (organoclay-carbon black and organoclay-silica) in comparison with organoclay alone. Higher shear force generated during mixing in presence of carbon black or silica filler in the matrix resulted in better exfoliation of organoclay, thereby providing superior reinforcement and excellent mechanical properties.

4.2.8 Conclusions

a) Nanocomposites based on SBR/BR blends with organoclay showed remarkable improvement in mechanical properties like hardness, modulus, tensile strength, elongation at break, breaking energy and tear strength compared to gum vulcanizate.

b) To meet the requirements of tire tread, special types of nanocomposites were developed with organoclay-carbon black and organoclay-silica dual filler systems based on SBR/BR blend.

c) The dual filler nanocomposites showed excellent mechanical properties and are well within the target performance range of passenger car radial tire tread compounds. The nanocomposites also fulfilled the requirement of abrasion properties; wet traction and dry traction which are very important for PCR tread application.

d) Since nanocomposites contain much lower dosage of filler, they show lower hysteresis loss which was reflected in lower Tan δ values at 60°C.

e) Nanocomposite based passenger car tread compounds showed lower rolling resistance without sacrificing other performance parameters like mechanical properties, tear properties, wear properties, wet traction and dry traction.

f) The properties achieved by dual filler nanocomposites with reasonably small amount of the filler content are close to commercial tread compounds that are highly loaded with fillers.

g) This investigation revealed the potential of nanocomposites which in future could be used as high performance passenger car radial tread to reduce rolling resistance and improve fuel economy in automotive transport.