CHAPTER 5

PREPARATION AND CHARACTERIZATION OF NR/BR NANOCOMPOSITES FOR TRUCK BUS RADIAL (TBR) TIRE TREAD APPLICATION

Truck bus radial (TBR) tire tread compounds are usually formulated using NR/BR rubber blends. The main focus of this investigation was to develop tread compounds from NR/BR blends having low hysteresis losses. To obtain the target properties, two different types of NR/BR nanocomposites were developed. The characterization of nanocomposites; the effect of organoclay as well as dual fillers on mechanical and dynamic mechanical properties of the compounds are reported and their salient properties are discussed in this Chapter.

Fig. 5.1- 10.00R20 TBR Tire

5.1 PREPARATION AND CHARACTERIZATION OF NANOCOMPOSITES BASED ON NR/BR BLENDS AND ORGANOCLAY.

5.1.1 Introduction

Ever since Toyota group introduced organoclay polyamide nanocomposites (Usuki,1993; Okada,1993), several researchers have studied a variety of polymer nanocomposites using organoclay. Clays such as montmorillonite are composed of silicate layers. The dimensions of the silicates are, approximately, 1 nm thickness and 100-1,000 nm in the lateral dimensions. Dispersion of such clays into polymeric materials is very difficult because of their hydrophilic nature, leading to formation of aggregates in the hydrophobic matrix. However, through clay surface modification, nanoclay can be made organophilic and, therefore, compatible with conventional organic rubbers. Such modified clays are called organoclay and they disperse readily in rubbers offers good mechanical properties.

In this investigation, a nanocomposites based on 70/30, natural rubber (NR)/ polybutadiene rubber (BR) blend and organoclay using XNBR as compatibilizer were prepared and characterized aiming for truck bus radial (TBR) tire tread applications. The performances of nanocomposites depend on several parameters such as nature of rubber, dosage of organoclay and most importantly exfoliation of the organoclay. Similarly organoclay dispersion also depends on parameters such as;

a) Polarity of compatibilizer (Carboxyl group % in XNBR)
b) Mixing techniques
d) Dosages of organoclay

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 nanocomposite. 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 5.1. The results and discussion incorporating the influence of each parameter on mechanical and dynamic mechanical properties of nanocomposites are elaborated in the subsequent sections.

5.1.2 Rheometric Properties

Rheometric studies show that organoclay has strong influence on cure rate. Nanocomposites based on NR/BR and organoclay cure much faster and are scorchier when compared to gum compound (without organoclay). The carboxyl content in XNBR has also influence on cure time and as its % increases, cure time moderately increases, however scorch safety remains unaffected. Nanocomposites prepared by 2 roll mill, solution methods and internal mixer exhibit comparable cure characteristics. The rheometric properties of all nanocomposites are shown in Table 5.2.

Table 5.1-Compound codes and brief descriptions

	Code	XNBR (phr)	Organoclay (phr)	Mixing Methods
Effect of carboxyl % in XNBR	**NBG**	**0.0**	**0.0**	**Internal Mixer**
	NB1	**XNBR-1 (10.0)**	**7.0**	
	NB4	**XNBR-4 (10.0)**	**7.0**	
	NB7	**XNBR-7 (10.0)**	**7.0**	
Effect of mixing methods	**OM**	**10.0**	**7.0**	**2 roll mill**
	SM			**Solution**
	IM			**Internal Mixer**
Effect of organoclay dosages variation	**F0**	**0.0**	**0.0**	**Internal Mixer**
	F4	10.0	4.0	
	F7	10.0	7.0	
	F10	10.0	10.0	

Table 5.2-Rheometric properties at 150°Cfor 30 minutes in MRD

		Min Torque, dN.m	Max Torque, dN.m	Ts2, Minute	Tc50, Minute	Tc90, Minute
Effect of carboxyl %	NBG	0.33	7.30	6.45	6.92	10.30
	NB1	0.53	8.19	2.10	2.52	4.53
	NB4	0.45	8.02	2.32	2.77	4.88
	NB7	0.37	7.43	2.82	3.28	5.68
Effect of mixing methods	OM	0.33	7.41	2.50	2.97	5.35
	SM	0.45	7.25	2.70	3.18	5.58
	IM	0.37	7.43	2.82	3.28	5.68
Clay dosages variation	F0	0.37	7.43	2.73	3.28	5.68
	F4	0.38	7.45	3.17	3.67	6.33
	F7	0.37	7.43	2.82	3.28	5.68
	F10	0.21	7.95	2.55	3.07	5.50

5.1.3 Mechanical Properties

It was observed that all the physical properties like modulus, tensile strength and elongation at break increases as carboxyl content in XNBR increases from NB1 to NB4 as shown in Fig. 5.2. Increase of 300% modulus in NB1, NB4 and NB7 compared to NBG (gum) are 50, 76 and 96% respectively. 7% carboxylated XNBR shows the highest tensile strength and energy at break; the increases are 68% and 126% respectively compared to gum vulcanizate (NBG). Similar trend is also observed in case of hardness, tear strength and tear energy as shown in Table 5.3. As carboxyl group percentage increases, the polarity of XNBR also increases; therefore the organoclay being polar in nature has greater interaction with the more polar rubber. Greater interaction between clay and XNBR result in better clay dispersion and due to this 7% XNBR shows enhancement of physical and tear properties. Hence, 7% XNBR was used for further investigation.

Table 5.3-Effect of carboxyl % in XNBR on physical properties

	Carboxyl %	Clay Phr	Hardness Shore A	M 300 MPa	T.S MPa	Energy at Break $J/m^2 \times 10^4$	Tear Strength N/mm	Tear Energy J
NBG	0	0.0	50	2.00	14.66	52.3	26.7	7.3
NB1	1	7.0	56	3.00	17.45	81.9	34.2	8.5
NB4	4	7.0	57	3.52	21.13	89.8	36.0	9.6
NB7	7	7.0	58	3.87	24.65	123.7	39.1	11.0

An appropriate mixing technique is very important for clay dispersion. The properties of nanocomposites prepared by three different mixing techniques were compared. Nanocomposites prepared by all the three mixing methods (OM, SM and IM) showed remarkable improvement of hardness, tensile strength, elongation at break and tear strength compared to gum compound (NBG) however, mixing using internal mixer (IM) showed better results compared with solution method (SM) and open two-roll mill (OM) mixing as represented in Fig. 5.3 and Table 5.4. It was noticed that clay mixing was extremely difficult in 2-roll mill. Solution method required a large quantity of solvent which had to be removed after mixing. In comparison to these techniques the internal mixer provided very easy and convenient mixing method and was adopted here for further investigation.

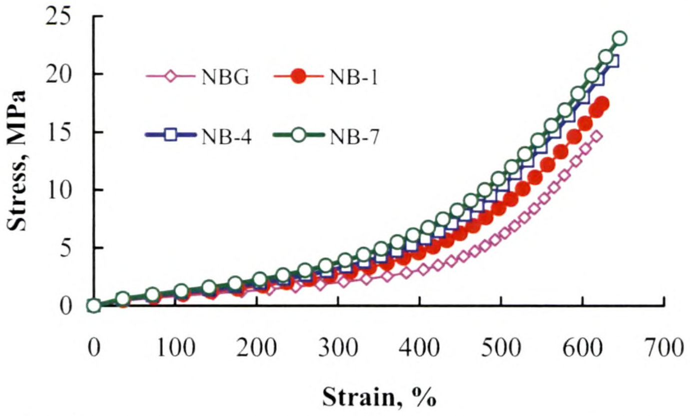

Fig. 5.2- Effect of carboxyl % in XNBR on stress strain properties of nanocomposites

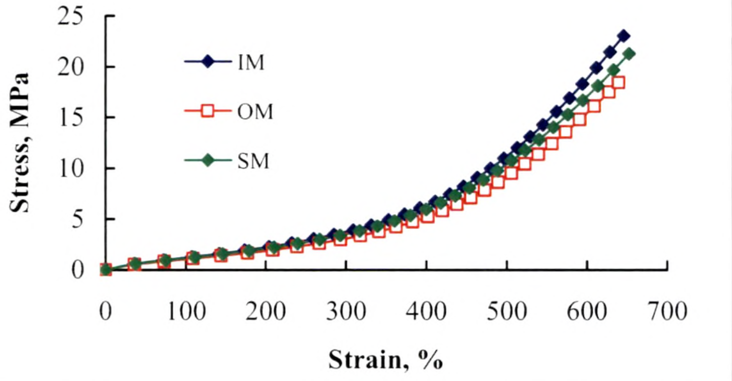

Fig. 5.3- Effect of mixing techniques on stress-strain properties on nanocomposites

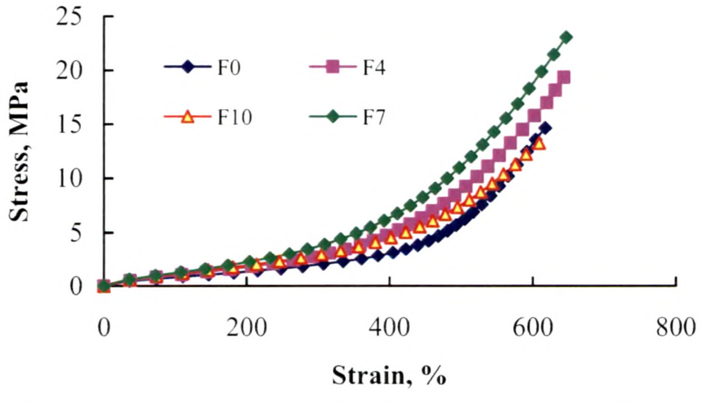

Fig. 5.4- Effect of organoclay dosages on stress strain properties of nanocomposites

Table 5.4-Effect of different mixing techniques on physical properties

		Hardness Shore A	M 300 MPa	T.S MPa	Energy at Break, J/m² x10⁴	Tear Strength N/mm	Tear Energy, J
OM	2-roll mill	55	3.35	18.46	90.5	35.3	8.7
SM	Solution	56	3.67	21.31	103.2	37.1	10.6
IM	Internal mixer	58	3.87	24.65	123.7	39.1	11.0

The influence of clay dosages on properties was investigated and the improvement of modulus, tensile strength , elongation at break and tear strength were observed as clay loading increases and reached the maxima at 7 phr. Further increase of clay phr resulted in deterioration of all properties as shown in Fig. 5.4 and Table 5.5. Mixing of 10 phr clay was very difficult and loss of properties is attributed to poor dispersion.

Table 5.5-Effect of clay dosages on physical properties

	clay (phr)	Hardness Shore A	M 300 MPa	T.S MPa	Energy at Break, J/m² x 10⁴	Tear Strength N/mm	Tear Energy , J
F0	0	50	2.20	14.91	91.9	27.0	7.6
F4	4	52	2.82	18.43	102.5	33.3	8.8
F7	7	58	3.87	24.65	123.7	39.1	11.0
F10	10	54	2.91	13.29	115.8	37.6	10.7

5.1.4 Dynamic Mechanical Properties

The viscoelastic properties of nanocomposite were measured by dynamic mechanical testing in the temperature range from -110°C to +60°C to capture the behavior of the rubber in the glassy as well as in the rubbery states. NR/BR gum compound shows two glass transition temperatures; one is at -95°C corresponding to BR and other is at -50°C corresponding to NR. NR and BR are physically miscible but thermodynamically not compatible and hence the two glass transition temperatures. There is no significant shift of glass transition temperatures observed in NR/BR-organoclay nanocomposite when compared with its gum compound. The dynamic mechanical properties of gum (NBG) and nanocomposites with 4 phr (F4) and 7 phr (F7) organoclay were studied and are presented in Fig. 5.5 to Fig. 5.7.

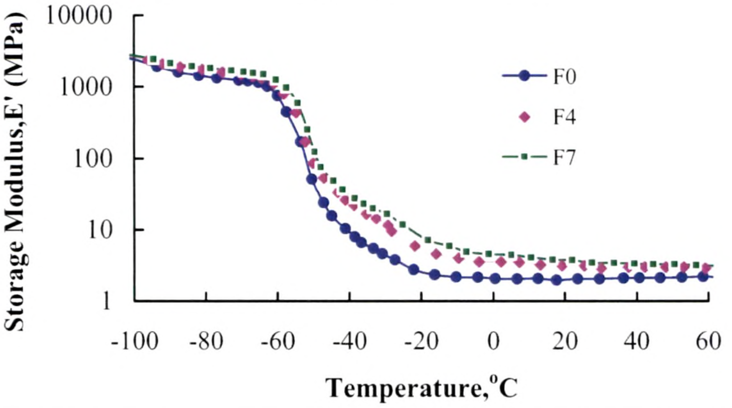

Fig. 5.5-Dynamic mechanical property: storage modulus versus temperature.

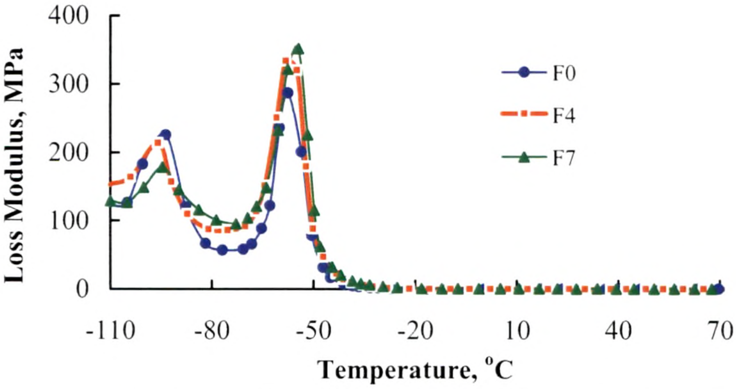

Fig. 5.6- Dynamic mechanical property: loss modulus versus temperature

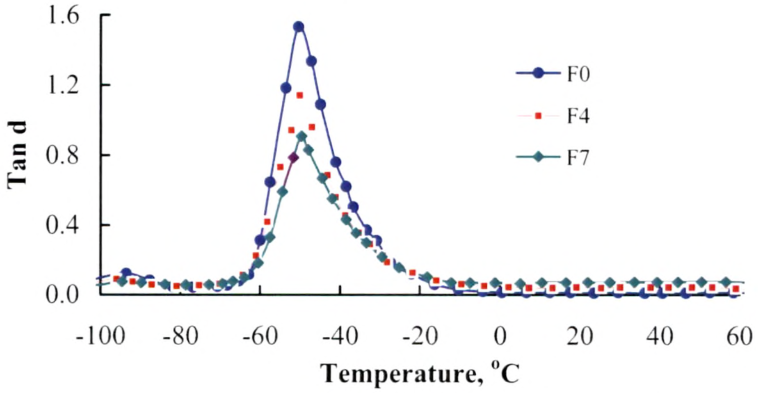

Fig. 5.7- Dynamic mechanical property: Tan δ versus temperature

Dynamic modulus of nanocomposite increases steadily with the increase of organoclay dosages at all temperature. Tan δ shows maximum value at glass transition temperature (Tg) which steadily reduces with increasing organoclay loading, indicating good polymer-filler interaction that the relaxation mechanisms. The increase of stiffness imparted by the organoclay in rubber matrix in the glassy states is due to the higher polymer-filler interaction thus reduces the damping characteristics of nanocomposite. Reduction of Tan δ is results of lowering of the damping characteristics.

5.1.5 X-Ray Diffraction (XRD)

High-resolution Wide-Angle XRD at lower angular range is 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.

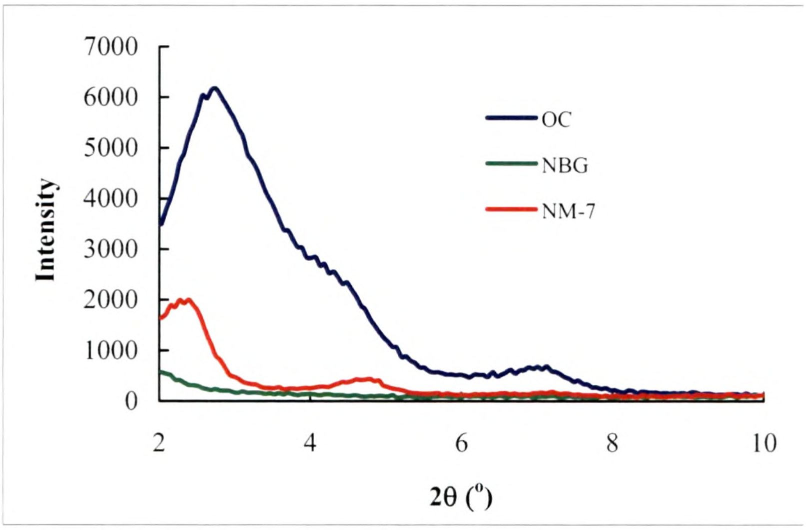

Fig. 5.8- X-ray diffraction patterns of the organoclay, Gum compound and nanocomposite with 7 phr organoclay

The XRD graphs of organoclay and NR/BR-clay (NB7) with 7 phr clay are shown in Fig. 5.8. The XRD studies also support the intercalated and exfoliated morphology of the nanocomposite.

XRD of organoclay showed the diffraction peaks at around 2.8°, 4.4° and 7.1° corresponding to d-spacing 3.15, 2.01 and 1.24 nm respectively. The nanocomposite (NB7) based on 7 phr clay shows the diffraction peaks at around 2.6° and 4.4° corresponding to d-spacing 3.4 nm (Intercalation) and 1.76 nm (layer collapse) nm respectively. Lower peak intensity in nanocomposite with 7 phr organoclay (NB7) at low d-spacing in comparison with organoclay indicates expansion of silicate layer in the nanocomposite (intercalation). The increase of d_{001}-spacing to 3.4 nm and shifting of d_{002} peak toward higher angle as well as decrease of peaks intensity indicate expansion of silicate layer. Absence of peaks at higher angle suggests exfoliated structure of nanocomposite.

The decrease in the intensity of intercalation peak (d =3.4 nm) is due to the decrease in the coherent layer scattering. The WXRD results can be explained on the basis of the intercalation of the polymer chains into the clay layers (Kim 2001), which lead to the disordering of the layered clay structure, thereby a decrease in the WXRD coherent scattering intensity being observed.

5.1.6 Transmission Electron Microscopy (TEM)

The filler dispersion was studied by TEM of ultrathin section of rubber prepared by ultra microtome at temperatures below glass transition temperature (Tg) of the rubber matrix. Fig. 5.9 shows TEM micrographs of NR/BR nanocomposite (scale bar: 0.5μm, 0.2 μm 50 nm). The dark lines in the TEM image are the intersections of the silicate layers. As shown in Fig. 5.9, organoclay are well dispersed in the rubber matrix and many parts of the organoclay in the NR/BR nanocomposites were separated from the original layers.

The NR and BR are hydrocarbons having non polar in nature whereas organoclay is polar material. The hydrocarbon nature of rubber favours more filler–filler interaction than rubber filler interaction. Introduction of XNBR, a polar rubber as compatibiliser gives higher Flory-Huggins interaction parameter that favours the penetration of rubber into the inter layers of organoclay (Kim, 2001). TEM micrographs reveal a disordered layered structure in NR/BR-clay nanocomposite. The morphology appears to be exfoliated with some intercalation of the silicate layers. The dark regions are the hard layered silicates while the light regions are soft rubber matrix.

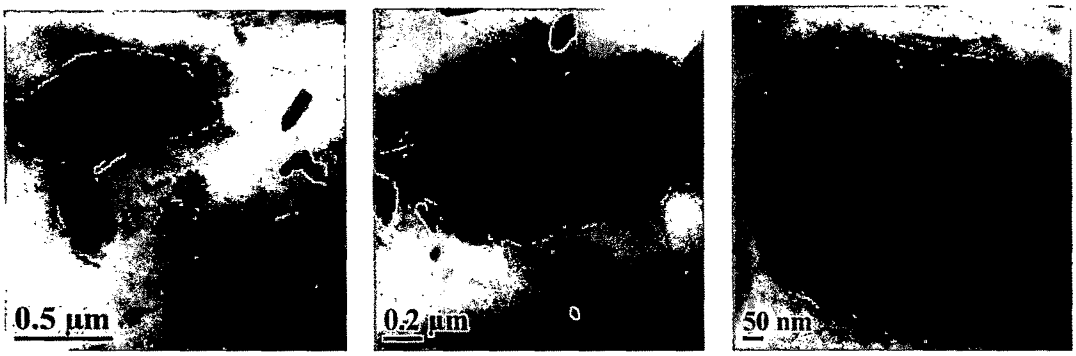

Fig. 5.9- TEM images of nanocomposite with 7 phr organoclay.

5.1.7 Conclusions

Investigations on nanocomposites of NR/BR (70/30) with organoclay (Closite®15A) using XNBR as a compatibiliser reveals the following:

I. All mechanical properties like modulus, tensile strength and elongation at break increases as the carboxyl content of XNBR increases from NB1(1% carboxyllation) to NB7 (7% carboxyllation). As carboxyl % in XNBR increases, the surface energy of the rubber increases which leads to higher interfacial interaction between filler and polymer (Das *et al*, 2008).

II. The mixing technique used also influences the organoclay dispersion and ultimately the mechanical properties. Internal mixer lead to the best clay dispersion and mechanical property enhancement followed by solution mixing and 2 roll mill. The mixing temperature (140°C) and high shear force in internal mixer has influence on the filler-polymer interaction which may be the reason for better clay dispersion and properties of nanocomposite compared to solution and 2 roll mill mixing.

III. The NR/BR-organoclay nanocomposite with 7 phr organoclay was found optimum as it exhibited the best physical properties like hardness, modulus, tensile strength, elongation at break and dynamic mechanical properties. The XRD study of the same nanocomposite reveals the silicate layers were expanded. TEM image also shows the intercalated and exfoliated morphology of the nanocomposite.

IV. The strong interfacial interaction between highly polar XNBR and organoclay played an important role in clay dispersion with in the rubber matrix. Strong interaction between carboxyl group and polar organoclay formed a thermodynamically stable composite and help clay dispersion when mixed with rubber.

5.2 DEVELOPMENT AND CHARACTERIZATION OF HIGH PERFORMANCE NANOCOMPOSITES BASED ON NR/BR BLENDS AND DUAL FILLER SYSTEM

5.2.1 Introduction

The objective of this investigation was to develop nanocomposites for truck bus radial (TBR) tire tread with reduction in the rolling resistance of the tire. To attain this objective nanocomposites of NR/BR (70/30) with organoclay (Closite®15A) using XNBR as a compatibiliser were formulated and characterized. Although substantial improvement of mechanical properties such as 300% modulus, tensile strength and elongation at break were attained with 70/30 NR/BR blend and 7 phr organoclay but other performance requirements of tire treads such as traction, tire wear and durability were not met with organoclay alone.

In case of tire tread application hardness and low strain modulus such as 50% and 100% modulus are also very important since tire handling; cornering and steering response depend on these properties. Similarly abrasion resistance is very critical for tire wear and durability.

Table 5.6-Compound descriptions (NR/BR: 70/30)

Code	XNBR (7% carboxyllation)	Organoclay (Closite 15A)	Carbon Black (N220)	Silica (HDS)	Silane, X 50-S (50% Si 69 + 50% CB)
NM-7	10.0	7.0			
Control-3			***50.0***		
NC-10	10.0	5.0	10.0		
NC-15	10.0	5.0	15.0		
NC-20	10.0	5.0	20.0		
Control-4				***45.0***	***10.0***
NS-10	10.0	5.0		10.0	2.0
NS-15	10.0	5.0		15.0	3.0
NS-20	10.0	5.0		20.0	4.0

Organoclay alone could not provide all desired properties; hence the concept of ***dual filler system*** was explored so that required compound properties could be obtained without substantially increasing hysteresis losses. The details of the raw materials used, compound formulations, preparation of dual filler nanocomposite, testing and characterization methods are described in ***Chapter 3*** and briefly described in Table 5.6 for reference. In this section, the results obtained for dual filler nanocomposites are elaborated.

5.2.2 Filler Characterization and Dispersion

In this investigation, three different fillers namely carbon black (N220), highly dispersible silica and organoclay (modified Na-MMT) were used. The particle size distributions of all the fillers are presented in Chapter-4. The other characterization such as BET surface area and DBP absorption were also described in Chapter-4.

The dispersion of carbon black and silica fillers in organoclay-carbon black and organoclay-silica dual filler nanocomposites were studied by Dispergrader (Opigrade, Sweden). A freshly cut thin rubber sample was placed in the sample holder. Surface of the sample was scanned and the image of the test sample surface was instantly presented on the monitor, powerfully magnified, side by side with one of the reference picture. Sample image was automatically classified against reference images stored in the software. The dispersion is rated by 1 to 10 scale where 10 represents best filler dispersion. The dispersion of organoclay-carbon black and organoclay-silica were 7.5 and 6.6 respectively.

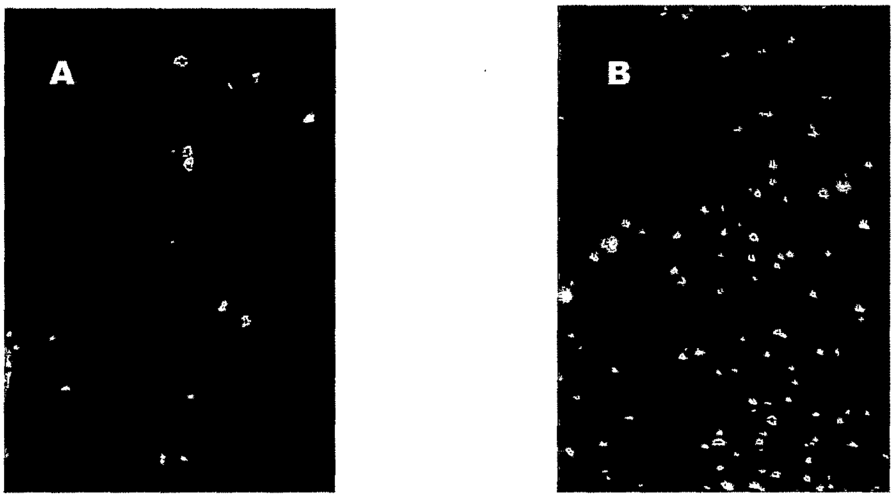

Fig. 5.10-(A) Organoclay-carbon black and (B) Organoclay-silica filler dispersion

5.2.3 Rheometric Properties

All the nanocomposites showed scorch safety 2.0 ± 0.5 and optimum cure time 5.6 ± 0.75 minutes. The rheometric modulus increases with increasing dosages of carbon black or silica filler in the nanocomposites as shown in Table 5.7. All organoclay-carbon black nanocomposites have similar optimum cure time (Tc_{90}) and Tc_{90} of all organoclay-silica nanocomposites are close to each other.

Table 5.7-Compound rheometric properties (MDR 150°C/30 minutes)

	Min torque dN.m	**Max torque dN.m**	**Ts2 Minutes**	**Tc90 Minutes**
NM-7	***2.82***	***7.43***	***2.82***	***5.68***
NC-10	2.20	8.38	2.20	4.72
NC-15	2.13	9.09	2.13	4.70
NC-20	2.07	9.98	2.07	4.77
NS-10	2.78	8.18	2.78	5.53
NS-15	3.02	8.66	3.02	5.95
NS-20	3.03	9.48	3.03	6.12

5.2.4 Mechanical Properties

The nanocomposite NM-7 showed excellent tensile strength and was close to Control compounds but hardness and 100% modulus were much lower than the Control compounds. These mechanical properties required for tire tread application could not be achieved by organoclay filler alone. Therefore, nanocomposites based on dual filler system comprising with organoclay-carbon black and organoclay-silica were developed. In dual filler system, 10, 15 and 20 phr of carbon black or silica were added along with 5 phr of organoclay. In NR/BR blend 7 phr organoclay was found to be optimum and offered the best properties, however in case of carbon black or silica filler, optimum properties observed in the range of 50 to 60 phr, hence 1 phr organoclay loading is approximately equivalent to 8-10 phr loading of carbon black or silica filler. It was observed that with an increased dosage of the second filler (carbon black or silica) mechanical properties of the nanocomposite improved substantially. The properties of nanocomposite developed with 5 phr organoclay and 20 phr carbon black or silica were close to the properties range of TBR tire tread compound as reported in Smithers report (Tire Analysis, TBR for emerging growth markets", Smithers Scientific Services, 2001, 2008).

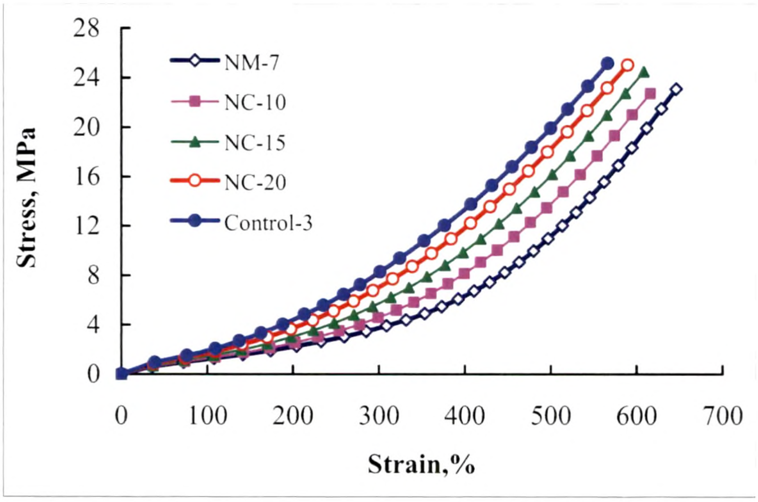

Fig. 5.11- Stress-strain properties of Control-3, organoclay and organoclay –carbon black dual filler nanocomposites

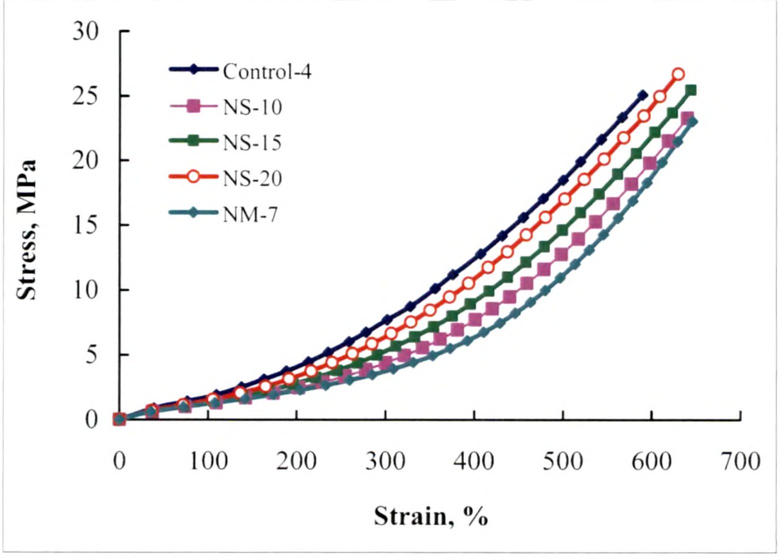

Fig. 5.12- Stress-strain properties: Control-4, organoclay and organoclay –silica dual filler nanocomposites

Stress strain curves of nanocomposite based on NR/BR with organoclay-carbon black and organoclay-silica are shown in Fig. 5.11 and 5.12 respectively along with Control compounds. The stress- strain properties of NC-20 is very close to Control-3 which has 50 phr carbon black filler. Similarly, NS-20 showed similar stress-strain properties to Control-4 which has 50 phr silica filler. Hence with much lower volume fractions of filler in the dual filler nanocomposites, properties similar to 45 to 50 phr carbon black or silica are obtained.

The reinforcement obtained from organoclay depends on two factor (a) loading of filler and (b) extent of intercalation and exfoliation of organoclay in the rubber matrix. During mixing, higher the shear force better is the filler dispersion. Incorporation of silica or carbon black in addition to organoclay generates much more shear force than organoclay alone and hence as a result highly exfoliated nanocomposite is formed. The increase of carbon black or silica filler increases the viscosity of rubber which generates greater shear force during mixing and processing. The excellent mechanical properties obtained using dual filler nanocomposites are to these aspects. Beside mechanical properties, other performance properties like tear strength, abrasion loss and heat build up of all the nanocomposites were also within the target limits of truck bus radial tread compound as shown in Table 5.8.

Table 5.8-Mechanical properties of nanocomposites

Properties	Typical range	NM-7	Control-3	NC-20	Control-4	NS-20
Hardness, Shore A	60 - 70	58	66	64	64	62
100% Modulus, MPa	1.5 - 2.5	1.26	1.82	1.72	1.62	1.50
300% Modulus, MPa	6.0 - 10.0	3.87	9.16	7.10	8.32	6.39
Tensile Strength, MPa	22.0 min	24.7	23.2	25.8	24.9	28.0
Elongation at Break, %	420 min	665	554	651	596	646
Tear Strength, N/mm	65 - 110	39.1	81.0	38.5	107.0	70.1
DIN Abrasion Loss, mm^3	70 - 110	180	88.0	94.0	99.0	106.0
Heat Build Up (ΔT), °C	20 - 30	12	28.0	18.0	26.0	16.0
Breaking Energy, $J/m^2 x 10^4$	-	123.7	129.9	136.4	146.2	155.7

5.2.5 Viscoelastic Properties

Viscoelastic properties of nanocomposites were determined by dynamic mechanical measurement in shear mode and presented in Fig.5.13 to Fig. 5.15. Different dynamic properties such as storage modulus (G'), loss modulus (G''), Tan δ have a great influence on viscoelastic behaviors of the compounds and their performance during applications.

Rolling resistance is related to the hysteresis behavior of compounds. Hysteresis loss is greatly influenced by filler-filler interaction. Higher is the filler-filler interaction, higher will be the hysteresis loss. Tan δ, which is the ratio of loss modulus to storage modulus of the compound, represents the hysteresis loss of the compound. In a tire tread compound, Tan δ at 60°C represents tire rolling resistance and lower is the value; lower will be the rolling resistance. Filler-filler interaction is accounted by measuring the difference in shear modulus (ΔG) at very low strain ($G_0 \sim 0.1\%$) and very high strain ($G\infty \sim 100\%$) 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 results in big difference between low strain modulus and high strain modulus between as observed during strain sweep experiment. Higher filler-filler interaction leads higher reduction of modulus and thus indicates higher 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 has much lower Payne's effect in comparison with carbon black and silica based commercial tread compounds (Control-3 and Control-4) as shown in the Fig. 5.13 and Fig.5.14 respectively as well as in Table 5.9 and these are due to lower volume fraction (lower dosages) of filler and greater filler-polymer interaction compared to the commercial tread compounds. In strain sweep, Tan δ values show a maxima when filler aggregates breaks which is seen in Fig. 5.15. Higher Tan δ_{max} also indicates higher hysteresis loss in the compounds and higher rolling resistance in tire. Nanocomposites with organoclay-carbon black dual fillers showed higher Payne's effect than the corresponding organoclay-silica dual filler. This is attributed to the presence of silane coupling agent which react with hydroxyl group of silica and breaks the strong filler network thereby reducing the filler-filler interaction remarkably.

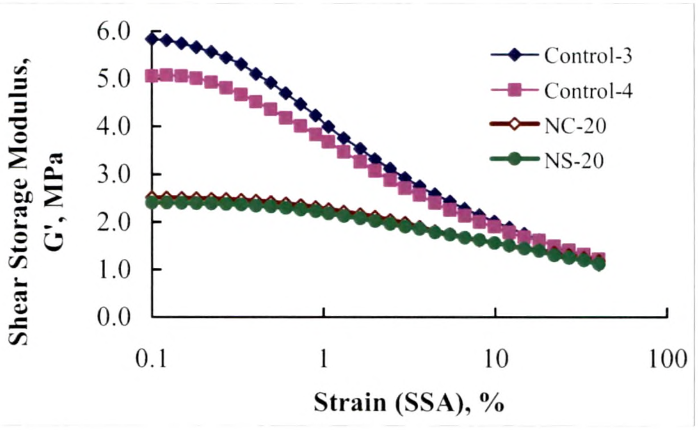

Fig. 5.13- Shear storage modulus versus strain at 60°C

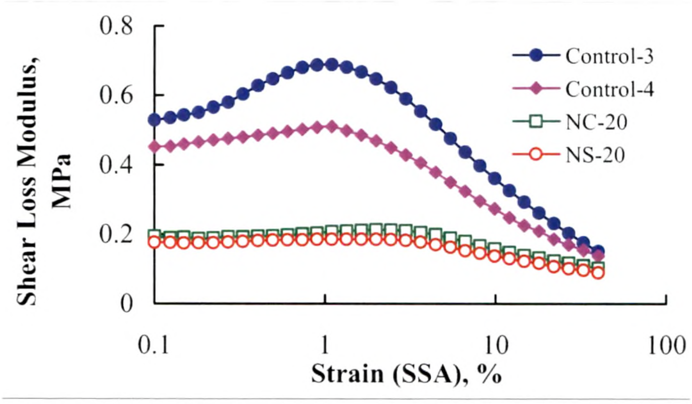

Fig. 5.14- Shear loss modulus versus strain at 60°C

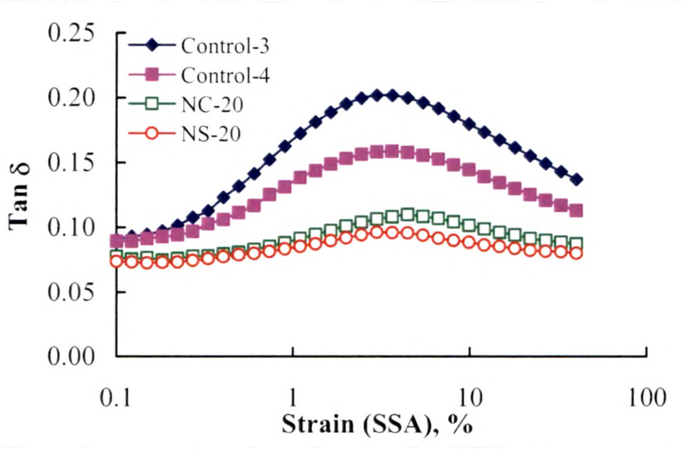

Fig. 5.15- Tan δ versus strain at 60°C

It was observed that organoclay-carbon black dual filler nanocomposite (NC-20) has 72% lower Payne's effect which leads to the reduction of 45% Tan δ_{max} values compared to carbon black based commercial tread compound (Control-3). Similarly organoclay -silica dual filler nanocomposite (NS-20) showed 68% lower Payne's effect and 40% lower Tan δ_{max} comparison with silica based commercial tread compound (Control-4). All nanocomposite based tread compounds showed much lower Tan δ values at 60°C when compared with Control compounds as shown in Fig. 5.15; hence these will have much lower rolling resistance in tire.

Table 5.9-Payne's effect

	Shear Modulus at Low Strain, Go (MPa)	Shear Modulus at very high Strain, G∞ (MPa)	Payne' Effect, ΔG, (MPa) [ΔG= Go- G∞]	Loss Modulus, G'' (MPa)	Tan δmax
Control-3	5.83	1.10	4.73	0.689	0.202
NC-20	2.52	1.18	1.34	0.213	0.110
Control-4	5.08	1.21	3.87	0.510	0.159
NS-20	2.40	1.12	1.29	0.186	0.096

5.2.6 X-Ray Diffraction (XRD) Study

The X-ray diffraction patterns were determined for organoclay, organoclay nanocomposites, and nanocomposites with dual filler system. X-ray diffraction peaks at 2θ angles and corresponding d-spacing of organoclay, clay nanocomposite and dual filler nanocomposites are presented in Table 5.10 and Fig. 5.16.

Diffraction peaks at low 2θ angles and reduction of peaks at higher 2θ angles in the nanocomposite revealed that d-spacing between silicates layers increased in the nanocomposite materials. The d_{001}-spacing increased to 3.88 nm in nanocomposite (NM-7) from 3.12 nm in organoclay and it was further increased to 4.0 nm in organoclay-carbon black dual filler based nanocomposite (NC—20). The dual filler based nanocomposite (NC—20) showed much higher d_{001}-spacing compared to organoclay nanocomposite. The increase of d_{001}-spacing in nanocomposite indicates that the layer silicate structure of organoclay gets expanded. Incorporation of carbon black further expanded the layer silicate structure and improved the dispersion as well as distribution of organoclay and resulted in better intercalated/exfoliated structure and resulted in excellent mechanical properties of the nanocomposites.

Similar to carbon black, incorporation of silica filler also improved the dispersion as well as distribution of organoclay and resulted in much better exfoliated structure than that observed for organoclay – carbon black that 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 studies.

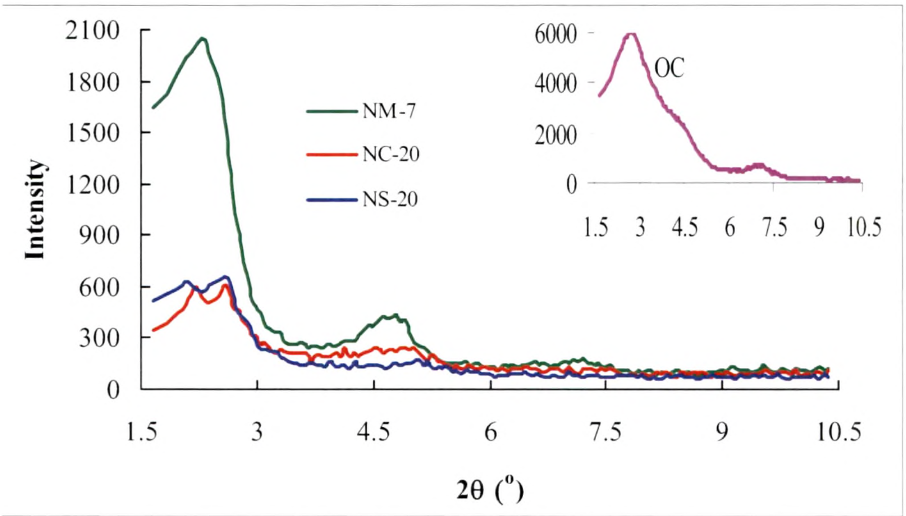

Fig. 5.16- XRD of organoclay and dual filler nanocomposites

Table 5.10-d-spacing (nm) in XRD study

Organoclay OC		Nanocomposite NM-7		Organoclay-carbon black nanocomposite NC-20		Organoclay-silica nanocomposite NS-20	
Angle 2θ	d-spacing (nm)	Angle 2θ	d-spacing (nm)	Angle 2θ	d-spacing (nm)	Angle 2θ	d-spacing (nm)
2.81	3.15	2.28	3.88	2.2	4.00	2.075	4.26
4.37	2.02	4.75	1.86	2.58	3.40	2.62	3.37
7.25	1.22	7.19	1.23				

5.2.7 Transmission Electron Microscopy (TEM) Study

The filler dispersion in the nanocomposites was studied by transmission electron microscopy (TEM). TEM images were taken at different magnifications from 0.5 microns to 50 nm. The exfoliated morphology of organoclay in the nanocomposite (NM-7) is presented in Fig. 5.17.

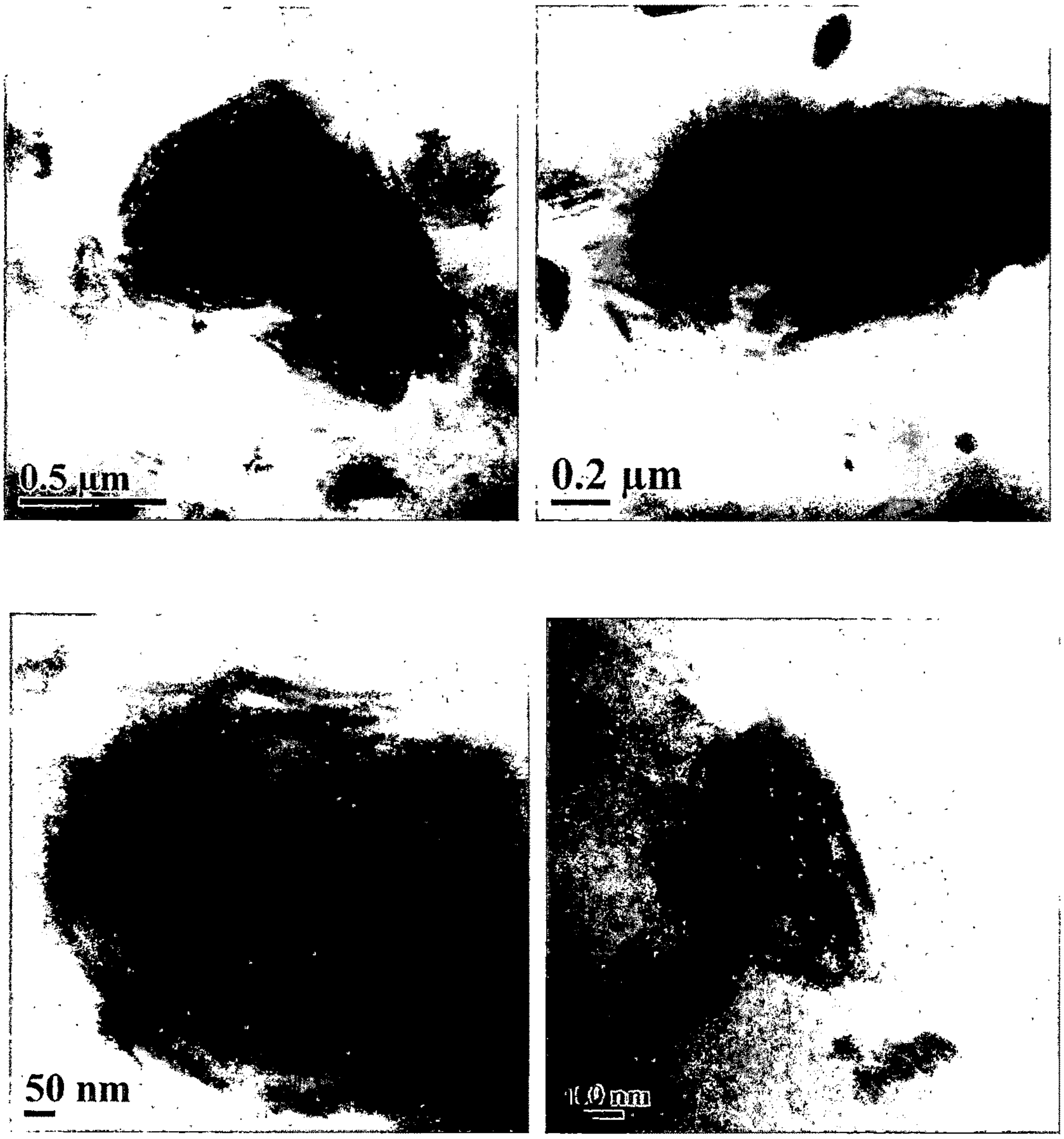

Fig. 5.17- TEM images of NR/BR organoclay nanocomposites (NM-7)

TEM images of organoclay-carbon black dual filler nanocomposite (NC-20) are presented in Fig. 5.18. Highly exfoliated structure of organoclay was observed in the NR/BR rubber matrix. In organoclay-carbon black dual filler system the TEM images of NC-20 showed a large extent of exfoliation of the organoclay, which appear to have a fiber like structure in the image whereas carbon black particles have a spherical shape and are darker in color. The distribution of both organoclay and carbon black are very fine in the nanocomposite material as seen in Fig. 5.18.

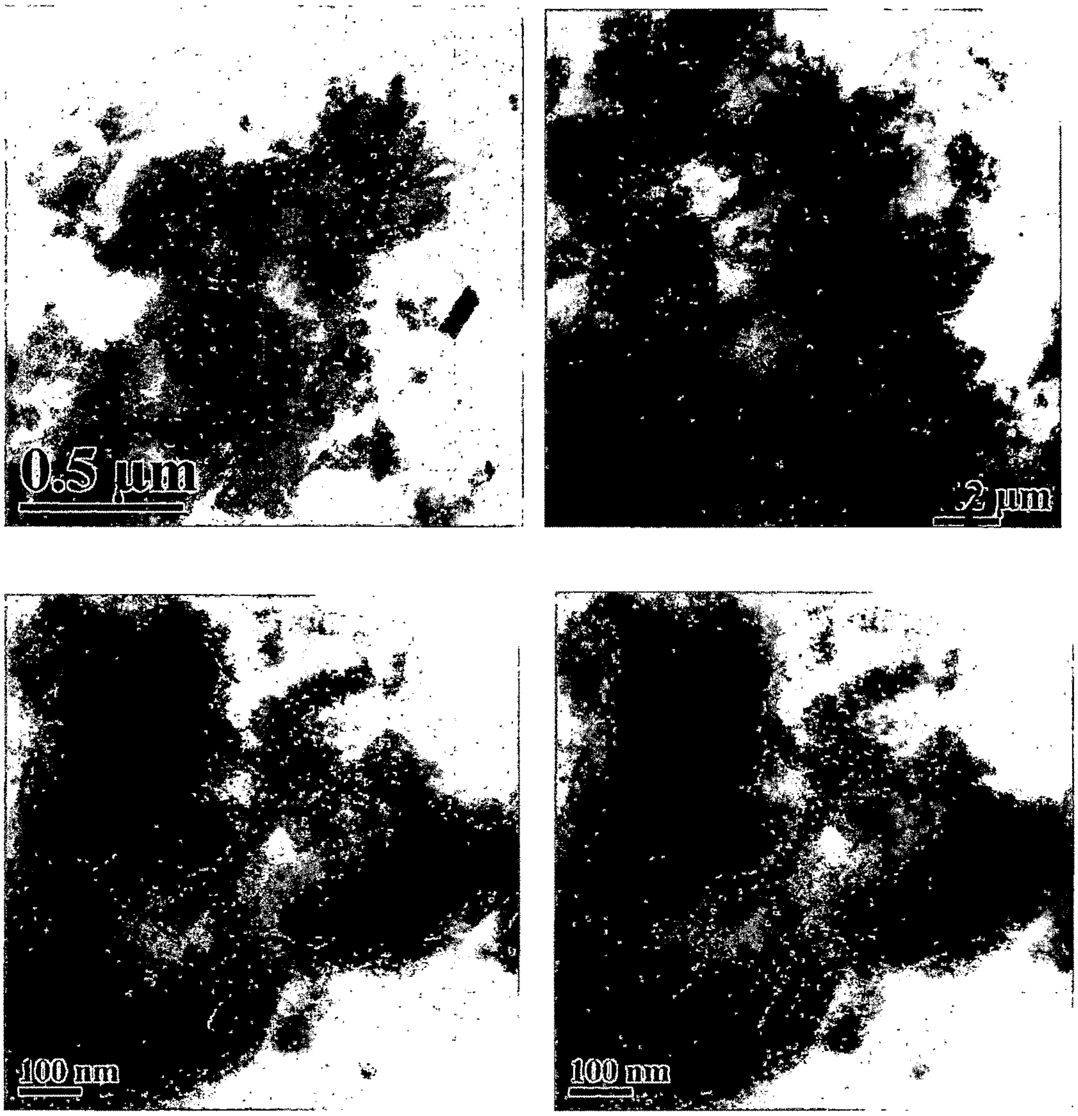

Fig. 5.18- TEM images of NR/BR organoclay-carbon black nanocomposites (NC 20)

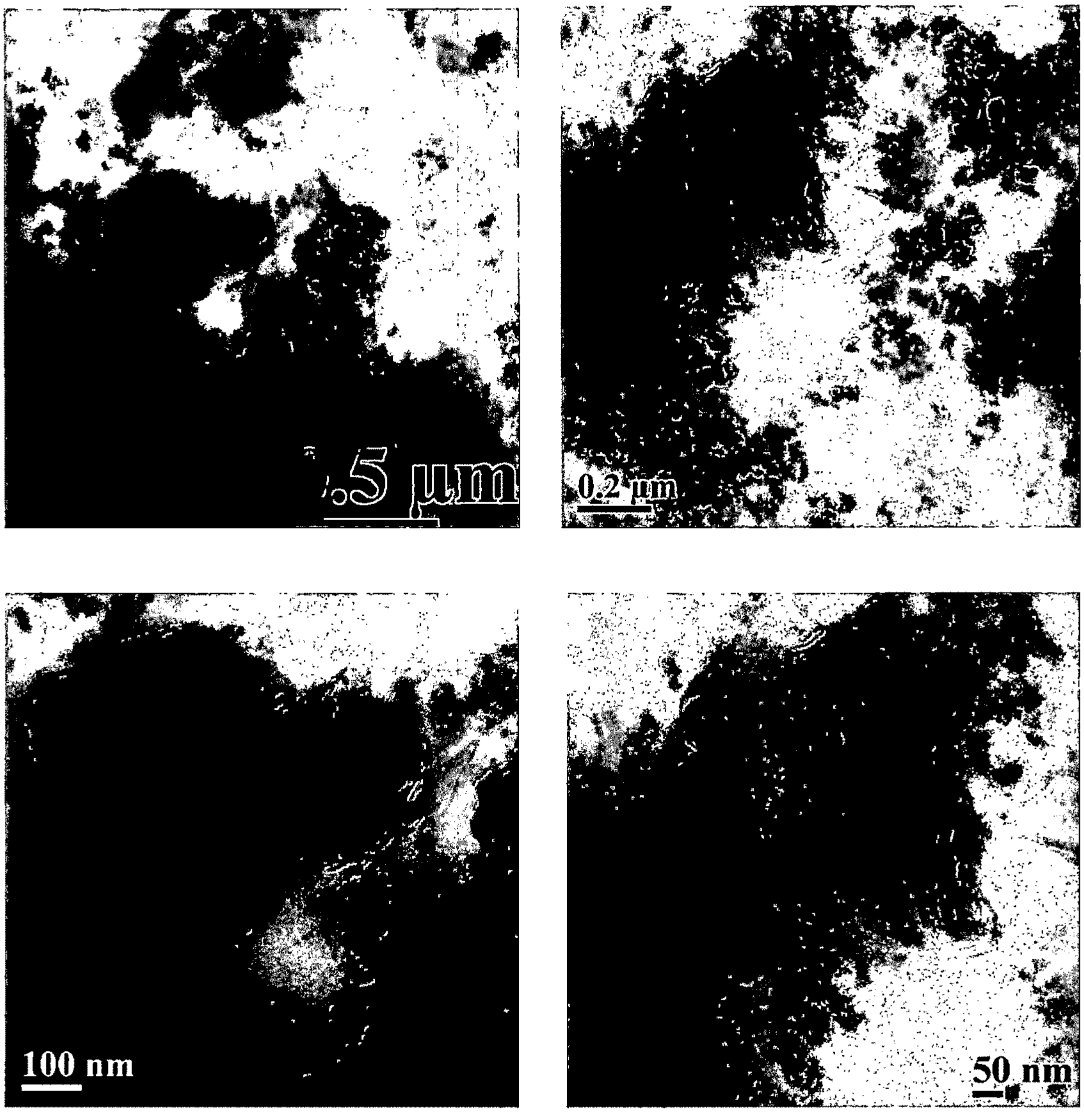

Fig. 5.19- TEM images of NR/BR organoclay-silica nanocomposites (NS 20)

TEM images of nanocomposites (NS-20) with organoclay-silica dual filler system showed a large extent of exfoliation of the organoclay mixed with some intercalated structure, which appear to be a fiber like in nature as seen from the image. Uniform distribution of organoclay and silica are observed in the NR/BR rubber matrix shown in Fig. 5.19. Presence of silane further enhanced the exfoliation of organoclay in organoclay-silica dual filler nanocomposite since it reacts with surface hydroxyl group of silica and organoclay as well thereby enhancing filler-polymer interaction.

Much better exfoliation of the organoclay was observed in both organoclay-carbon black and organoclay-silica dual filler systems compared to organoclay alone. This is attributed to the higher shear force generated during mixing in the presence of carbon black or silica filler in the matrix that resulted in greater exfoliation of organoclay, thereby providing superior reinforcement and excellent mechanical properties.

5.2.8 Conclusions

Nanocomposites based on NR/BR blends with organoclay showed excellent improvement of mechanical properties (Table 5.3 to 5.5) when compared with gum vulcanizate for example in the nanocomposite having NR/BR 70:30 and 7 phr organoclay there was 93 % enhancement in 300% modulus; 68% in Tensile strength; 47% in tear strength and 136% in Breaking Energy.

In spite of remarkable improvement of the above mentioned properties, organoclay nanocomposite did not fully meet the requirements of TBR tread compounds because for TBR tire tread applications, hardness, low strain modulus as well as abrasion resistance are very important. To meet these requirements, nanocomposites based on NR/BR blend were developed with organoclay-carbon black and organoclay-silica dual filler systems. The dual filler nanocomposites showed excellent mechanical properties which are comparable to commercial tread (Control) compounds and also fulfilled the requirements of Hardness, Modulus, Abrasion resistance and Tear strength for tread application. They meet the target performance range for TBR tread compounds.

Tan δ at 60°C indicates lower rolling resistance of the compound and lower the value lower is the rolling resistance. The reduction organoclay-carbon black nanocomposite (NC-20) had 45% less Tan δ_{max} compared to Control-3. Similar reduction of Tan δ_{max} (40%) was observed in organoclay-silica nanocomposite (NS-20) in comparison with Control-4. This clearly shows dual filler nanocomposite (NC-20 and NS-20) will give much lower rolling resistance in tire without sacrificing other performance parameters like mechanical properties, tear properties, wear properties and traction. This investigation revealed the potential of nanocomposites which in future could be used as TBR tire tread to reduce rolling resistance and improve fuel economy in commercial automotive transport.