

Tapas Ranjan Mohanty¹, Arup Kumar Chandra¹, Vivek Bhandari¹ and Santanu Chattopadhyay² 1. Global R & D Centre, Apollo Tyres Ltd., Oragadam, Sriperumbudur, 602105, Tamil Nadu, India

2. Rubber Technology Centre, IIT Kharagpur, Kharagpur 721302, West Bengal, India

Abstract: A novel carbon black (CB) and nanoclay (NC) filled system in Natural rubber (NR) matrix has been developed for steel cord tyre ply compound with optimized performance properties. The effect of partial replacement of CB (N-220) by two different kinds of nanoclay (Cloisite-20A and Cloisite-30B) on the adhesion properties has been extensively investigated. The nanocomposites have shown improved adhesion properties between steel cord and rubber (aged and unaged) i.e. pull out force and rubber coverage (%), for relatively lower loading of both Cloisite 20A and Cloisite 30B (3 phr). The addition of nanoclay at lower loading (upto 3 phr) leads to an increase in the overall performance of the rubber compound. Due to nano filler reinforcement, the cohesive strength of the nanocomposites increases, but it is still lower than the adhesive force between steel cord and rubber. As a result the failure is mostly cohesive with higher pull out force. The adhesion improvement is more significant in case of 3phr Cloisite 30B. Cloisite 30B contains polar modified quaternary alkyl ammonium ions as intercalants in its gallery spacing, which may form hydrogen bonding with the resin network available near the copper sulphide bonding layer and leads to better rubber reinforcement and higher pull out force. Dynamic contact angle measurement, transmission electron microscopy (TEM) and low angle X-ray diffraction (XRD) studies have been carried out to explain these phenomena.

Key words: Nanoclay, nanocomposites, adhesion, steel cord ply skim compound, radial tyre.

1. Introduction

Tyre is a complex composite consists of several types of rubbers, fillers, reinforcing fibres, steel cords and various other ingredients which are used in the rubber formulations and while building it [1]. The major strength of a tyre comes from the body ply or carcass. The materials used for reinforcement in the ply are mainly steel cords or organic textile cords. However, with growing demand from the automotive manufacturing companies and general consumers for better tyre performance properties such as mileage, load carrying capacity, durability, cushioning, low rolling resistance, puncture resistance etc, lead the researchers to look for various types of reinforcing materials for tyre. To address all these diametric requirements, steel cord has grabbed attention as a major reinforcing material, especially for carcass and belt of a radial tyre. The adhesion between various heterogeneous components of a tire is very important during its service life [1]. Good adhesion between the rubber skim compound and brass plated steel cord plays a crucial role in order to absorb the impact properly and to bear the load that comes on the tyre [2-4].

Since last 15-20 years, nanoclays have been used as potential reinforcing agent for various elastomers. There are several types of nanoclays available and these nanoclays with high aspect ratio offer a wide varieties of property enhancement at very low level of loadings, owing to the nanometric dimension and dispersion [5-9]. Most of the researchers have mainly

Corresponding author: Tapas Ranjan Mohanty, scientist, research fields: rubber nanocomposites, steel cord adhesion. E-mail:tapas9787@gmail.com.

studied the influence of the usage of nanoclays on the mechanical, thermal and physical properties of various polymers. On the other hand, literatures revealing the effects of nanoclays on the adhesion behaviour of elastomers are very less in number. There are only few studies about the effect of MMT based nanoclay on the adhesive behaviour of acrylic elastomer [10, 11]. The effect of laponite nanoclay on the pressure sensitive adhesive tack of acrylic adhesives was studied by Wang *et al.* [12]. The tremendous improvement in the autohesive tack behaviour of BIMS rubber using needle like sepiolite nanoclay is well justified by Dinesh *et al.* [13].

However, the effect of nanoclay on steel cord to rubber adhesion has not been widely established. The main objective of the present work is to study the effect of nanoclay on the adhesion behaviour of NR **CB-NC** based hybrid composite and its implementation as a steel cord ply compound. In this present work, effect of partial replacement of CB (N220) in the control formulation of steel cord ply compound for a truck-bus-radial (TBR) tyre by two different types of organoclay (Cloisite-20A & Cloisite-30B) have been studied. The pull-out adhesion force have been studied in conjunction with measurement of various other technical properties to understand its impact on steel cord rubber adhesion.

2. Experimental

2.1 Materials

Ribbed smoked sheet (RSS-III), viscosity ML (1+4) $100 \text{ }^{\circ}\text{C} = 70 \text{ was supplied by 'Belthangady Taluk}$ Rubber Workers Marketing and Processing Co-operative Society Ltd.', India. Cloisite 20A dihydrogenated (Dimethyl tallow quaternary ammonium modified MMT) having specific gravity 1.7 g/cc, mineral purity = 98.5%, mean particle size in between 2-13 µm and basal spacing of 3.15 nm was procured from Southern Clay Products, USA. Cloisite-30B [Methyl bis (ethyl alcohol) tallow quarternary ammonium modified MMT] having specific gravity = 1.98 g/cc, mineral purity = 98%, mean particle size in between 2-13 µm and basal spacing of 1.85 nm was also procured from the same organization (Sourthen Clay Products. USA). Intermediate super abrasive furnace black, ISAF (N220) was obtained from Philips Carbon Black Ltd., India having the following characteristics: iodine absorption no. = 121 g/kg; DBP absorption no., 10^{-5} $m^{3}/kg = 114$; compressed DBP absorption no., 10^{-5} $m^3/kg = 98$; nitrogen absorption surface area = 114 m^2/g ; and tint strength = 116%. Phenol Formaldehyde resin (PF resin) was supplied by Sumitomo Bakelite, Europe having pH = 5.5 and softening point around 100 °C. Cobalt stearate was purchased from OMG, GmbH. Brass coated steel cord was supplied by Baekart Pvt. Ltd. Other compounding and curing additives (ZnO, Peptizer 40% DBD, TDQ, 6PPD, active silica granular, Calcium stearate, Sulphur, DCBS, CTP, insoluble sulfur oil treated 20%) were purchased from standard Indian suppliers (analytical grade).

2.2 Preparation of Nanocomposites

The steel cord ply compounds were prepared by mixing in lab scale Banbury (FAMM Ltd., Mumbai, India) with a rotor speed of 50 rpm. The total mixing was done through four stages, which are depicted below as per sequence. The rotor used was a tangential type and the fill factor was about 0.80. After the fourth stage mixing in Banbury the compound was passed through two-roll mill to achieve a sheet of 7.2 mm thickness and stored for 24 h. Optimum cure time for the composites were determined by Moving Die Rheometer (MDR 2000 Alpha Technologies, U.S.A) at 160 °C, 30 minutes. The sheets were moulded for 15 min at 160 °C by compression moulding using a curing press (Moore Press, United Kingdom). The sheets were then cooled at room temperature. The details of the samples along with their respective designations are presented in Table 1.

Ingredients	A	B		D ,	F
RSS-III	100.0	100.0	100.0	100.0	100.0
NC (Cloisite 30B)	-	3.0	-	5.0	
NC (Cloisite 20A)	-	-	3.0	-	5.0
N-220	55.0	52.0	52.0	50.0	50.0
ZnO	8.0	8.0	8.0	8.0	8.0
Rubber peptizer 40% DBD	0.25	0.25	0.25	0.25	0.25
PF resin	2.5	2.5	2.5	2.5	2.5
TDQ	2.0	2.0	2.0	2.0	2.0
6-PPD	1.0	1.0	1.0	1.0	1.0
Cobalt stearate	1.5	1.5	1.5	1.5	1.5
Active silica granular	0.35	0.35	0.35	0.35	0.35
СТР	0.3	0.3	0.3	0.3	0.3
Insoluble sulphur—oil treated 20%	4.5	4.5	4.5	4.5	4.5
Accelerator, DCBS	1.0	1.0	1.0	1.0	1.0

Table 1	Formulation NR-CB-NC	nanocomposites	(all ingredients are in	phr, parts p	er 100 g of rubber)
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2.2.1 Mixing Condition: 4-Stage Mixing

Stage-I Master batch—1 (Banbury at 50 rpm, 5-6 minutes)

Addition of ingredients/operation:

- Rubber
- Rubber peptizer
- Nano clay (NC)
- Carbon black (CB)*
- ZnO
- Dump at 140 °C

Stage-II Master batch—2 (Banbury at 50 rpm, 5-6 minutes)

Addition of ingredients/operation:

- Stage-I compound
- Carbon black (CB)*
- PF resin
- TDQ, 6PPD, ZnO
- Dump at 140 °C

Stage-III Master batch—3 (Banbury at 50 rpm, 5-6 minutes)

- Addition of ingredients/operation:
- Stage-II compound
- Cobalt stearate, active silica granular
- Dump at 135 °C

Stage-IV Master batch—4 (Banbury at 20 rpm, 3-4 minutes)

Addition of ingredients/operation:

- Stage-III compound
- DCBS, CTP, sulfur
- Dump at 100 °C

*CB was mixed in two stages. In the second stage, 20 phr of CB was mixed for all the formulations and remaining CB was mixed in the first stage.

2.3 Testing and Characterization

2.3.1 Low Angle X-Ray Diffraction

To measure the change in gallery spacing of modified layered silicates, organically X-ray diffraction (XRD) test was conducted in a Rigaku Miniflex CN 2005 X-ray diffractometer equipped with CuKa radiator (30 kV, 10 mA, Rigaku Corporation, Tokyo, Japan). The diffraction data were obtained within a goniometer angle (2 θ) range of 2°-10° (wide angle XRD at lower angular range) at a rate of 1°·min⁻¹. The d-spacing of the clay layers was calculated using Bragg's equation $(n\lambda = 2d \cdot sin\theta)$; where n is the order of Bragg's diffraction (here n =1), λ is the wavelength of X-ray (Cu target), d is the interplanar distance, and θ is the angle of incidence of X-ray.

2.3.2 High Resolution Transmission Electron Microscopy

The rubber samples for TEM analysis were prepared by ultra cryo-microtomy method. The samples were microtomed using a Leica Ultracut EM FCS, Gmbh, Austria equipped with glass knives with cutting edge of 45° to get cryo-sections of 50 nm thickness. During ultra microtomy the sample temperature was maintained well below the glass transition temperature (Tg) of NR composites. The cryo-sections were then directly supported on a copper grid of 300-mesh size. Then the microscopic examination was performed on a transmission electron microscope (JEOL JEM-2100, Japan) operated at an acceleration voltage of 200 kV.

2.3.3 Non-isothermal Curing

The non-isothermal curing at different heating rates has been carried out using rubber process analyzer (RPA), RPA-2000 of Alpha Technologies, USA. The samples were heated according to the program of a constant heating rate (4, 7 and 10 °K/min) from room temperature to 300 °C.

2.3.4 Tensile Properties

Tensile (dumbbell shaped) and Tear (angular) specimens were punched out from the moulded sheets using Hollow Die punch (CEAST, Italy). The tests were carried out in a Universal Testing Machine (Zwick Roell Z010, Germany) at a cross head speed of 500 mm/min at 25 ± 2 °C. Tensile and tear tests were carried out as per the ASTM D 412-98 and ASTM D 624-99 methods respectively. Results of tensile and tear tests for each sample were recorded as the average of five repeated observations. The standard deviations for modulus at 300% elongation, tensile strength (TS), elongation at break (EB%), and tear strength are ± 0.3 , ± 0.7 , ± 8.0 and ± 1.5 units, respectively.

2.3.5 Hardness

The hardness of each sample was measured by Shore A & IRHD Combined Model Hardness Tester (GIBITRE Instrument, Italy) as per ASTM D 2240 test method. The average of four observations has been reported here. 2.3.6 Ageing

2.3.6.1 Thermal Ageing (Aerobic)

Ageing test was carried out keeping the samples in an ageing oven at 100 °C for 48 hr to get a preliminary idea about the ageing characteristics of the samples.

2.3.6.2 Humidity Ageing

The test was carried out keeping the cured samples in a humidity chamber at a relative humidity of 96% and temperature of 70 $^{\circ}$ C for 3 days.

2.3.7 Dynamic Mechanical Analysis (DMA)

The dynamic mechanical thermal analysis was conducted using parallelepiped samples with dimensions 25 mm \times 10 mm \times 2 mm in a DMA machine (VA 4000 METRAVIB, France) in the tension mode. The dynamic properties were recorded at frequency=11 Hz, static strain= 5%, dynamic strain = 2% and temperature = 70 °C for steel-cord ply compound.

2.3.8 Steel Cord Pull-Out Adhesion Test

The testing was carried out as per ASTM D 2,229. The specimens for T-test were cured at 153 °C for 30 minutes in a four cavity steel cord adhesion mould. Pullout force was determined as the maximum force exerted by the tensile tester on a T-test sample during the pullout test at 100 mm/min cross head speed. Rubber coverage (defined as a percentage of the steel cord surface covered by rubber), the relative extent of rubber covered on pulled out cord was observed by naked eye. Each value reported was an average of eight samples.

2.3.9 Contact Angle Measurement

The contact angle (θ) measurements of NR-CB-NC nanocomposites samples were done in a contact angle meter (Kernco, Model G-II from Kernco Instruments, EI Paso, TX). Measurements were carried out with water (triply distilled) in a vapor saturated air at 25 °C in a closed sample box. The volume of the sessile drop was maintained as 5 µl in all cases using a microsyringe.

Each contact angle is the mean of at least five measurements with a maximum error in θ of $\pm 1^{\circ}$.

3. Results and Discussion

3.1 XRD Patterns of NR-CB-NC Nanocomposites

Fig. 1 represents the X-ray diffraction patterns of the NR-CB-NC nanocomposites. The compound B (containing 3phr Cloisite 30B) shows two diffraction peaks, one at $2\theta = 6.45^{\circ}$ and the other at $2\theta = 2.31^{\circ}$, which are the characteristic peaks of the dispersed organoclay (Cloisite-30B). The major peak at $2\theta =$ 2.31° corresponds to the average basal spacing (d-spacing) of $38.4A^{\circ}$ which is substantially higher than that of pristine Cloisite 30B (i.e., $18.5 A^{\circ}$). Similarly for compound C (containing 3phr Cloisite 20A), two diffraction peaks were observed, one at 2θ $= 2.33^{\circ}$ (d spacing $38.1A^{\circ}$) which is much higher than that of pristine Cloisite 20A (i.e. $24.2A^{\circ}$) and the other at $2\theta = 6.27^{\circ}$.

Thus, for both compound B and compound C an intercalated structure along with certain level of exfoliation has occurred. These minor peaks at $2\theta = 6^{\circ}-7^{\circ}$ corresponding to lower level of d-spacing indicate the formation of clay aggregates. For

compound D and compound E, the major peaks appeared at $2\theta = 2.47^{\circ}$ (d spacing $35.9A^{\circ}$) and $2\theta = 2.41^{\circ}$ (d spacing $36.8A^{\circ}$) respectively. From the values of d spacing it is clear that for composites containing 5 phr NC also there is an increase of average basal spacing, but comparatively lesser than 3 phr loaded composites). However the tightness of clay aggregates is more in case of compound containing 5 phr of NC which is indicated by one more additional sharper peak at $2\theta = 5^{\circ}$.

3.2 Morphology of NR-CB-NC Nanocomposites by TEM

The HR-TEM photomicrographs of various NR-CB-NC nanocomposites are shown in Fig. 2. From Fig. 2a (B: 3phr Cloisite 30B) and Fig. 2b (C: 3 phr Cloisite 20A), it can be seen that nanoclay is well dispersed throughout the entire matrix. The clay platelets are randomly oriented along the entire rubber matrix for lower loading of NC upto 3 phr. For the compound B containing 3 phr of Cloisite 30B with 52 phr N220, the CB shows preferential association with rubber as well as with NC layers. This leads to formation of hybrid nanostructures i.e. nanoblocks,



Fig. 1 XRD patterns of NR-CB-NC nanocomposites.



Fig. 2 TEM photomicrographs of NR-CB-NC nanocomposites at 10 kX magnification: (a) Compound B, (b) Compound C, (c) Compound D and (d) Compound E.

nanounits, halo and nano channels. The formation of these hybrid nanostructures corroborate to a significant improvement in the dispersion and hence enhances the overall performance properties. Certain level of clay exfoliation can be observed in this case. In case of compound C containg 3 phr of Cloisite 20A with 52 phr N220, the observation (Fig. 2b) to some extent is similar as that of compound B, but compound B (Fig. 2a) shows the best dispersion among all. For compounds D and compound E containing 5 phr Cloisite 30B and Cloisite 20A respectively with 50 phr N220, from the TEM photomicrographs (Figs. 2c and 2d), it appears to be aggregated with some partial intercalation of the silicate layers. This may be due to overdose of nanoclay. The filler-starved regions are also visible in the TEM micrograph (Figs. 2c and 2d).

3.3 Cure Characteristics NR-CB-NC Nanocomposites

3.3.1 Isothermal Curing

The reduction in scorch time (t_2) and the increase of

the cure rate with increasing amount of NC are significant (Table 2) because the incorporated organoclay contains quaternary alkyl ammonium ion. Benzothiazole accelerators when combine with amines produce benzothiazyl anions which accelerate the cleavage rate of cyclic sulfur [14, 15] ultimately resulting in faster curing of the rubber. The maximum torque (M_{max}) as well as delta torque (ΔM) values are also higher for nanocomposites as compared to the control compound A containing only carbon black. This may be due to greater extent reinforcement because of nano filler.

3.3.2 Non-isothermal Curing

Tyre is a complex composite having different rubber components (thicker and thinner). Although a particular curing condition is set, but the realistic curing of a tyre is a non-isothermal process. Hence the non-isothermal curing at different heating rates has been carried out using rubber process analyzer (RPA) to study the effect of NC on the activation energy required for curing. Table 3 represents the RPA curing

		P			
Sample	M _{min} (dNm)	M _{max} (dNm)	ΔM (dNm)	Scorch time t_2 (min)	Optimum cure time t ₉₀ (min)
А	2.52	23.0	20.48	2.83	7.50
В	2.90	26.0	23.10	2.35	7.30
С	2.80	26.3	23.50	2.43	7.22
D	2.60	26.1	23.50	2.20	6.84
Е	2.45	25.3	22.85	1.95	6.55

 Table 2
 Cure characteristics of NR-CB-NC nanocomposites.

Table 3 RPA data for the curing of NR-CB-NC nanocomposites	at different heating rates.
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Sample	β (°K/min)	Tp (°K)	$1/T_{\rm P}^* 10^3 (^{\circ}{\rm K}^{-1})$	lnβ
	4	448	2.232142857	1.386294361
А	7	457	2.188183807	1.945910149
	10	464	2.155172414	2.302585093
	4	445	2.247191011	1.386294361
В	7	455	2.197802198	1.945910149
	10	463	2.159827214	2.302585093
	4	443	2.257336343	1.386294361
С	7	454	2.202643172	1.945910149
	10	461	2.169197397	2.302585093
	4	440	2.272727273	1.386294361
D	7	453	2.207505519	1.945910149
	10	463	2.159827214	2.302585093
	4	439	2.277904328	1.386294361
E	7	453	2.207505519	1.945910149
	10	462	2.164502165	2.302585093

data of NR/CB/NC nanocomposite at different heating rates. In each case the peak temperature shifts from a higher value to a lower value with the change in heating rate from higher side to lower side. Slower heating rates give the sample more time to cure resulting a smaller value of peak temperature [16].

However, many equations have been developed to calculate the activation energy (E_a) for non-isothermal curing process. In our present study, we have used Ozawa-Flynn-Wall method based on Doyle's approximation [16] for the calculation of Ea and is expressed as follows:

 $ln\beta = Const. -1.052E_a/RT_p \qquad (1)$ where, $\beta =$ Heating rate, T_p is the peak temperature, E_a is the activation energy, R is the gas constant.

A plot of $\ln\beta$ versus 1/Tp from Table 3, should give a straight line with a slope of 1.052 E_a/R , as shown in Fig. 3. The E_a values, calculated from the slope are listed in Table 4. The Ea values obtained from Eq. (1) showed a decrease trend for NR-CB-NC filled nanocomposites as compared to NR-CB control composite. Therefore, it is concluded that the NC particles acted as catalyst which increases the speed of curing reaction by lowering the activation energy for the reaction as explained earlier due to presence of quaternary ammonium ion.

3.4 Physico-Mechanical Properties

The various stress-strain properties of NR-CB-NC nanocomposites are represented in Tables 5 and 6. respectively. The compounds B and C containing 3 phr of Cloisite -30B and Cloisite 20A respectively show higher value of modulus (100, 200 and 300%) among all composites may be due to proper dispersion (exfoliation) of NC within the rubber matrix. The increasing modulus and hardness may enhance the cohesive strength of the rubber compound and ultimately





Fig. 3 Ozwa plot of NR-CB-NC nanocomposites: (a) Compound A, (b) Compound B, (c) Compound C, (d) Compound D and (e) Compound E.

Table 4	Value of activation ener	gy (E _a) of NR-CB-NC	nanocomposites.
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	80 (u)	1
Sample		Activation energy E _a (kJ/mol)
A		94.4
В		83.2
С		82.0
D		64.4
Е		63.8

Table 5	Mechanical	properties of NR-CB-NC	c nanocomposites.
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Samula	Tensile strength (Mpa)		Elongation at break (%)			Hardness (Shore A)			
Sample	Unaged	Aged	Change (%)	Unaged	Aged	Change (%)	Unaged	Aged	Change(%)
Α	25.5	16.82	-34.0	405	201	-50.4	73	80.5	+10.3
В	27.4	19.7	-28.1	420	205	-51.2	78	84	+7.7
С	26.9	18.8	-30.1	423	210	50.4	77	84	+9.1
D	24.5	16.9	-31.0	425	216	-49.2	76	82.5	+8.6
Е	23.9	15.5	-35.1	429	206	-52.0	76	83	+9.2

	Modulus (MPa)								
Comm1.		100%			200%			300%	
Sample	Unaged	Aged	Change (%)	Unaged	Aged	Change (%)	Unaged	Aged	Change (%)
А	3.83	7.25	+89.3	9.22	15.6	+69.2	15.72	16.82	+7.0
В	4.91	8.80	+79.2	10.50	17.03	+62.2	17.02	17.7	+4.0
С	4.75	8.64	+81.9	10.70	17.10	+59.8	17.50	18.0	+2.9
D	4.14	7.54	+82.1	9.44	15.24	+61.4	16.08	16.4	+2.0
Е	4.05	7.23	+78.5	9.28	Х	Х	15.62	15.88	+1.7

Table 6 Mechanical properties of NR-CB-NC nanocomposites.

increases the compound rupture energy. Since some of the polymer molecules remain intercalated within the clay galleries, it may allow the slippage of rubber molecules leading to an increase in the EB (%) values of the nanocomposites compared to control compound A, which is consistent with our earlier published literatures [17-18]. The compounds B & C show an optimum balance between physical properties.

3.5 Dynamic Mechanical Properties

The storage modulus and tan δ values of various steel cord adhesion samples were measured using DMA machine, operated at frequency = 11 Hz, static strain = 5%, dynamic strain = 2%, temperature = 70 °C. Figs. 4 and 5 represent the hysteresis and storage modulus values of various NR-CB-Organoclay nanocomposites (including the control compound) respectively.

The compounds containing 3 phr of NC (B and C) show comparatively lower value of tan\delta at 70 °C indicating a lower hysteresis irrespective of the type of organoclay used. This may be due to enhanced polymer-filler interaction due to nanometric dispersion of the filler. Again nanoclay filled compounds compared to control compound (A) show increment in storage modulus values due to same reason.

3.6 Adhesion Properties

Since tyre is subjected to dynamic application, adhesion between rubber skim compound and steel cord is a basic requisite in steel cord reinforced tyres. But, steel cord itself does not adhere to rubber, so brass coating is given on the surface of steel cord. During tyre curing process, the brass plating reacts with the sulphur present in the rubber compound to form an adhesion inter-phase [2]. Copper sulphide plays a vital role for the adhesion, but zinc sulphide usually co-exists [3]. Copper and zinc oxides and hydroxides are also formed at the adhesion inter phase [4]. The chemistry behind the adhesion at the rubber-brass interface has been discussed extensively in several literatures over the last three decades [19-28]. But still it is not well understood how the copper sulfide layer interacts with the rubber. It is thought that the dendritic structure of copper sulfide forms a tight, physical interlocking with the vulcanized rubber [19].

The effect of NC loading on the adhesion of the nanocomposites with brass plated steel cord was analyzed by steel cord pull-out adhesion test. The pull-out force (N) and rubber coverage (%) of various adhesion samples for steel cord ply compound are depicted in Figs. 6 and 7 respectively. From the figures, it is observed that there is considerable increment in pull out force as well as rubber coverage for compound B and compound C containing 3 phr of Cloisite-30B and Cloisite-20A respectively for both unaged and humid aged samples.

As highlighted by Van Ooij et al. and Chandra et al. since the metal to rubber adhesion interface consists of copper sulfide, zinc sulfide and zinc oxide layers, there are in total at least five possible modes of failure [22, 25]:

- Cohesive failure of the rubber
- Adhesive failure of the sulphide-rubber interface

• Cohesive failure of the sulphide layer



Fig. 4 Hysteresis (tano at 70 °C) of NR-CB-NC nanocomposites.



Fig. 5 Storage modulus (E' at 70°) for NR-CB-NC nanocomposites.



Fig. 6 Pull-out force (N) of NR-CB-NC nanocomposites.



Fig. 7 Rubber coverage (%) of NR-CB-NC nanocomposites.

- Adhesive failure at the sulphide-ZnO interface
- Adhesive failure of the ZnO-metal interface

Again it was explained by Chandra et al. for normal as well as under aerobic ageing, the adhesion energy in general is appreciably higher than the compound rupture energy [22]. This indicates that chances of cohesive failure within rubber matrix is more than that of the failure at adhesion inter phase. To avoid this cohesive failure, higher reinforcement of the rubber compound is required. The addition of nanoclay at lower loading (up to 3 phr) leads to an increase in the reinforcement of the rubber compound probably due to formation of hybrid nano networks. The rubber to brass bonding due to the formation of hybrid nanostructures in NR-CB-NC nanocomposites for 3 phr loading has been schematically represented in Fig. 8. For lower loading of NC (upto 3 phr), the formation of hybrid nano structures like (nanounit and halo) leads to a significant improvement in the dispersion and hence enhances the overall reinforcement. This ultimately increases the cohesive strength of the nanocomposites offering greater resistance to separation upon stressing and possibly could be the reason for obtaining higher pull-out force values for compound B and compound C compared to the control compound A. But the cohesive energy is still lower than the adhesion energy which led to cohesive failure of the compound during pull out rather than adhesive failure with a higher pull out force value.

In addition; since nanoclay contains adequate no. of hydroxyl (Si-OH, Al-OH) groups on their surface, it strengthens the adhesion interface by forming hydrogen bonds with the resin network formed near the copper sulfide interface. However, the adhesion improvement is more prominent in case of Cloisite 30B. This can be argued that since Cloisite-30B contains polar modified quaternary alkyl ammonium ions as intercalants in its gallery spacing, it may even more facilitate the formation hydrogen bonding with the resin network available near the copper sulphide bonding layer and probably that leads to better rubber reinforcement and higher pull out force. During vulcanization process, the polar phenol formaldehyde resin molecules migrate out of the rubber because of incompatibility and move towards the adhesion interface between rubber and brass surface. At this interface, the resin forms tightly cross linked interpenetrating network structure with the copper sulphide dendrites. The formed interpenetrating network structure is responsible for the reinforcement of weak boundary layer adjacent to adhesion interphase and strengthens the adhesion. Since Cloisite-30B contains polar modified quaternary alkyl ammonium ions as intercalants in its gallery spacing, there may be chances of formation of hydrogen bonding with resin which will further strengthen the network. Consequently it enhances the adhesion between rubber and brass. This plausible mechanism has been schematically explained in Fig. 9.



Fig. 8 Schematic diagram: Typical rubber to brass bonding illustrating the dendritic morphology of Cu_xS and interlocking of rubber due to the formation of hybrid nanostructures in NR-CB-NC nanocomposites for 3 phr loading.



Fig. 9 Schematic diagram: Enhancement in rubber to brass adhesion due to the formation of hydrogen bonding between Organic modifier of Cloisite-30B and Resin in NR-CB-NC nanocomposites.

With further increasing the loading of Cloisite-30B or Cloisite-20A up to 5phr (compound D and compound E respectively), the pull-out force and rubber coverage show a kind of decrement in both unaged and humid aged conditions. This may be attributed to a poor dispersion or formation of agglomerates resulting poor reinforcement as evident from both TEM morphology and physical properties measurements, which ultimately reflected in lowering adhesion properties. The other reason may be related to the insufficient growth of copper sulfide layer (Cu_xS). As already discussed Cu_xS is a prerequisite for good adhesion. Thus the optimum growth of copper sulfide layer is necessary to maximize the contact interface between the rubber and the brass, resulting in good adhesion [27, 28]. But in case of 5 phr NC loaded compounds (compound D compound E), the Ea activation energy values obtained from non-isothermal curing (Table 4) are much less compared to the control (compound A) as well as 3 phr NC loaded compounds (compound B and compound C). Probably because of very fast rate of curing (low activation energy) for 5 phr NC loaded compounds, there may be chances of insufficient growth of Cu_xS . It is always essential to delay the crosslinking process long enough to build a Cu_xS layer of critical thickness [19]. Hence in the case of 5 phr NC loaded compounds, insufficient thickness of Cu_xS layer might have led to adhesive failure. Consequently lower values of pull-out force and rubber coverage were obtained in these cases.

3.7 Contact Angle Measurement

The surface characteristics of any composite largely govern the wetting phenomena and hence the adhesion behavior [29-31]. Contact angle measurement of liquids on solid surfaces is a technique for quantifying the wettability and surface characteristics of solids [29]. Wetting properties of the nanocomposites were studied using dynamic contact angle measurement with water. Table 7 represents the mean contact angle of NR-CB-NC nanocomposites. The variation of contact angle of the nanocomposites with respect to nanoclay loading for both Cloisite-30B and Cloisite-20A is

represented in Fig. 10.

The work of adhesion (W_A) for the nanocomposites was calculated using the Young-Dupré equation (Eq.

(2)). W_A is the work required to separate the solid composite surface and liquid drop.

$$W_{\rm A} = (1 + \cos\theta)\gamma_{\rm I} \tag{2}$$

Table 7	Contact angle and work of adhesion of NR-CB-NC nanocomposites.					
Sample	Contact angle θ (°)	Work of adhesion W_A (mJ/m ²)				
А	111.6	45.5				
В	105.1	53.24				
С	106.3	51.8				
D	113.1	43.75				
E	119.0	37.1				



Fig. 10 Variation of contact angle (°) with NC loading of NR-CB-NC nanocomposites.



Fig. 11 Variation of Work of adhesion (W_A) with NC loading of NR-CB-NC nanocomposites.

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Fig. 12 Schematic diagram: Contact angle and wettability of NR-CB-NC nanocomposites.

where, γ_1 is the surface tension of the liquid used for the contact angle measurement. Here we have taken γ_1 = 71.99,the surface tension of water at 25 °C.

The plot of work of adhesion (W_A) of the nanocomposites with respect to nanoclay loading for both Cloisite-30B and Cloisite-20A are represented in Fig. 11. The work of adhesion can be linked to the filler matrix interaction of filler with a liquid comparable with the virgin polymer [31]. Even though the liquid (water) selected do not imitate the neat polymer exactly, an attempt was done to correlate the work of adhesion of the nanocomposites with the filler matrix interaction [31].

The TEM and XRD studies revealed the efficient dispersion of nano clay up to 3 phr. Consequently the effective dispersion of nanoclays into the rubber matrix may be the cause for an increase in the work of adhesion. The wettability of rubber at the filler surface and the adhesion forces involved at the rubber-filler interface is a critical parameter for the reinforcement. Adequate wetting at the interface leads to ease of bond formation and subsequently offers greater resistance to separation upon stressing. The variation of contact angle and wettability of NR-CB-NC nanocomposites is schematically represented in Fig. 12. For lower level replacement of CB with NC (3 phr Cloisite-20A/ Cloisite-30B), the wettability is sufficient enough to form stronger polymer-filler network. But with further increase in the NC loading up to 5 phr (compound D & E), the contact angle values increases which indicates poor wettability and lower reinforcement.

4. Conclusions

The partial replacement of CB (N220) by organoclay (Cloisite-20A & Cloisite-30B) in the control formulation of steel cord ply compound for a truck-bus-radial (TBR) tyre has lead to an all round improvement, specially the pull out adhesion force and other related properties. It has been explained on the basis of following factors.

The addition of NC at lower loading increases the rubber reinforcement and cohesive strength of the nanocomposites (compound B and C), but it is still lower than the adhesive force between steel cord and rubber. As a result the failure is mostly cohesive with higher pull out force for compound B and C compared

to control compound A. But at higher loading of NC, the formation of agglomerates results poor reinforcement and consequently lowers the adhesion properties.

The contact angle and work of adhesion values also indicates poor wettability and lower reinforcement for 5 phr loaded sample.

The other reason for lower pull out force values in case of 5 phr NC loaded compounds is insufficient growth of Cu_XS layer because of extremely lower activation energy and faster curing of these formulations. Ultimately this leads to poor adhesive strength.

The resin forms tightly cross-linked interpenetrating network structure with the Cu_XS dendrites. In case of cloisite 30B, polar modifier quarternary alkyl ammonium ion present in the gallery of cloisite 30B forms hydrogen bonding with the resin network. This attributes to further enhancement of pull out force for compound B compared to all other nanocomposites.

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