

# Phosphorylated Cashew Nut Shell Liquid Prepolymer Modified Kaolin as a Reinforcing Filler for Rubber Vulcanizates—Comparison with SRSO Modified Kaolin and Cloisite

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**Abstract:** NR (natural rubber) based and its blend with BR (polybutadiene rubber) and NBR (nitrile rubber) composites were synthesized using reinforcing filler and other relevant additives. PCNSL (phosphorylated cashew nut shell liquid) modified kaolin, SRSO (sodium salt of rubber seed oil) modified kaolin and commercially available cloisite 30b were used as filler for reinforcement to achieve improved mechanical properties. Kaolin was modified with PCNSL either in two methods, by solvent treated method or sodium salt method and varying concentrations were prepared for comparison. No rate of intercalation was found with solvent treated PCNSL, but achieved with sodium salt of PCNSL. While comparing SRSO and SPCNSL, it is found that better intercalation and property improvement were achieved with only SRSO, since it possesses up to 18 carbon atoms in the side chain than the PCNSL with 15 carbon atoms side chain.

**Key words:** PCNSL, SRSO, cloisite, intercalation, comparison, NR.

## 1. Introduction

Physico-mechanical property characterization of rubber composites for potential industrial applications has been studied from long years back. The research on rubber composites arrived at a point that, through the inclusion of micro/nano particles as reinforcing filler, will improve all the strength properties under assorted conditions. Among the fillers layered silicate materials found a prime position as it adds reinforcement to the composites. Since long back kaolinite and MMT (montmorillonite) are extensively used as reinforcing filler for polymer, but in the pristine state they provide only modest kinetic effect. The research on clay modification was begun in 1980s by researchers at Toyota's Central Research and

Development Laboratories and the first clay nanocomposite commercialized was nylon 6 using quaternary ammonium ion modified MMT as filler [1]. The intercalated and exfoliated structure of unmodified MMT was studied by Pojanavaraphan et al. [2], by compounding NR latex/clay aerogel composite through freeze drying technique and they achieved dispersed clay composite formation at 3 phr of MMT loading. Gonzalez et al. [3] prepared NR/MMT nanocomposites in only one step by using poly(ethylene glycol) which behaves as a dispersing agent causing the intercalation of rubber chains into the silicate galleries and providing substantially improved clay dispersion and they have found that both PEG and MMT affect the enhancement of mechanical properties.

Like MMT, kaolinite also has been extensively used in the industry from long back, as a reinforcing additive because of its unique surface property.

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Braggs et al. [4] modified kaolin clay with chloro dimethyl octadecylsilane and studied its electrochemical property before and after modification. The electrochemical and rheological data obtained provide strong evidence for the presence of reactive hydroxyl groups on its surface and the interaction of these groups with modifiers. Menon [5] and Menon et al. [6] modified kaolin clay using PCNSL (phosphorylated derivative of cashew nut shell liquid) and studied its effect as a multifunctional additive for composites. A typical semi-efficient NR vulcanization system modified with bromo derivative of PCNSL shows improvement in the flame retardancy of vulcanizates by the progressive increase in limiting oxygen index. The self-adhesion strength of NR compounds modified with PCNSL studied, with respect to contact time, contact pressure, storage time and concentration of PCNSL, from the 180° peel test showed a maximum at 10 phr of PCNSL due to the interfacial diffusion property. Rheological properties, stress relaxation properties, cure characteristics and physico-mechanical properties of NR modified with PCNSL prepolymer have been studied by Menon et al. [7-10].

Recently Sreelekshmi et al. [11] used PCNSL modified kaolin as hybrid filler along with silica in NR and its blend composites with BR (polybutadiene rubber). The detailed characterization using TGA (thermogravimetric analysis), FTIR (Fourier transform infrared spectroscopy), TEM (transmission electron microscope), SEM (scanning electron microscope) and XRD (X-ray diffraction) shows that PCNSL could act as a coupling agent and compatibilizer between kaolin and rubber. Peter et al. [12] synthesized NR composites containing modified kaolin filler and they obtained improved physico-mechanical properties by the load of 8 phr of PCNSL modified kaolin. The present paper describes the specific property enhancement obtained while adding solvent treated PCNSL and the sodium salt of PCNSL in single NR (natural rubber) and its blend vulcanizate, which were

compared with the SRSO (sodium salt of rubber seed oil) and commercially available cloisite added composite.

## 2. Materials and Methods

### 2.1 Materials

BCK (best coated grade kaolin) (Cation Exchange Capacity 2.90 meq NH<sub>3</sub>/100 g; surface area 14.30 m<sup>2</sup>/g, particle size 1,112 nm) was supplied by M/s. English India Clays, Ltd. (EICL), Thiruvananthapuram, India. Laboratory grade (Sigma Aldrich) NaOH and hydrazine hydrate (HH) were used. Commercial grade of RSO (saponification value 202.9 mg KOH/g; iodine value 136.2 g I<sub>2</sub>/100 g) was purchased from M/s. Murugesan & Sons, Virudhunagar, Tamilnadu, India. CNSL (cashew nut shell liquid) was obtained from M/s. Adarsh Cashews, Sanoor, India. NR (grade, Ribbed Smoked Sheets, RSS-5) and synthetic rubbers such as BR and NBR (nitrile rubber) were purchased from the local market. Commercial grades of rubber chemicals such as zinc oxide (White seal; ACPL-P999), sulfur (“Rub-O-Sulf”), mercaptobenzothiazole (MBT, “PILCURE”) and stearic acid (“Lubstric”; Godrej Industries Ltd.) were obtained from M/s. Ceyenar Chemicals, Kottayam, India.

### 2.2 Organo-Modification of Kaolin

PCNSL was synthesized by the phosphorylation of CNSL at 180 °C according to a patented procedure developed by Pillai et al. The organo-modification of kaolin with PCNSL was done either in two methods. Like SRSO, PCNSL was used to prepare its sodium salt and the salt is used for the intercalation process. A sodium ethanoate solution is used for the preparation of PCNSL salt. First PCNSL is dissolved in ethanol and after completing the solvation, add prepared NaOH solution and continue the mechanical stirring for a period of 48 h. In another method PCNSL was used as such for the intercalation, in presence of

suitable solvent. Thoroughly dissolved solution of PCNSL in toluene was used to modify kaolin after keeping under stirring in a mechanical stirrer (REMI Motor) at 2,000 rpm speed for a period of 48 h. Weighed amount of kaolin is added in 5% and 3.75% solution of PCNSL in toluene in separate reaction vessel and stirred separately. The stirred solution is filtered under vacuum filtration, dried, powdered and labeled as PBTs. Such prepared solution is again vacuum filtered by washing with alkaline solution for 5 times. A volume of 20 mL of 1 N ammonia solution is used for each washing and the sample is dried and labeled as PBTA. Organomodification of kaolin with SRSO was detailed in our previous published paper [13].

**2.3 Compounding of Vulcanizates**

Nanocomposites based on single and blend vulcanizates containing modified and unmodified filler were mixed on a laboratory size: open two roll mixing mill (roll size: 6" × 12", model-Ravi

Engineering Works, New Delhi) at a friction ratio of 1:1.05, nip gap of 0.5 mm and at room temperature as per ASTM D 3182-89 (2011). The mixed, rolled stock was homogenized by passing endwise 6 times. The test specimens were prepared by compression molding at 150 °C, 70 kg/cm<sup>2</sup> for 5 min on an electrically heated hydraulic press (model-INDUDYOG, New Delhi). The formulation of compounds expressed as parts per hundred of rubber (phr) is given in Tables 1-3.

**2.4 Analytical Techniques Used for the Characterization of Kaolin and Vulcanizates**

Powder x-ray diffraction measurements of cloisite, unmodified and organomodified kaolins were carried out on a XEUSS SAXS/WAXS system with Fit 2D software using a Genix micro source (Xenocs) operated at 50 kV and 0.3 mA with Cu K $\alpha$  (1.5406 Å) radiation. Silver behenate was used for distance calibration from sample holder to detector and the optimized distance was 221.75 mm. To get well refined

**Table 1 Composition of NR/NBR blend vulvanizates with varying filler.**

Sample code	NR	NBR	Filler (4 phr)
NR 0	100		0
NR PBT	100		10 PBT
NR PBTA	100		10 PBTA
NBR* PBT	80	20	10 PBT
NBR* PBTA	80	20	10 PBTA
NR C30B	100		C30B
NBR* C30B	80	20	C30B
NR srsok	100		srsok
NBR* srsok	80	20	srsok
Base mix	ZnO-5, SA-2, MBT-2, S-2		

\* NBR-NR/NBR blend.

**Table 2 Composition of vulvanizates with varying filler.**

Sample code	BCK	PCNSL	10 PBTA*
NP 2	4.168	2.095	
NP 4	4.124	4.173	
NP 6	4.13	6.083	
NR 2			2.018
NR 4			4.013
NR 6			6.017
NR 8			8.013
Base mix	NR-100, ZnO-5, SA-2, MBT-2, S-2		

\* Alkali washed 10% PBT.

**Table 3** Composition of NR/BR blend vulcanizates with varying rubber.

Sample code	NR	BR
N100	100	0
N80 B20	80	20
N50 B50	50	50
N20 B80	20	80
B100	0	100
Base mix	ZnO-5, SA-2, MBT-2, S-2, PBTA 10*-4	

\* Alkali washed 10% PBT.

spectrum, samples were exposed to x-ray for 10 min. All the measurements were done in transmission mode between a range of  $2\theta$  ( $3^\circ$ - $40^\circ$ ). Functional group analysis of PCNSL, unmodified and modified kaolins were done on an FTIR spectrometer (Perkin Elmer Spectrum II) under mid IR spectral range,  $400$ - $4,000$   $\text{cm}^{-1}$ , using KBr as the reference sample. The sample along with KBr was ground well; a transparent pellet was made and characterized under IR. All spectra were corrected for the presence of moisture and carbon dioxide in the optical path. Molecular mass of the samples was confirmed with JEOL JM AX 505 HA mass spectrometer performing fast atom bombardment for producing molecular ions, using suitable solvent in which the sample is completely dissolvable.

Fracture behavior of composites was studied using a scanning electron microscope (ZEISS, EVO 18 special edition system) operated at 20 kV. The fracture ends of specimens were mounted on aluminum stubs and gold coated to avoid electrical charging during examination. The micrographs were obtained at magnifications ranging from 500 to 20,000. Thermal analysis of pristine and modified kaolins was done in Perkin Elmer, Pyris diamond TG/DTA system by heating the sample from room temperature to  $1,050$   $^\circ\text{C}$  at a progressing rate of  $20$   $^\circ\text{C}/\text{min}$  under nitrogen atmosphere. Thermal degradation measurements of vulcanizates were done in Perkin Elmer, Pyris diamond TG/DTA system. The TGA apparatus permits continuous weighing and recording of changes in weight of a reaction system on heating

from room temperature to  $700$   $^\circ\text{C}$  at a rate of  $20$   $^\circ\text{C}/\text{min}$  in nitrogen atmosphere. Swelling study of the samples was done on the basis of ASTM D 471-97 (1998). A test piece of known weight was cut from the press-molded rubber sample. The sample was mesmerized in pure toluene at room temperature in order to allow the swelling to reach diffusion equilibrium. At the end of this period the test piece was removed, the loose solvent rapidly removed by blotting with filter paper and the swollen weight immediately measured. The CLD is calculated using Flory-Rehner equation  $V_r = [(D - FT) / \rho_r] / \{[(D - FT) / \rho_r] + [A_0 \times \rho_s]\}$ , where D—deswollen weight, F—fraction of insoluble components, T—initial weight,  $\rho_s$ —density of solvent,  $\rho_r$ —density of vulcanizate and  $A_0$ —difference of final weight and initial weight. DMA measurements were carried out on strips with a dimension of 4 mm width, 20 mm length and 0.2 mm thickness, over a temperature range of  $-90$  to  $50^\circ\text{C}$  at a frequency of 1 Hz under tension mode on TRITEC 2000B instrument. The tensile and tear properties of the vulcanizates were measured on a Universal Testing Machine (Instron 3345) as per ASTM D 412 and ASTM D624-86 respectively, at a cross head speed of 500 mm/min.

### 3. Results and Discussion

#### 3.1 Organo-Modification of Kaolin with SRSO and PCNSL

The SRSO intercalated kaolin was characterized and analyzed in detail and is published in our previous paper [13]. Infrared absorption spectra of sodium salt

of PCNSL have been studied in the region of 500 to 4,000  $\text{cm}^{-1}$  and the typical IR spectra are shown in Fig. 1. Spectra were analyzed to determine the relative intensity of the IR bands responsible for the different phosphate units. As seen from Fig. 1, the frequencies of predominant absorption peaks are characterized by: a broad peak near 3,000  $\text{cm}^{-1}$ , a weak peak around 2,300  $\text{cm}^{-1}$ , doublets in the region 1,500  $\text{cm}^{-1}$  and a sharp peak around 1,000  $\text{cm}^{-1}$ . The sharp doublet and a broad peak around 3,000 to 2,800  $\text{cm}^{-1}$  in the PCNSL spectrum is because of the stretching of P-OH bond, which becomes a single broad peak in the PCNSL sodium salt spectrum at 3,300  $\text{cm}^{-1}$ . The broad spectrum indicates the presence of organic moiety with in PCNSL, since the peak is of P-O-metal

stretching. Also the small broad peak present at around 2,300  $\text{cm}^{-1}$  shows the presence of organic content within the starting compound. The doublet found at 1,455 and 1,624  $\text{cm}^{-1}$  in the PCNSL spectrum is compiled to a single peak and a new peak transmits at 1,380  $\text{cm}^{-1}$ , in the case of sodium salt and is because of the bending of P-O-metal bond. A sharp peak found at 538  $\text{cm}^{-1}$  indicates the presence of metal, thus confirming the conversion of PCNSL to its sodium salt.

The molecular mass calculated for PCNSL and its sodium salt using MALDI is given in Fig. 2. Chemically the molecular mass of PCNSL is 379, which is accurately obtained from mass spectrum. While successively converting PCNSL to its sodium

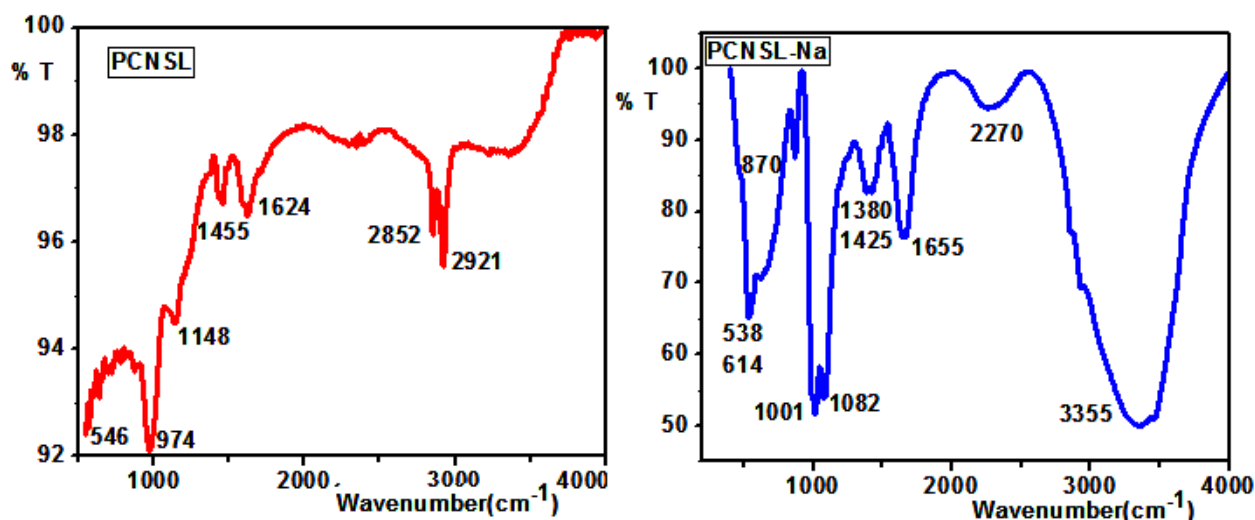


Fig. 1 FTIR spectrum of PCNSL and sodium salt of PCNSL.

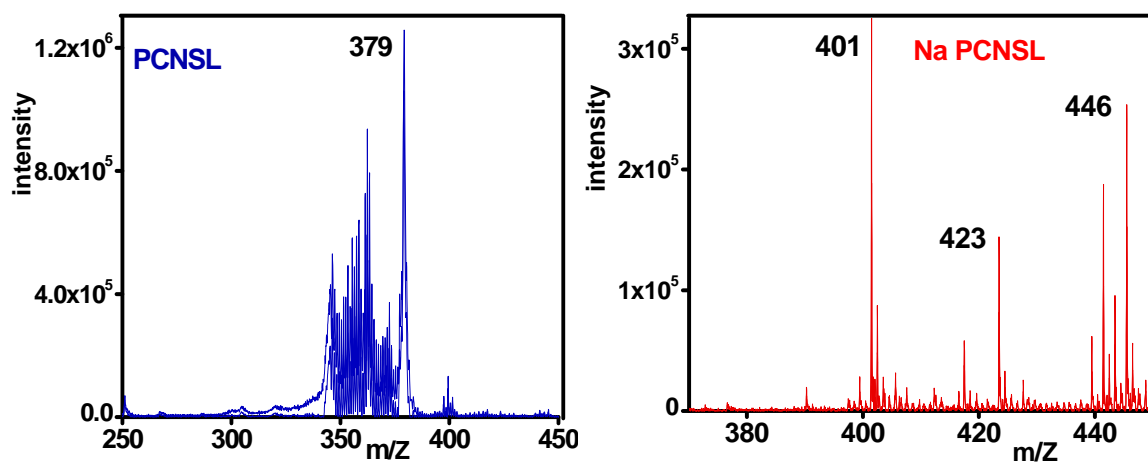


Fig. 2 MALDI of PCNSL and sodium salt of PCNSL.

salt, the molecular mass increases. While one OH is converting to salt, (M/Z) is increased to 401, and if two OHs are converted, then the M/Z increases to 423 and so on. From this we could confirm the metallic nature of PCNSL.

The FTIR spectrum of “solvent treated PCNSL along with kaolin” by varying concentration is shown in Fig. 3. For PCNSL the characteristic peaks are transmitted at 2,852 and 2,921  $\text{cm}^{-1}$ , which corresponds to P-OH stretching vibration, and for kaolin two strong sharp peaks transmitted at 3,620  $\text{cm}^{-1}$  and 3,694  $\text{cm}^{-1}$ , which are characteristics of inner hydroxyl and outer surface hydroxyl vibration respectively. But for toluene treated PCNSL along with kaolin which are labeled as PBT, both the characteristic peaks correspond to kaolin and PCNSL is transmitted in each PBT. As PCNSL and kaolin reacted to form PBTs, the intensity of both peaks at around 2,900  $\text{cm}^{-1}$  and 3,600  $\text{cm}^{-1}$  decreases and shows variation in percentage transmittance. The peaks at around 1,500  $\text{cm}^{-1}$  are because of the transmission due to aliphatic stretching vibration. In the case of PBTs, the transmittance of peaks at 1,500

$\text{cm}^{-1}$ , shows change with variation in concentration. For PBT 10, it is found with highest transmittance because of more layer dispersion.

### 3.2 Comparison of SRSO Intercalated BCK with PCNSL Modified BCK and Cloisite

#### 3.2.1 Thermal Stability

The TGA measurements done for the SRSO modified kaolin have been compared with the values corresponding to PCNSL modified kaolin and commercial cloisite 30 B, which is plotted in Fig. 4. Thermal analysis is done within a temperature range of 0 °C to 800 °C, and  $t_{10}$  is calculated for each sample by doing the closed scanning between a temperature range of 250 °C to 550 °C and the data are given in Table 4. It is found that cloisite is least thermally stable as compared to others, and while modification the PCNSL modified samples are more thermally stable than SRSO modified one. Since the SRSO with 18 carbon atoms side chain undergoes earlier decomposition than PCNSL with 15 carbon atoms side chain, the thermal stability decreases and highly stable systems can use the PCNSL modified one.

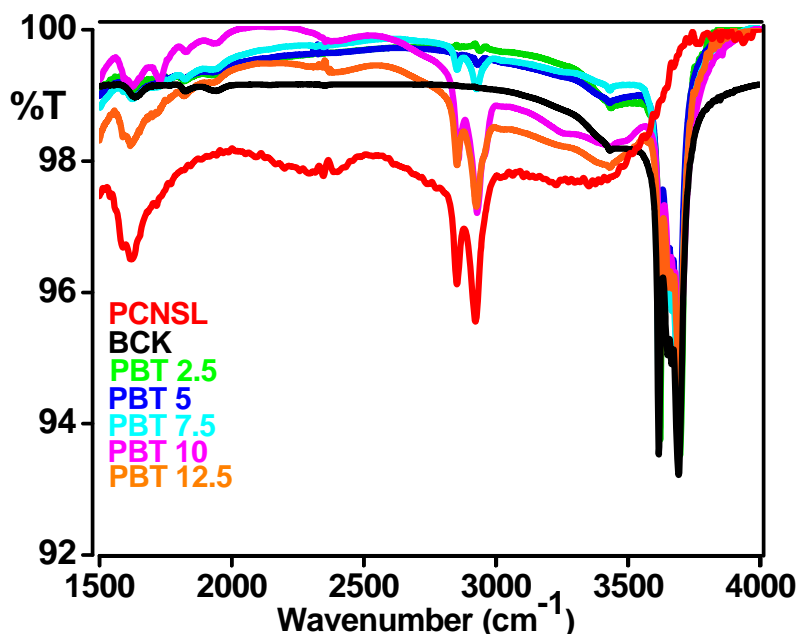


Fig. 3 FTIR spectrum of PCNSL and solvent treated PCNSL.

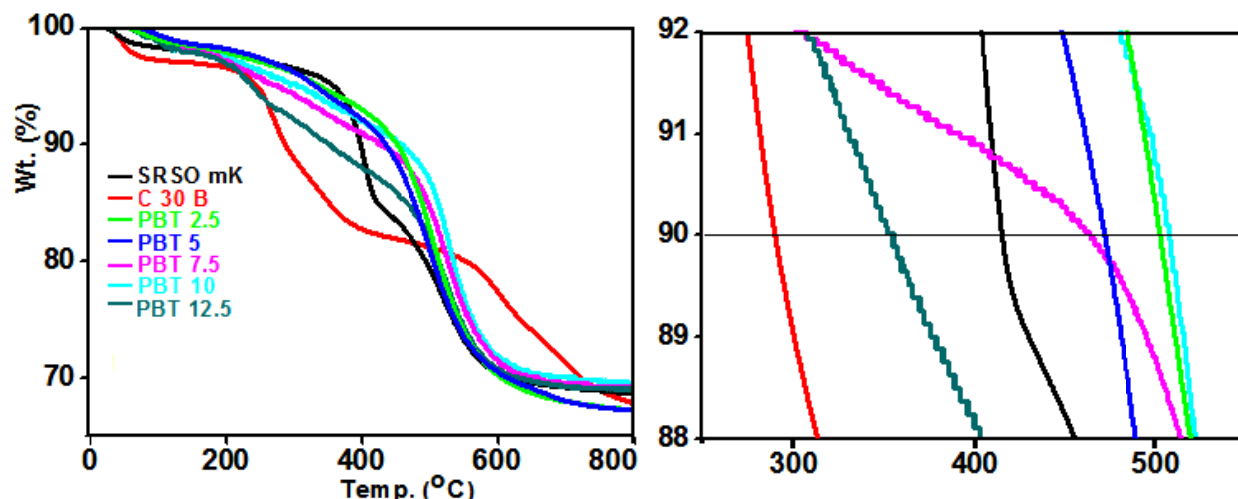


Fig. 4 TGA of cloisite, PCNSL modified and SRSO modified kaolin as filler.

Table 4 Decomposition temperature and weight loss of unmodified and modified fillers.

Sample code	$T_{10}$ (°C)*	Total weight loss (%)
SRSO BCK	415	23.3
Cloisite 30b	290	32.5
PBT 2.5	502	19.1
PBT 5	471	23.6
PBT 7.5	463	38.8
PBT 10	508	24.9
PBT 12.5	354	36.1

\* Temperature for 10% decomposition.

Table 5 DLS data of cloisite, unmodified and modified kaolins.

Sample	Diameter (nm)	Intensity (%)	Width (nm)
K*	1,112	69	378
K-SRSO	352	88	21
PBT 10	767	94	168
PBTA 10	759	92	181
Cloisite 30b	< 2 $\mu$	10	-
	< 6 $\mu$	50	-
	< 13 $\mu$	90	-

\* Kaolin.

While comparing each PBT, it is found that PBT 10 is more thermally stable, since the PCNSL included between the kaolin layers at that concentration is strongly cross-linked to each other, and if further increasing the PCNSL concentration, the thermal stability is decreasing.

### 3.2.2 Particle Size Measurement from DLS

The particle sizes of kaolin, cloisite and modified kaolin were measured on the basis of dynamic light scattering in water solvent, and the diameters obtained

in nanometer were tabulated and given in Table 5. While comparing the particle size, kaolin and cloisite are micron in size, however modified kaolin is nanometer in size. In the modification process, SRSO causes more penetration between the layers of kaolin than PCNSL, however whilst comparing the PBT 10 with its alkaline washed form, both are showing nearby rate of intercalation. By the SRSO modification, the diameter of kaolin platelets was reduced to 352 nm along with a width of 21 nm.

While modification, cations can absorb on the surface of clay layers which results in a more positive surface charge and enhances the repulsive force between clay particles and favors the dispersion state of clay. Thus from the DLS data obtained, it is found that SRSO causes more intercalation between kaolin platelets as compared to PCNSL modification, since it possess up to 18 carbon atoms in the side chain than the PCNSL with 15 carbon atoms side chain.

### 3.2.3 Interlayer Expansion

The XRD spectrum of SRSO modified kaolin, PCNSL modified kaolin and cloisite are given in Fig. 5. The highest *d* spacing is obtained with SRSO modified one at 4.67 nm while compared to other, which indicates that the rate of intercalation of SRSO is stronger than PCNSL. The highest degree of SRSO intercalation on kaolin is associated with the longest side chain present in that as compared to PCNSL. But within PCNSL, the solvent treated kaolin (both PBT10 and PBTA 10) does not give any intercalation and only the sodium salt of PCNSL is giving intercalation and increases the *d* spacing to 1.12 nm. For the commercial cloisite, the interlayer spacing is 1.85 nm, which shows that the SRSO modified kaolin is more dispersed one than commercially available cloisite. Hence the SRSO modified kaolin can be

suitably used for particular applications.

### 3.3 Physico-Mechanical Properties of Vulcanizates

The kaolin clay duly intercalated with SRSO and PCNSL was used as reinforcing filler for rubber and the vulcanizates were properly masticated out. Both single and blend rubber compositions were prepared by varying either rubber concentration or by varying filler concentration. The NR/BR and NR/NBR blends were prepared and characterized. The vulcanizates such mixed were cured under optimum cure time and were characterized further and compared with vulcanizates containing commercial filler cloisite. Within solvent treated PBTs, the one obtained with highest dispersion and thermal stability, was used for mixing with rubber, as a filler and that is PBT 10. The alkaline washed PBT 10 was also used in rubber in order to do a comparison, which is labeled as PBTA 10.

#### 3.3.1 Cross Link Density from Flory-Rehner Equation

The cross link density of single and blend vulcanizates with varying concentration of filler and rubber was calculated using toluene solvent and is given in Table 6 and Fig. 6. As the rubber unsaturation and filler network are more bonded with each other,

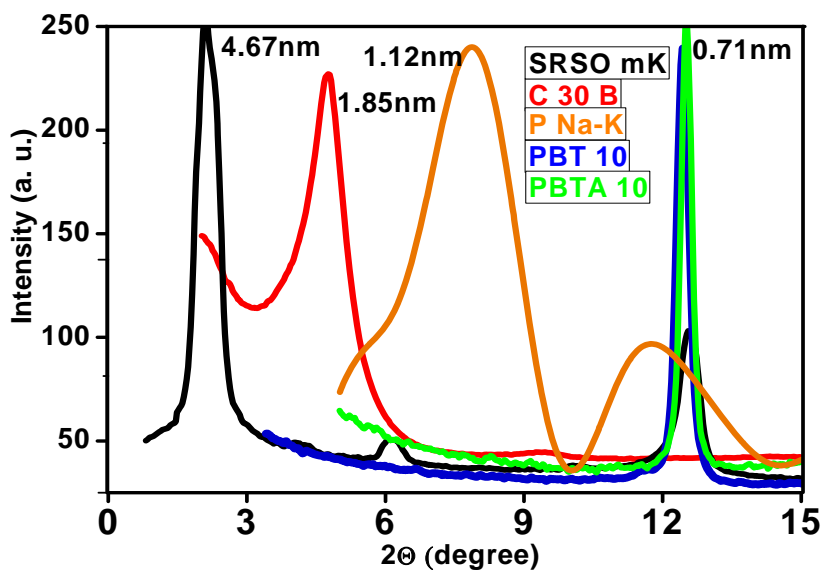


Fig. 5 XRD of cloisite, PCNSL modified and SRSO modified kaolin as filler.



Table 6 CLD index of NR-NBR blend vulcanizates with varying filler.

Sample	CLD
NR 0*	0.165
NR srsoK	0.192
NBR srsoK	0.188
NR Cloisite	0.156
NBR Cloisite	0.157
NR PBT	0.135
NR PBTA	0.174
NBR PBT	0.172
NBR PBTA	0.183

\* Nonfiller.

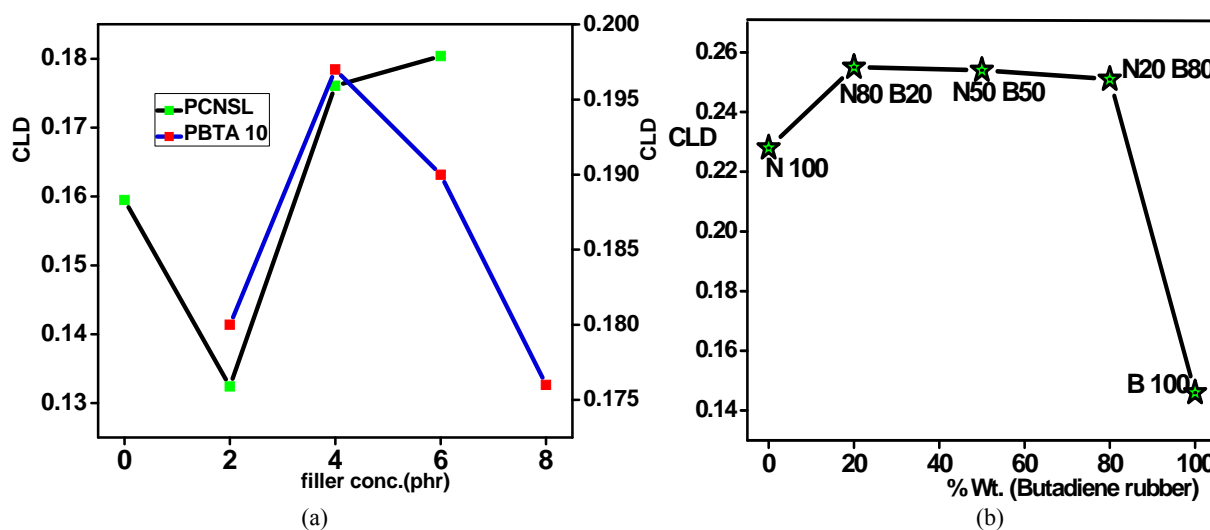


Fig. 6 CLD of vulcanizates varying filler (a) and blend composition (b).

the CLD is increasing, and it may vary with nature of filler, concentration of filler, concentration of rubber, alkaline/acid nature of modifier etc. From Table 6, it is found that as filler is adding to vulcanizate, its cross link capability is increasing, and with nature of filler it shows variation in CLD. Among cloisite and modified filler, the SRSO modified filler mixed vulcanizate is having highest CLD and cloisite mixed vulcanizate possesses only lowest CLD. While comparing single NR and blend NR/NBR rubber vulcanizate, it is found to be the blend having highest CLD because of strong unsaturation sites and polar nature of NBR available to getting bonded with filler.

From Fig. 6a, it is found that as the concentration of PCNSL is increasing, the CLD also increases since the side chain of PCNSL possesses strong unsaturation

sites, but if the concentration of alkaline washed toluene treated PCNSL modified kaolin (PBTA 10) is increasing, the high CLD is achieved with 4 phr of filler and after the addition it is decreasing. At higher concentration, the alkaline nature may cause decrosslinking. The PBTA 10 is used as a filler in weight percentage of 4 phr, for the preparation of vulcanizates with varying NR-BR blend ratio. The variation in CLD for the NR/BR blend is shown in Fig. 6b. It is found that for the pure BR vulcanizate, the cross link ability is very few as compared to other, even lower than the pure NR vulcanizate. The crosslink nature of vucanizates can be improved by blending different rubbers and varying the rubber concentration. From Fig. 6b, it is found that the blend ratio with NR-80 & BR-20 possesses high CLD

among other.

3.3.2 Modulus, Strength & Elongation

The tensile strength, elongation and modulus calculated using UTM for the aged and unaged vulcanizates with varying concentration of filler and rubber were given in Tables 7-10. Tensile strength gives the indication of the resistance of a material to breaking under tension; however elongation at break expresses the capability of a material to resist the changes of shape without crack formation. Usually modulus describes the elasticity or the tendency of an object to deform along an axis when opposing forces are applied along that axis.

From Table 7, it is found that while the composites vary, PCNSL concentration, the modulus, tensile strength and elongation are increased during aging for each sample. During thermal aging the acidic nature of PCNSL and kaolin cause growth of bonding between unsaturation sites of rubber and filler. While

comparing between PCNSL concentration, at 4 phr the maximum modulus, elongation and strength are observed. The UTM data of vulcanizates with varying PBTA 10 concentration are given in Table 8. It is found that the vulcanizate with 4 phr of PBTA 10 is having highest modulus, elongation and strength and during aging the properties are increased for each sample. Compared to 48 h aging, the vulcanizates aged at 96 h are possessing maximum values because the instructure PCNSL alkaline nature and further the washed alkaline content enhances the stability of crosslinking.

From Table 9, while comparing the UTM values of NR/BR blend rubber vulcanizates, it is found that among blends, the best properties are achieved with NR-80 and BR-20 composition than other. Further increasing the concentration of BR, the strength of vulcanizate is decreasing, since the pristine BR mix is very weak as compared to pristine NR. So for a blend

**Table 7 UTM data of aged & unaged vulcanizates with varying PCNSL as filler.**

Sample	Specimen	Modulus 100% (Mpa)	Modulus 300% (Mpa)	Tensile str. (MPa)	Elong @ brk (%)
NP 2	Unaged	5.9	25.7	8.71	9,060
	Aged 48 h	6.5	31.8	10.55	7,744
	Aged 96 h	8.2	38.5	10.38	8,840
NP 4	Unaged	6.3	26.8	10.94	9,940
	Aged 48 h	8.3	38.2	11.46	8,660
	Aged 96 h	8.2	38	11.52	8,820
NP 6	Unaged	6.2	27.7	10.55	9,440
	Aged 48 h	7.7	37.5	10.79	5,800
	Aged 96 h	7.7	37.3	11.10	8,280

**Table 8 UTM data of aged & unaged vulcanizates with varying PBTA 10 as filler.**

Sample	Specimen	Modulus 100% (Mpa)	Modulus 300% (Mpa)	Tensile str. (MPa)	Elong @ brk (%)
NR 2	Unaged	8.2	34	6.8	7,024
	Aged 48 h	7.8	28.8	10.71	9,280
	Aged 96 h	10.2	42.2	11.38	9,300
NR 4	Unaged	8.3	35	10.85	8,310
	Aged 48 h	9.8	46	12.26	9,340
	Aged 96 h	10.4	47.2	12.45	9,360
NR 6	Unaged	8.5	34.5	9.9	7,880
	Aged 48 h	7.4	25.4	10.31	8,160
	Aged 96 h	9.8	45	10.01	9,060
NR 8	Unaged	7.3	29.2	10.93	7,616
	Aged 48 h	7.6	29.5	9.76	8,560
	Aged 96 h	9.5	44.2	12.47	8,760

**Table 9 UTM datas of NR/ BR blend vulcanizates with varying blend composition.**

Sample	Specimen	Modulus 100% (Mpa)	Modulus 300% (Mpa)	Tensile str. (MPa)	Elong @ brk (%)
N100	Unaged	0.492	0.954	21.711	3,539
	Aged 48 h	0.545	1.058	26.472	3,409
	Aged 96 h	0.527	1.019	19.27	3,084
N80 B20	Unaged	0.848	1.091	19.092	3,131
	Aged 48 h	0.926	1.532	23.326	2,463
	Aged 96 h	0.835	1.366	18.106	3,014
N50 B50	Unaged	0.734	1.07	3.139	1,489
	Aged 48 h	0.627	1.138	3.434	1,500
	Aged 96 h	0.618	1.121	2.494	1,120
N20 B80	Unaged	0.601	1.402	2.45	973
	Aged 48 h	0.709	1.22	2.135	650
	Aged 96 h	0.700	1.21	1.617	455
B100	Unaged	0.579	1.317	1.716	542
	Aged 48 h	0.796	1.398	1.829	548
	Aged 96 h	0.755	1.35	1.643	464

**Table 10 UTM data of NR/ NBR blend vulcanizates with varying filler.**

Sample	Modulus 100% (Mpa)	Modulus 300% (Mpa)	Tensile str. (Mpa)	Elong @ brk (%)
NR PBT	6.00	21.83	7.31	8,980
NBR PBT	7.20	27.3	8.5	8,900
NR PBTA	8.20	33.3	10.86	9,160
NBR PBTA	8.80	34.8	11.46	9,340
NR C30B	6.43	23.78	12.36	3,739
NBR C30B	6.44	25.85	14.73	3,759
NR srsok	8.83	38.88	16.93	6,860
NBR srsok	9.18	41.98	19.52	6,900

composition N80 B20 can be selected for suitable application than any other composition. The UTM data of NR/NBR blend rubber vulcanizates with varying filler are given in Table 10. Similar to cross link density, the NR/NBR blend is having highest strength and modulus than single system because both the rubber will pose some stress against strain. While comparing between filler, SRSO modified filler containing vulcanizate is having higher properties than PCNSL modified and cloisite, because of filler-rubber network stability. Also while comparing between alkaline washed PCNSL modified kaolin and unwashed PCNSL modified kaolin, the vulcanizate with washed filler is cured better and has good properties.

### 3.3.3 Crystallinity and Interlayer Spacing

XRD of NR/BR blend rubber vulcanizates with

varying blend composition, having  $2\theta$  from  $5^\circ$  to  $40^\circ$  and  $2\theta$  from  $9^\circ$  to  $15^\circ$  is plotted in Fig. 7. Since the vulcanizates contain both amorphous rubber and crystalline filler, the corresponding XRD will appear with broad and sharp peaks. For the 1:1 composition, the peak intensity is very less, since the rubbers are equally crosslinked with each other and also with filler. For the 80/20 composition, the filler causes intercalation thereby the base peak at 0.71 nm will shift to higher spacing, however N80 B20 ( $2\theta = 9.8^\circ$ ) composition having highest intensity as compared to N20 B80 ( $2\theta = 10.2^\circ$ ). For the single NR (N 100) and BR (B 100) vulcanizate system, the base peak is scattered at 0.71 nm and no intercalation was observed.

XRD of NR/NBR blend rubber vulcanizates with varying filler composition, is plotted in Fig. 8. Since the

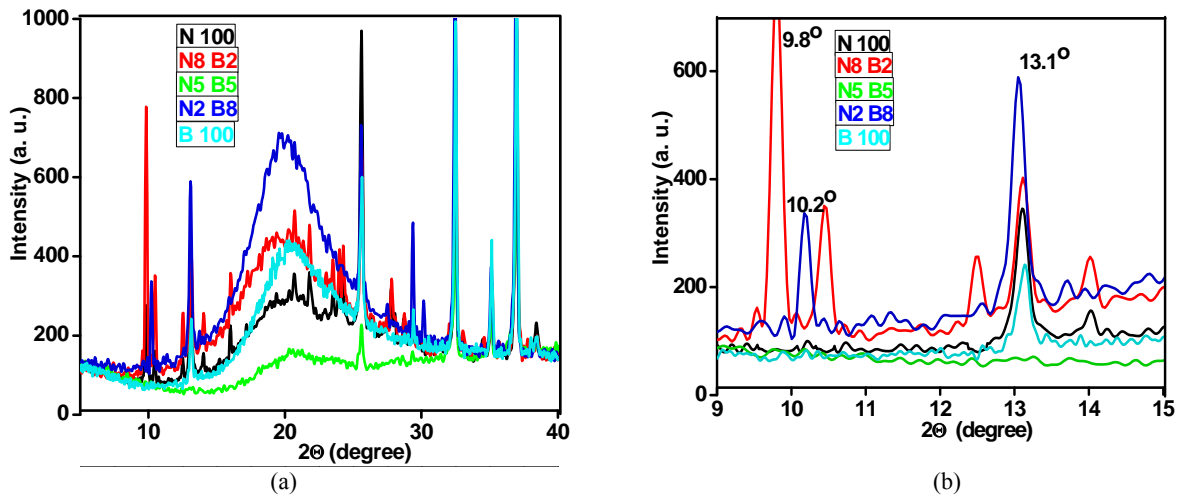


Fig. 7 XRD of NR/BR blend vulcanizates with varying blend composition having 20: (a) 5°-40°; (b) 9°-15°.

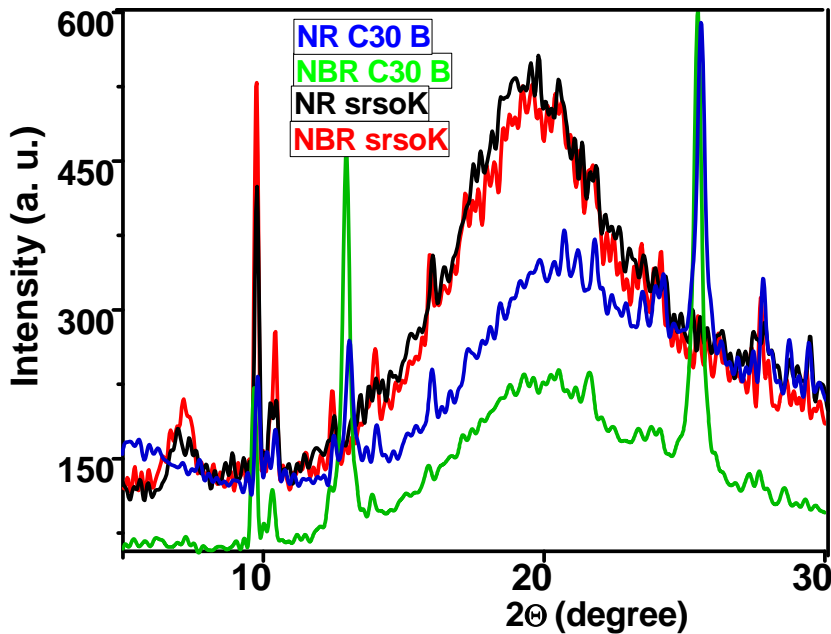


Fig. 8 XRD of NR/NBR blend vulcanizates with cloisite and SRSO modified kaolin as filler.

vulcanizates are having same NR/NBR composition (80/20), the XRD of both the vulcanizate with each filler is scattering at identical  $2\theta$ . But by varying the filler, it is found that for the vulcanizate with SRSO modified kaolin is having higher  $d$  spacing than the vulcanizate with cloisite 30 b.

### 3.3.4 Glass Transition Temperature and Damping Factor

Storage modulus predicts the strength or stiffness of vulcanizate which is calculated by measuring the

strain possess in a sample while applying a stress. Storage modulus of vulcanizates with PCNSL modified and SRSO modified kaolin as filler, is shown in Fig. 9 between temperature ranges of  $-90\text{ }^{\circ}\text{C}$  to  $0\text{ }^{\circ}\text{C}$ . The modulus, glass transition and damping parameters of vulcanizates observed from DMA are given in Table 11. As the stiffness of the vulcanizate increases, the storage modulus ( $E'$ ) also increases, and from the figure it is found that PCNSL modified kaolin with 10% concentration is having higher storage

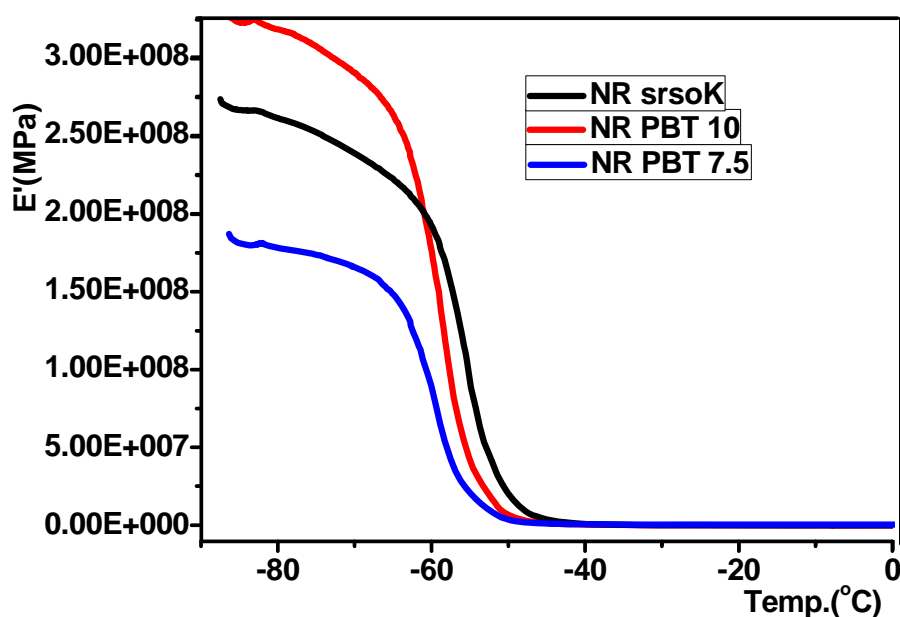


Fig. 9 Storage modulus of vulcanizates with PCNSL and SRSO modified kaolin as filler.

Table 11 DMA data of vulcanizates with PCNSL and SRSO modified kaolin as filler.

Composition	$T_g$ (°C), from $E''$	$T_g$ (°C), from Tan $d$	Tan $d$	$E'$ (S M) (Pa)	$E''$ (L M) (Pa)
NR srsoK	-55.43	-49.18	1.89	2.7289E8	4.8488E7
NR PBT 7.5	-59.54	-48.78	1.92	1.8728E8	6.1161E7
NR PBT 10	-49.40	-45.20	1.72	3.2804E8	3.4454E7

modulus value than a 7.5% concentration PCNSL and SRSO modified kaolin. Loss modulus of vulcanizates with PCNSL modified and SRSO modified kaolin as filler is shown in Fig. 10. As the rubber chains and filler network more cross linked each other, the strength of the vulcanizate will increase, and thus the mobility of molecules within the vulcanizate will decrease. If the chains present in the vulcanizate undergo motion, some energy will lose and that is measured as loss modulus. From the figure it is found that for the PBT 10 filled vulcanizate the loss modulus is lower than the other; however it predicts the strength and mobility of composite.

The damping factor is proportional to the energy loss due to mobility of composite molecules and the tan delta spectrum of vulcanizates is shown in Fig. 11. Tan delta is calculated from the ratio of storage modulus and loss modulus and as the composite

stability increases, the peak height will decrease. From the maximum of peak height, the tan delta value is calculated and the glass transition temperature can be predicted from this. The glass transition temperature ( $T_g$ ) is an indication of transition from glassy to rubbery state, which can either be predicted from the loss modulus or tan delta curve. Generally the  $T_g$  calculated from loss modulus curve will be lower than that calculated from tan delta curve. The glass transition values of vulcanizates are given in Table 11. As the strength of composite increases, the temperature that needs for the transition from glassy to rubbery state also increases, in the sense among three composites the one filled with PBT 10 is having highest  $T_g$ .

### 3.3.5 Thermal Decomposition

TGA plots for the NR/BR blend rubber vulcanizates with varying blend composition and NR/NBR blend

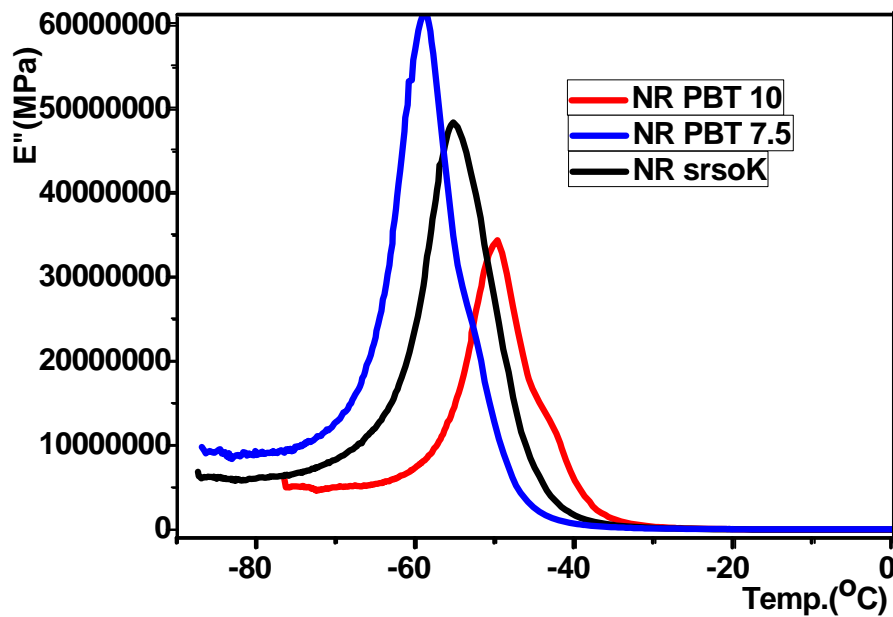


Fig. 10 Loss modulus of vulcanizates with PCNSL and SRSO modified kaolin as filler.

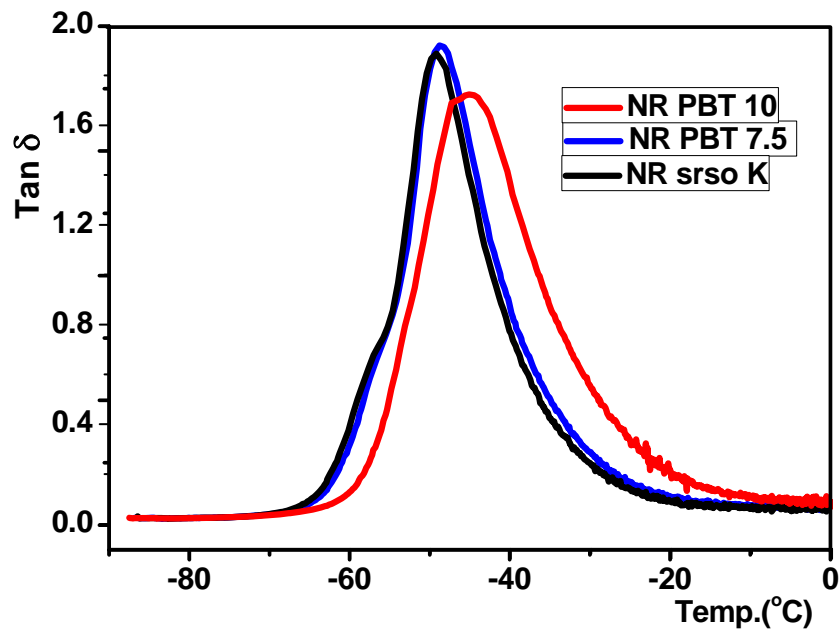


Fig. 11 Tan  $\delta$  of vulcanizates with PCNSL and SRSO modified kaolin as filler.

vulcanizates with varying filler, between a temperature ranges of 0 °C to 700 °C are given in Fig. 12 and the temperature needs for 10% and 50% decomposition are given in Table 12. It is found that the thermal stability is increased with BR concentration and the blend is more stable thermally than the single rubber system. While comparing filler

SRSO modified filler is making NR/NBR blend more stable and for single NR system, PCNSL modified filler is giving more stability.

### 3.3.6 Fracture Morphology

The fracture surface morphology of pristine rubbers such as NR and NBR and NR/NBR blend vulcanizates with SRSO modified filler and cloisite filler is shown

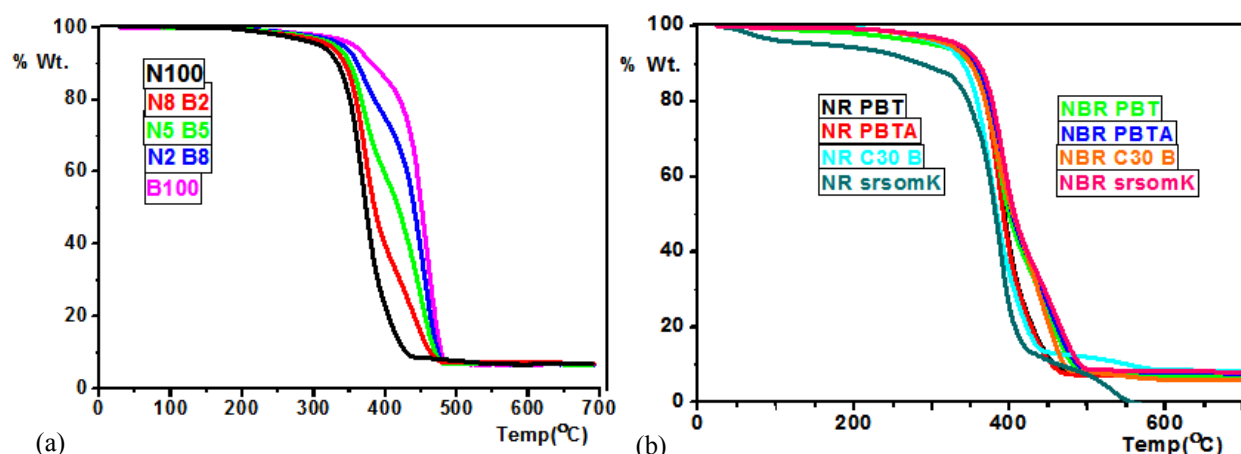


Fig. 12 TGA of NR/BR blend vulcanizates with varying blend composition (a) and NR/NBR blend vulcanizates with varying filler (b).

Table 12  $T_{10}$  values of vulcanizates.

Sample code	$T_{10}$ (°C)
NR PBT	353
NR PBTA	352.6
NBR PBT	350.4
NBR PBTA	358
NR C 30b	342
NBR C 30b	350.7
NR srsomK	287
NBR srsomK	362
N 100	333
N80 B20	342
N50 B50	351
N20 B80	360
B100	381

in Fig. 13. The chain cross linking within the NR network is clear from the figure, however NBR has a polar cross linking surface. While adding SRSO modified kaolin as filler on the vulcanizate, it will give uniform dispersion on the matrix surface than the cloisite filler. The NR vulcanizates with varying concentration of PCNSL filler and the vulcanizates with varying concentration of modified PCNSL as filler are shown in Fig. 14. It is found that as the concentration of PCNSL increases, it will more uniformly distribute on the rubber matrix and the PBT 10 is more uniformly dispersed on the rubber matrix than PBT 7.5, and further the alkaline wash of the PBT 10 filler causes better dispersion and crosslink with the rubber matrix.

The NR/BR blend vulcanizates with varying concentration of rubber containing PBTA 10 as the filler is shown in Fig. 15. The fracture surface of N80 B20 is clearly showing the presence of uniformly distributed hexagonal clay platelets on the matrix surface. The 1:1 combination of NR and BR causes uniform distribution of filler but is agglomerated.

Based on the physico-mechanical studies done for the single and blend rubber vulcanizate, with varying filler, the following Fig. 16 is proposed to explain the mechanism of strain produced on a composite while applying a stress. It is found that when a stress is applied on a composite containing pristine PCNSL as the filler, the vulcanizate will undergo a strain in the same direction of applied stress. The composite will



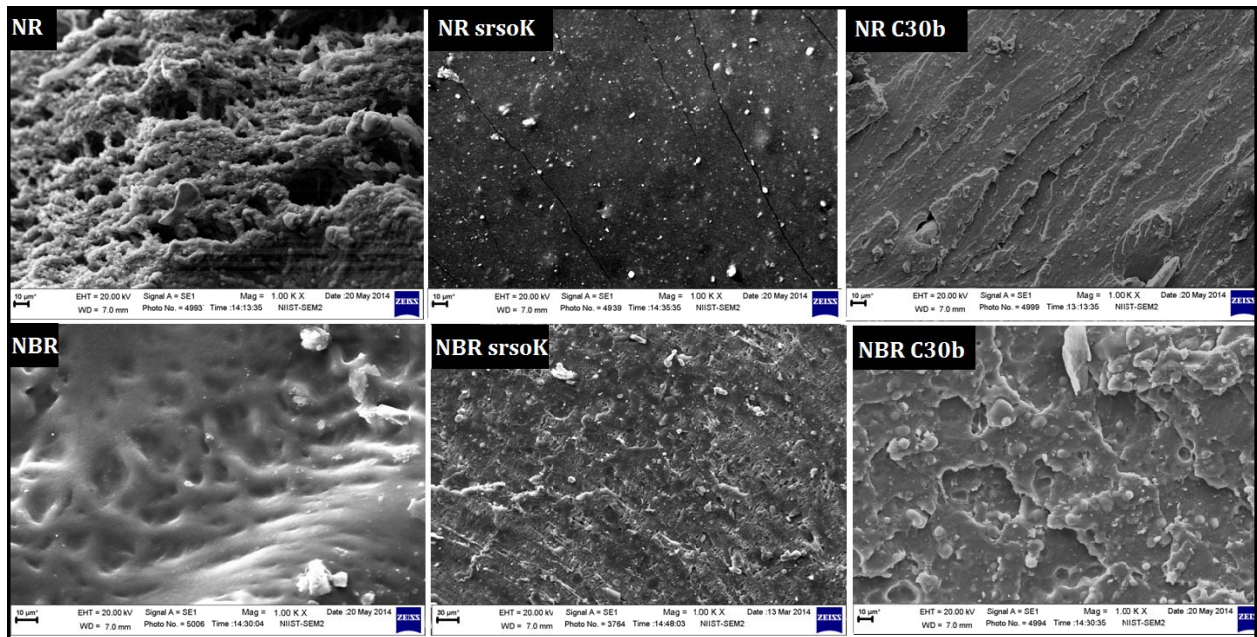


Fig. 13 Fracture SEM of pristine rubber and cured rubber with varying filler.

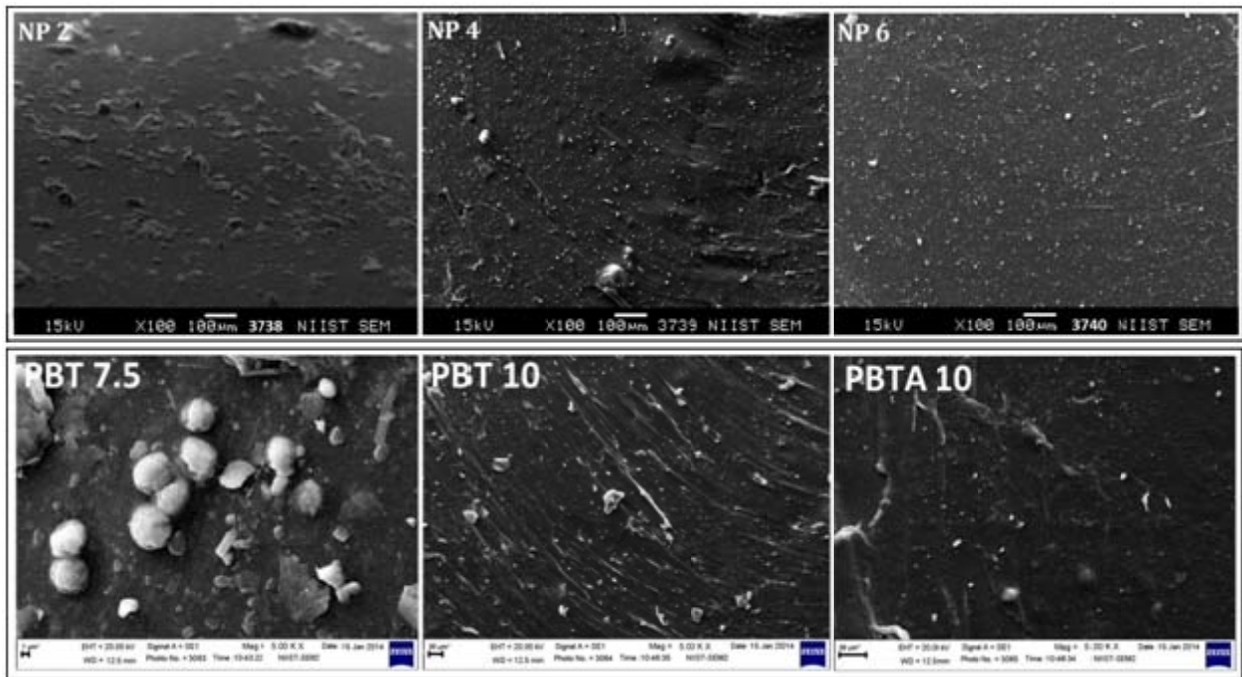


Fig. 14 Fracture SEM of vulcanizates containing PCNSL and PBTs as filler.



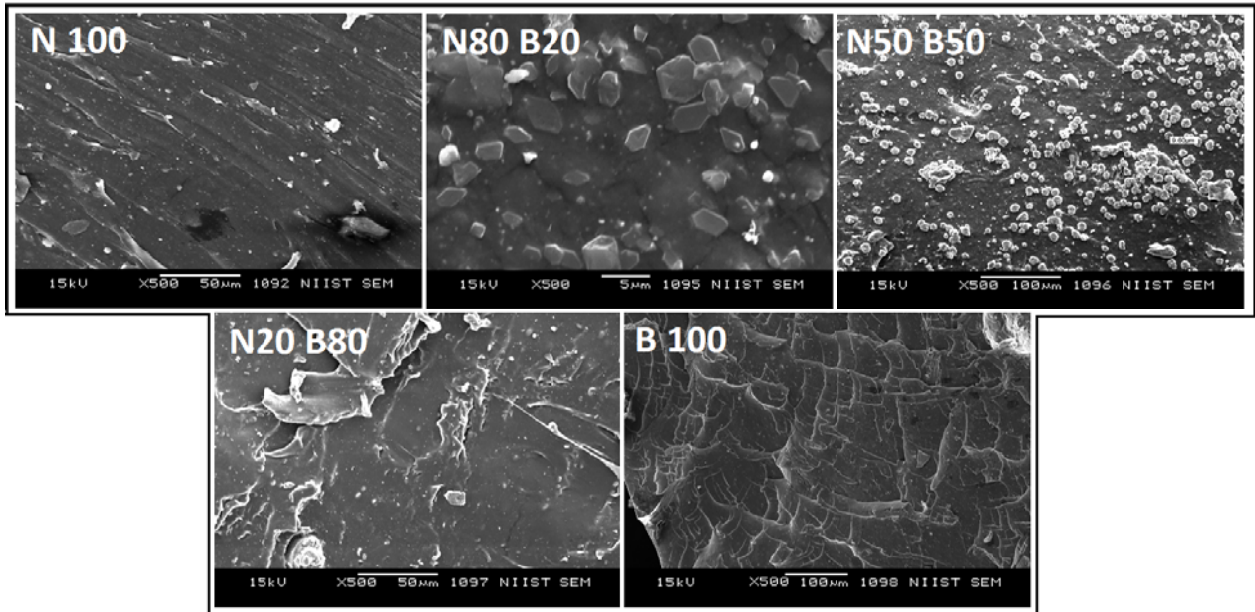


Fig. 15 Fracture SEM of vulcanizates with varying blend composition.

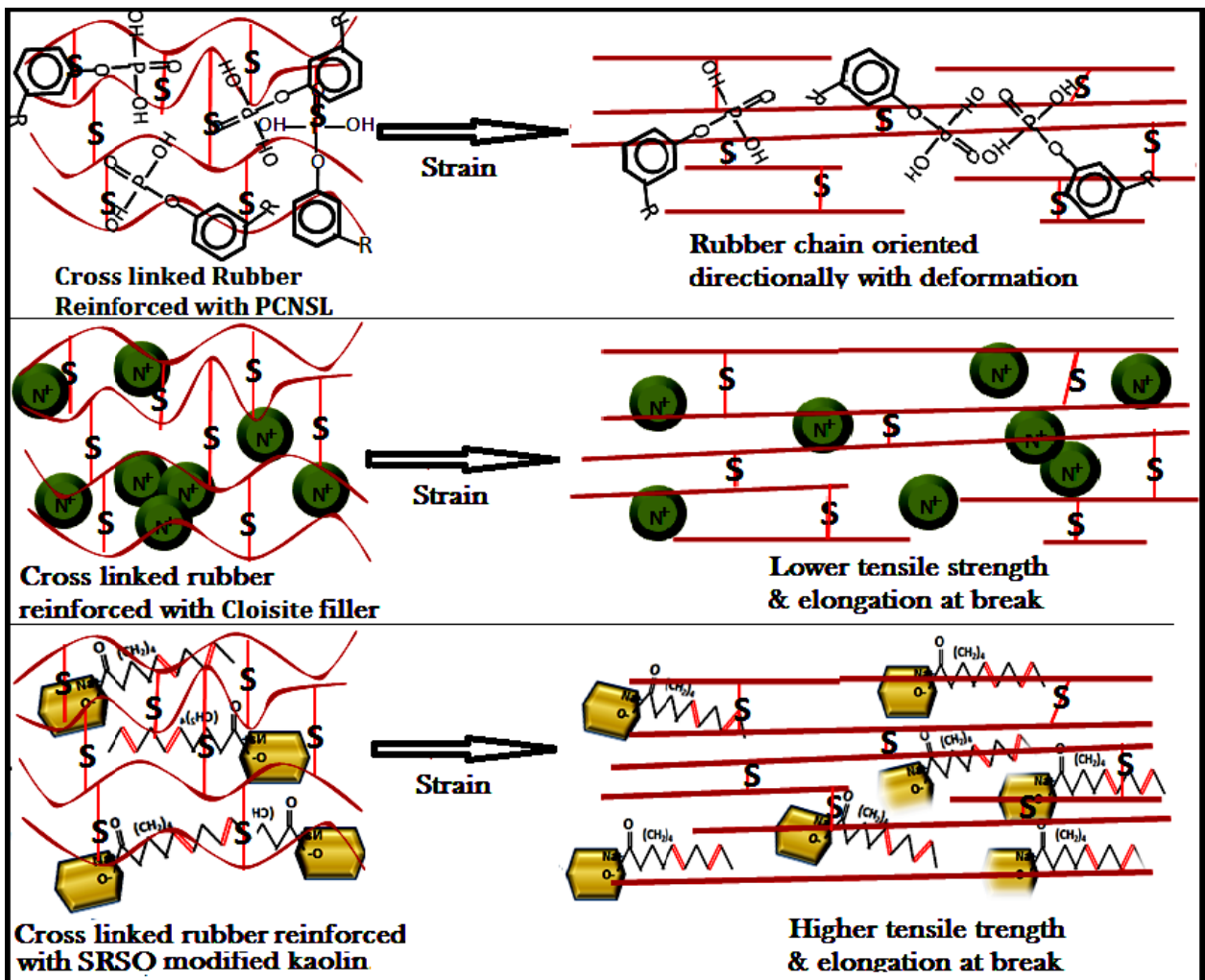


Fig. 16 Rate of stress in a cross linked rubber under strain.

elongate and get deformed. The rate of elongation and deformation of the composite is compared with composites containing cloisite and SRSO modified kaolin as filler. It is found that among the three composites, the rate of deformation is lower in the one filled with modified kaolin as filler, since it is better cross linked with the rubber than the other fillers.

#### 4. Conclusions

The SRSO modified kaolin has been compared with the values corresponding to PCNSL modified kaolin and commercial cloisite 30 B. While comparing the thermal stability it is found that cloisite is least thermally stable, and while modification the PCNSL modified samples are more thermally stable than SRSO modified one. Since the SRSO with 18 carbon atoms side chain undergoes earlier decomposition than PCNSL with 15 carbon atoms side chain, the thermal stability decreases and highly stable systems can use the PCNSL modified one. From the DLS data obtained, it is found that SRSO causes more intercalation between kaolin platelets as compared to PCNSL modification, since it possesses up to 18 carbon atoms in the side chain than the PCNSL with 15 carbon atoms side chain.

The kaolin clay duly intercalated with SRSO and PCNSL was used as reinforcing filler for rubber along with cloisite. Among cloisite and modified filler, the SRSO modified filler mixed vulcanizate is having highest CLD and cloisite mixed vulcanizate is possessing only lowest CLD. While comparing single NR and blend NR/NBR rubber vulcanizate, it is found to be the blend having highest CLD because of strong unsaturation sites and polar nature of NBR available to get bonded with filler. As the concentration of PCNSL is increasing, the CLD also increases since the side chain of PCNSL possesses strong unsaturation sites, but if the concentration of alkaline washed toluene treated PCNSL modified kaolin (PBTA 10) is increasing, the high CLD is achieved with 4 phr of filler and after the addition it is decreasing. At higher

concentration, the alkaline nature may cause decrosslinking. The mechanical properties and post-thermal and acid aging properties of NR blends at different blending ratios are investigated herein. The experimental results show that the tensile strength of NR/BR blends increases with increasing NR content. Studies about aging and mechanical properties of blend rubber vulcanizates with varying composition tell that the tensile strength of NR/BR blends decreases after prolonged ageing.

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