Friction and wear study of NR/SBR blends with Si_3N_4Filler

IOP Conf. Series: Materials Science and Engineering **346** (2018) 012015 doi:10.1088/1757-899X/346/1/012015

Friction and wear study of NR/SBR blends with Si_3N_4 Filler

A GaneshKumar, G Balaganesan *and M S Sivakumar

[1]Department of Applied Mechanics, Indian Institute of Technology Madras, Tamil Nadu, India 600036.*Corresponding author E mail: gbganesh@iitm.ac.in

Abstract. The aim of this paper is to investigate mechanical and frictional properties of natural rubber/styrene butadiene rubber (NR/SBR) blends with and without silicon nitride (Si_3N_4) filler. The rubber is surface modified by silane coupling agent (Si-69) for enhancing hydrophobic property. The Si_3N_4 of percentage 0 1, 3, 5 and 7, is incorporated into NR/SBR rubber compounds with 20% precipitated silica. The specimens with and without fillers are prepared as per standard for tensile and friction testing. Fourier transform infrared (FTIR) spectroscopy test is conducted and it is inferred that the coupling agent is covalently bonded on the surface of Si_3N_4 particles and an organic coating layer is formed. The co-efficient of friction and specific wear rate of NR/SBR blends are examined using an in-house built friction tester in a disc-on-plate (DOP) configuration. The specimens are tested to find coefficient of friction (COF) against steel grip antiskid plate under dry, mud, wet and oil environmental conditions. It is found that the increase in tensile strength and modulus at low percentage of Si3N4 dispersion. It is also observed that increase in sliding friction co-efficient and decrease in wear rate for 1% of Si_3N_4 dispersion in NR/SBR blends. The friction tested surfaces are inspected using Scanning Electron Microscope (SEM) and 3D non contact surface profiler.

1. Introduction

Natural and synthetic rubbers are used in numerous applications in the manufacture of a variety of products. Blending of various types of rubber enhances the properties superior to those of individual rubber. The mechanical properties of NR/SBR blends are expected superior to their individual properties. NR/SBR is a special type of blend which is suitable for variety of applications from race car tyres to footwear. The SBR component enhances toughness and NR provides superior resilience and energy return when they are blended. Many researchers have made attempt to study on frictional properties of rubber that are used as tires, power-transmission belts, soles, floors, and high performance water-lubricated bearings. In such studies, the experimental conditions are considered similar to the functions of the products. For example, the motion between the friction surfaces for tyres or belts is a combination of rolling and sliding. The coefficient of friction and wear rate for visco elastic materials against steel depend mostly on the rubber composition, test duration and test method [1]. Also, coefficient of friction (COF) is affected by contact conditions, such as normal load, contact pressure, sliding speed, energy dissipation. A pin-on-disc apparatus was used to measure COF for wet, dry, and contaminated environmental conditions. The authors concluded that the highest friction coefficients are obtained for dry conditions and when no contaminants were present [2].

Many researchers have studied the friction and wear behaviour of rubber composites. Satoru Maegawa et.al [3] have developed an adhesion friction model to explain the normal load dependence of the coefficient of friction. It is presented by some researchers [4] that increase in precipitated silica

dispersion in rubber compounds showed optimum wear resistance and high COF. Yan-long Tai et.al[5] found that modified Si_3N_4 nano particles enhances physical properties, wear resistance and low rolling resistance to SBR, especially, when the dispersion is 0.5–1.5%.

Rubber composites have received a great deal of attention due to their high performance and wide range of applications, such as seals, automobile tyre treads, hoses, soles and gloves [6]. Generally silica is used as reinforcing filler in non-black rubber products to improve the mechanical, frictional properties and hardness. Several ceramics are used as co-reinforcing filler and provide desired tribological properties, but there are difficulties to get a wide range of applications in rubber. Dispersion of these fillers into rubber matrix is challenge due to strong tendency to reunite due to its high surface energy. Hence surface modification of fillers is essential step to enhance filler dispersion. There are three methods to modify fillers using small molecular coupling agent (SMCA) [7,8], macro molecular coupling agent (MCA) by one step process [9,10] and surface grafting modification(SGM) by two step process. It is found that the mechanical properties of NR/SBR/ Bagasse ash rubber composites are greatly improved by addition of bis[3-(triethoxysilyl)propyl] tetra sulfide (TESPT or Si69). The mechanical property-promoting mechanism is due to carbon–silicon bonding with rubber molecules and siloxane linkages with the bagasse ash silica in the rubber composites. The optimum Si69 is about 2 wt% for treatment of bagasse ash particles which is found to enhance the mechanical properties of NR and SBR. Some researchers [11,12] inferred that this coupling agent(Si-69) covalently bonds on the surface of Si_3N_4 particles and formation as an organic coating layer.

In this study, the mechanical and frictional properties are studied experimentally for NR/SBR blends with and without Si_3N_4. The Si_3N_4 fillers are surface modified by silane coupling agent (Si-69). The Si_3N_4 filler is varied from 1 to 7 weight % of NR/SBR and also rubber compounds are dispersed with 20% precipitated silica. The specimens with and without fillers are prepared as per standard for tensile and friction testing. The effect of filler dispersion is to be studied for these properties. The co-efficient of friction and specific wear rate of NR/SBR blends are examined using an in-house built friction tester in disc-on-plate (DOP) arrangement. The friction tested surfaces are inspected in Scanning Electron Microscope (SEM) and 3D non contact surface profiler.

2. Experimental details

2.1 Raw materials

The NR/SBR blends with and without Si_3N_4 fillers were prepared using elements in table 1. NR and SBR are considered equal amount. The natural rubber grade RMA-1X was supplied by Manasi Traders (Ambattur, Chennai), and styrene–butadiene rubber grade SBR1502 was supplied by Vignesh Chemicals (Ambattur, Chennai). The Si_3N_4 was manufactured and supplied by the Tokuyama Siam Silica Co., Ltd of grade Hi-Sil TOKUSIL 233. The average particle size and specific area of Si_3N_4 are 23-34μm and 0.154 m^2/g, respectively, as measured by a particle size analyser (Laser Particle size analyser, Microtrac S3500,USA). Bis[3-(triethoxysilyl)propyl]tetrasulfide (designated as Si69), $[(C_2H_5O)_3–Si–(CH_2)_3–S_4–(CH_2)_3–Si–(C_2H_5O)_3]$, was supplied by Behn Meyer Chemical (T) Co., Ltd. (Bangkok, Thailand) is used as a chemical coupling agent.

Table 1. Elements used with NR/SBR blends

Material	Content (%)
Zinc oxide(Zno)	5
Stearic acid	2
Marcaptobanzothiozloe(MBT)	0.5
Diphenylguanidine(DPG)	0.2
Sulfur	3.0
Polyethylene glycol	1.0
Precipitated silica	20
Silicone nitride (Si_3N_4)	0,1,3,5 and 7

2.2. Sample preparation

Si_3N_4 fillers of 1%, 3% and 7% percentage were considered for this study. The surface treatment of Si_3N_4 fillers was done using silica coupling agent. The Si_3N_4 filler was dispersed in petroleum ether and coupling agent of about 20% was added into the dispersing flask. Shear mixing was done using shear mixture at 1800 rpm at room temperature for 6 hours and the mixture was kept in the vacuum chamber for 24 hours to remove gas and air bubbles.

The rubber sample preparation was done in three steps namely mastication, compounding and molding processes. In the mastication step, the rubber was masticated on a laboratory two-roll mill for 4 minutes continuously. In the compounding step, the rubber and fillers were compounded with prepared vulcanization chemicals on the two-roll mill for 25 minutes in which sulfur was added after 20 minutes. The compounds were kept at 28°C and 50% relative humidity. The resultant rubber compounds were then compression-molded using a hydraulic press (model MGLP-50AT; Mach Group Co., Ltd., Samut Prakan, Thailand) at 100 bar and 165°C curing temperature in order to produce vulcanized rubber.

2.3. Characterization

The modified and unmodified Si_3N_4 were tested in a FTIR spectrometer to find absorbance and wave number. Curing time and delta torque values of the rubber compounds were measured using an oscillating die rheometer (ODR) and the specimens were tested at a temperature of 165°C. Tensile properties of the rubber vulcanite were tested according to ASTM D412-06c. Figure 2(a) shows the specimens made for tensile testing. Modulus value was predicted at 100% elongation of the specimen. Tests were carried out using universal testing machine (Model Z050TH, Zwick Roell Testing Machines Pvt. Ltd,) at a speed of 500mm/min. A hardness durometer (Shore A, DIN 53-505,Y2K Testing Machines,) was used for hardness test. The test condition was accordance with ASTM D2240-05. The results were averaged from five sets of test data.

2.4 Friction and wear test

The friction test was performed using in-house made experimental setup as illustrated in figure 1. The test specimen of size 80 mm diameter and 4mm thickness was used. The hardness of the rubber is 55 durometer. Figures 2(b) and (c) show the specimens before and after the friction test. The synthetic rubber sample pads were bonded to the bottom of a steel plate using a holding disc. Weights were added to the plate for a total vertical force of 19 kg. The pad/weight arrangement was pulled across the anti skid plate at a constant rate of 50 mm per minute, using hydraulic system. The reactive force was measured with a Syscon make load cell, model number SI - 4000 of capacity 50 kg. The force data was recorded using digital storage oscilloscope. Each sample was tested using a straight pushin dry condition. The coefficient of static friction μ_s is given by,

$$\mu_{s=\frac{F_{smax}}{F_N}} \quad (1)$$

WhereF_{smax}, is maximum static force and F_N is normal force by mass.

The coefficient of kinetic friction is denoted asμ_k, and is expected less than the coefficient of static friction for the same materials.

$$\mu_{k=\frac{F_k}{F_N}} \quad (2)$$

Where,F_k, is force to push the mass during piston movement.

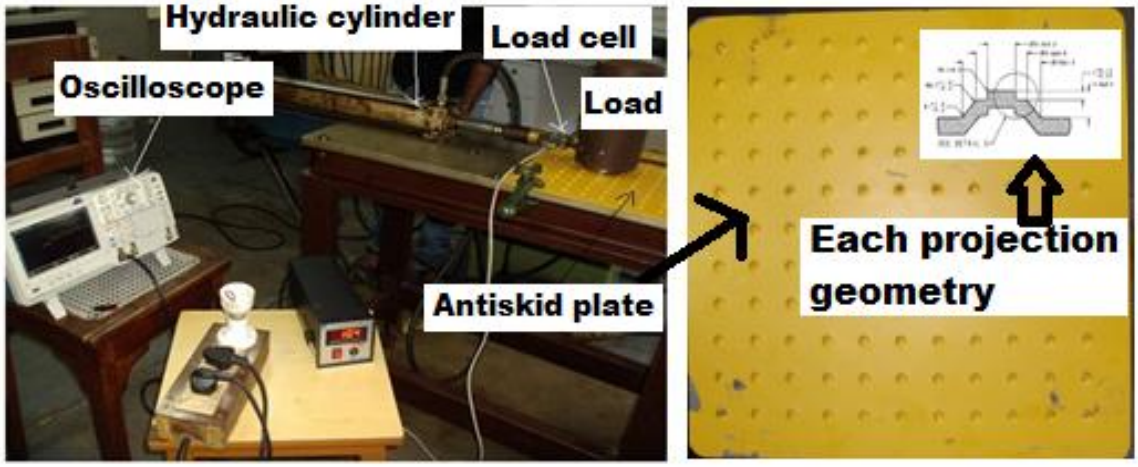

Figure 1. Experimental setup for friction test

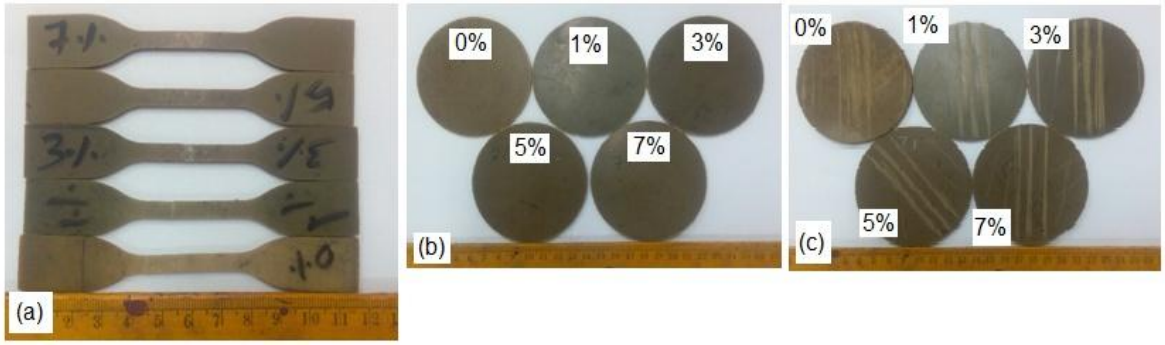

Figure 2. (a) Tensile test Specimens (b) Specimens-before friction testing (c) Friction tested specimens

Thus the coefficients of friction are a measure of the frictional force between a pair of surfaces in contact. Higher the coefficient of friction, higher the frictional force and hence lesser the tendency to slip/skid. Three data sets for each arrangement were made to account for possible variations in data collection. The Specific wear rate is calculated according to equation (3).

$$W_s = \frac{\Delta V}{F_N L} \qquad (3)$$

Where ΔV is the volume loss, F_N is the normal load, L is the sliding distance. The loss volume (ΔV) was calculated by converting mass loss into volume loss using density.

2. 5 Testing of the surface of specimens

The surface roughnesses of rubber samples were measured before and after friction test using non-contact roughness tester of Bruker make, model GT-K0. The surfaces of all the specimens were assessed using the same testing parameters and adjusted using vision software at a magnification of 10.9×, Sampling of 910.58nm, and array size 640×480. Morphology of the rubber from friction fractured surfaces was studied using SEM at 20kv accelerating voltage.

3. Results and Discussion

3.1 Characterisation of Si_3N_4 *filler by FTIR*

The modification of Si_3N_4 surface is done by reaction of hydroxyl groups and silanol groups formed as silane coupling agents. The grafting reaction is identified from the appearance of characteristic bands of silane coupling agents in modified-Si_3N_4FTIR spectra, such as –CH2–appearing at 2920–2950 cm^{-1}. Figure 3 shows FTIR spectra of modified Si_3N_4 and unmodified Si_3N_4. It is observed that the peak of –CH2– exists in all modified Si_3N_4. It is the evidence for silane coupling agent molecules presence on Si_3N_4. The graft reaction is confirmed by examining the –OH vibration on the surface of Si_3N_4 before and after grafting. Comparing the position of Si–OH peaks, it is found that the peak intensity of Si–OH is at 3445 cm^{-1}, antisymmetric stretching vibration of Si–O–Si is at 1097cm^{-1}, and symmetric stretching vibration and bending vibration of Si–O are observed at 787 and 467 cm^{-1} respectively. The reason is due to destruction of hydrogen bonds existing at the surface of Si_3N_4. The poor dispersion of SiO_2 is due to the fact that the hydroxyl groups on the surface of Si_3N_4 forming as hydrogen bonds resulting in easy aggregation of Si_3N_4 particles. Hence, the destruction of hydrogen bond favours the dispersion of SiO_2 particles in rubber matrix.

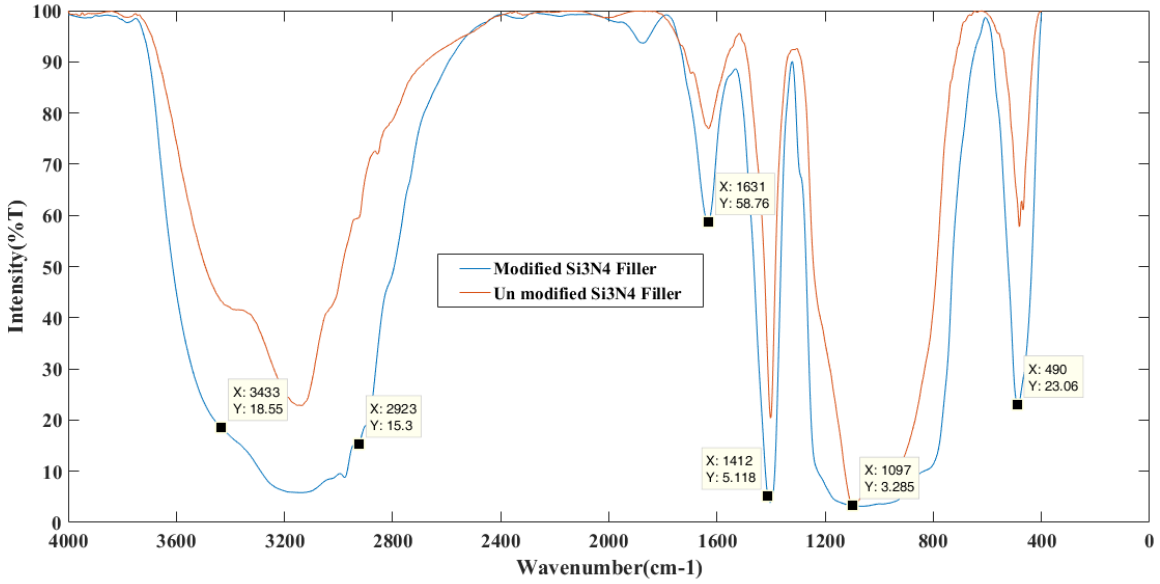

Figure 3. FTIR spectra of modified $Si_3N_4$and unmodified Si_3N_4

3.2 Curing characteristics

Table 2 shows the rheometric characteristics in terms of minimum and maximum values of torque (M_L and M_H respectively), the optimum curing time (Tc_{90}) and scorch time(ts_2), the cure rate index of NR/SBR blends with surface modified Si_3N_4 filler. It is observed that 11.5% increase in M_H value for 1% filler with reference to specimen without filler. This increase in the maximum torque is attributed to the presence of the surface modified filler in the matrix, which reduces the mobility of the molecules, having good interaction between modified filler and rubber blends. The minimum torque (M_L) is the measure of the stiffness of the vulcanized test specimen and is taken at the lowest point of the curve. It is increasing for 5% and 7% of filler dispersion. It is observed that optimum curing time (Tc_{90}) and the scorch time (Ts_2) values of NR/SBR blends with modified filler are decreased up to 7% filler dispersion when compared to specimen without filler. The cure rate index (CRI) values are increasing for the filler dispersion up to 7%. This is due to the poor interfacial interaction between rubber and filler at higher percentage loadings.

Table 2. Curing and mechanical properties of NR/SBR compounds with and without filler

Cure Characteristics at165°c and Mechanical properties	The properties for Si_3N_4 dispersion of				
	0%	1%	3%	5%	7%
M_L(kg cm)	25.34	23.85	23.85	26.63	27.90
M_H(kg cm)	67.95	75.82	71.24	74.70	81.64
Tc_{90}(Min)	4.09	3.66	3.29	2.89	2.95
Ts_2(Min)	1.1	0.96	0.77	0.60	0.62
CRI (Min^{-1})	33.44	37.07	39.37	43.66	44.91
Hardness shore A	48	55	52	55	55
Volume loss(mm^3)	42.54	48.78	46.97	49.34	49.21

3.3 Mechanical Properties

The mechanical properties tensile strength, elongation at break, tensile modulus and hardness shore A of NR/SBR blends with and without filler are determined. Figure 4 shows the tensile strength of the specimens with and without filler. Five specimens are tested for each percentage of filler dispersion and the peak values are averaged to predict tensile strength. It is observed that the increase in tensile strength about 16% for the specimen with 1% filler when compared to specimen without filler. The enhancement in the mechanical properties indicates a strong interaction between matrix and modified fillers and also indicates that the fillers are exfoliated or intercalated in rubber matrix. The tensile strength values are decreasing for higher percentage of filler dispersion. This is due to agglomeration of filler in the rubber blends. The formation of agglomeration reduces the interface area between the matrix and filler surfaces resulting stress concentration at weak points in the matrix and consequently low mechanical strength.

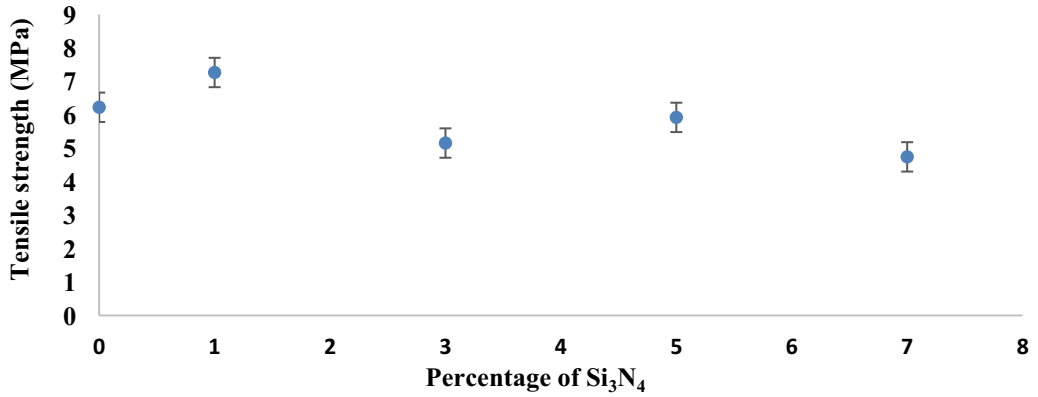

Figure 4. Tensile strength of NR/SBR compounds with and without Si_3N_4

Figure 5 shows for tensile modulus at 100% elongation of the specimens with and without fillers. The range of modulus values for the specimens with and without filler is between 1-1.5 Mpa. The modulus value of specimen with 1% is higher than other specimens. The increase in percentage of specimen with 1% filler is about 30% when compared to specimen without filler. Figure 6 shows the elongation percentage at failure of specimens. The elongation percentage of the specimen without filler is about 580%. The increase in elongation percentage for the specimen with 1% filler is about 16% when compared to specimen without filler.

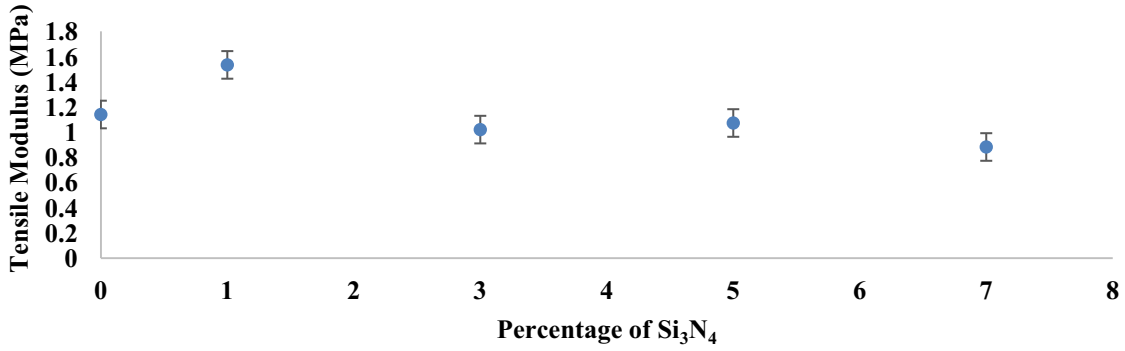

Figure 5. Tensile modulus of NR/SBR compounds with and without Si_3N_4 at 100% elongation

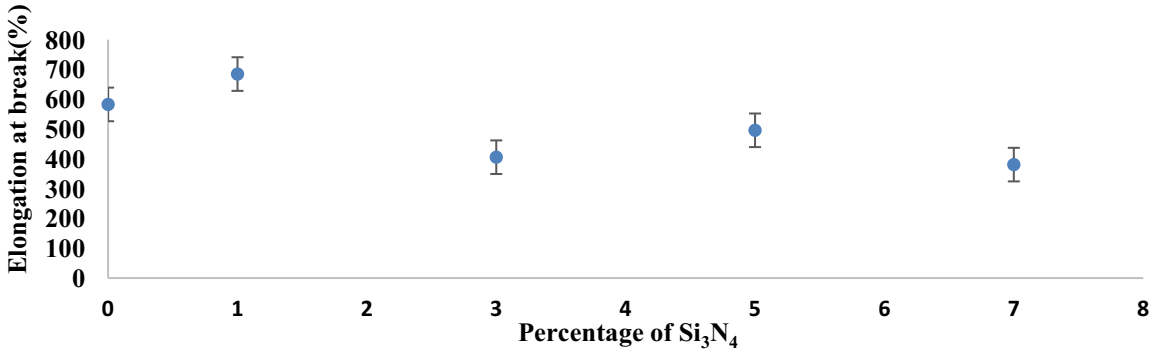

Figure 6. Elongation percentage of NR/SBR compounds with and without Si_3N_4 at the time of failure

3.4 Friction and wear test

Figure 7 shows the force - time plot for the friction testing of the specimens with and without filler at dry condition. The first peak load is considered as static friction force and successive peaks are due to interaction of rubber specimen with projections in the anti skid plate. The duration of test as per plot in the figure 7 is 100 -120 s. The total sliding distance for the test is about 100 mm. The static and kinetic coefficient of friction values are calculated using equations (1) and (2). The tests are also conducted for dry, wet, oil and mud environmental conditions. The separate specimen is used for conducting test in each condition. Five trials are conducted in each specimen. Table 3 shows the COF of NR/SBR composites at constant sliding speed of 50mm/minute against steel plate for various environmental conditions. The range of static COF at dry condition is between 0.34 - 0.5 and dynamic COF at same condition is between 0.2-0.35. The range of COF for other condition is between 0.3 -0.4 and the range of dynamic COF is less in each condition. It is observed that Si_3N_4 filler dispersion in rubber composites enhances COF (in both static and dynamic) and lowered specific wear rate. It is observed that Si_3N_4 filler is reinforcement to NR/SBR blends for better improvement of COF and wear resistance at low loading level (1%). For increase in percentage of Si_3N_4 filler makes agglomeration, so the overall performance of rubber composites decreases. It is concluded that the modified Si_3N_4 with silane provides compatibility and enhances the capacity of dispersion in NR/SBR blends, and which influences the properties of NR/SBR blends.

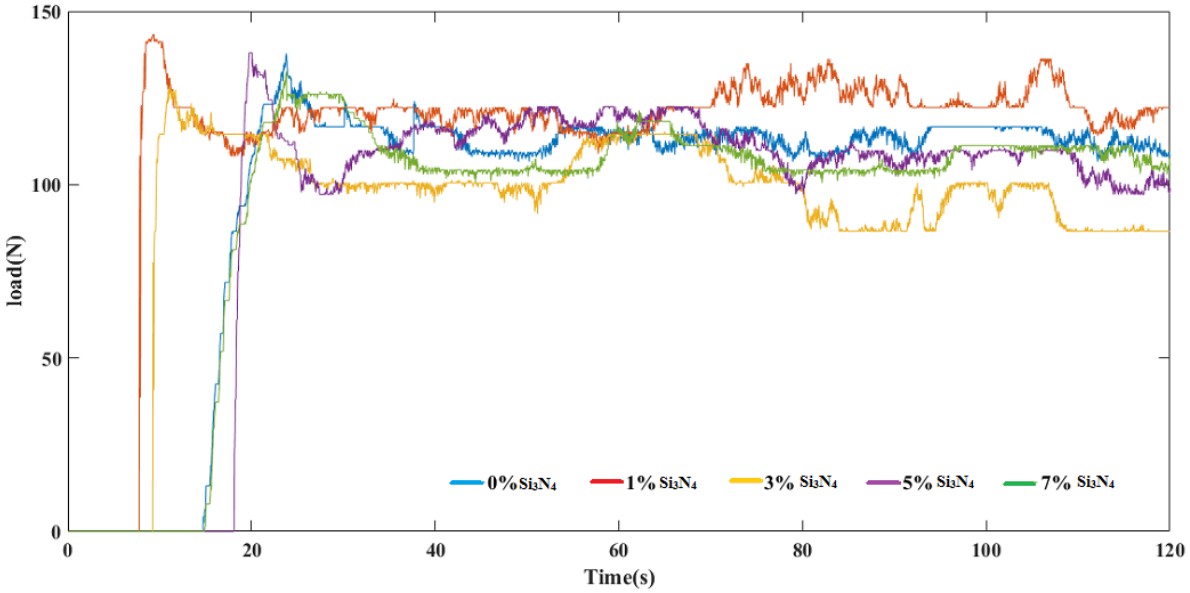

Figure 7. Load - time plot for friction test at dry condition

Table 3. Friction co-efficient of NR/SBR composites against steel antiskid plate in different condition

Sample	Dry Static	Dry Dynamic	Mud Static	Mud Dynamic	Wet Static	Wet Dynamic	Oil Static	Oil Dynamic
0%	0.343	0.215	0.319	0.204	0.307	0.193	0.298	0.219
1%	0.483	0.382	0.473	0.376	0.462	0.362	0.396	0.295
3%	0.312	0.201	0.294	0.198	0.289	0.182	0.273	0.175
5%	0.472	0.367	0.452	0.365	0.412	0.336	0.413	0.306
7%	0.455	0.337	0.403	0.342	0.403	0.331	0.410	0.312

The results indicate that the co-efficient of friction for rubber composites with and without Si_3N_4 particles, is reduced when friction occurred in other environmental conditions. The decrease in COF of rubber on steel with mud, water and oil is due to formation layers between steel plate and rubber specimens.

3.5 Micro morphology of composites by SEM

Figures 8(a) and (b) show the SEM micrograph of NR/SBR compounds without filler for before and after friction test on steel grip surface in dry condition. It is seen from SEM image in figure 8(b) that there is damage in surface due to sliding on steel grip projections. This is due to debonding of precipitated silica from matrix. Figures 9(a) and (b) show the SEM micrograph of NR/SBR compounds with 1% filler for before and after friction test. The damage in specimen after testing is higher when compared to specimen without filler. This is due to debonding of filler as well as precipitated silica in rubber blend. It is also observed that SEM images of worn rubber surface shows the debris of the filler particle on the surface of specimen caused by friction test.

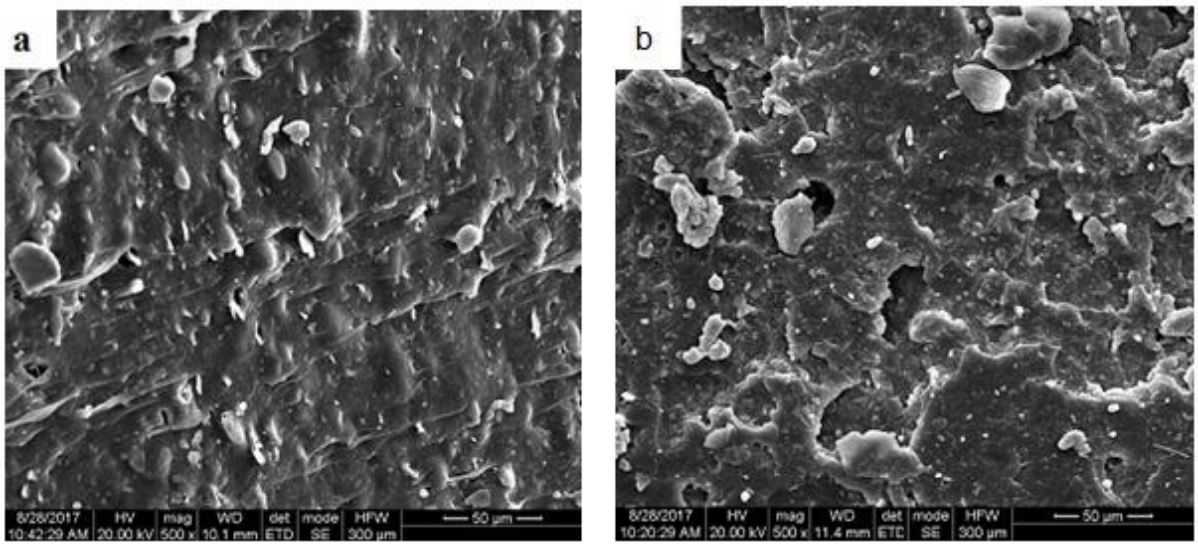

Figure 8. SEM micrograph of rubber specimen without filler (b) before friction test (b) after friction test

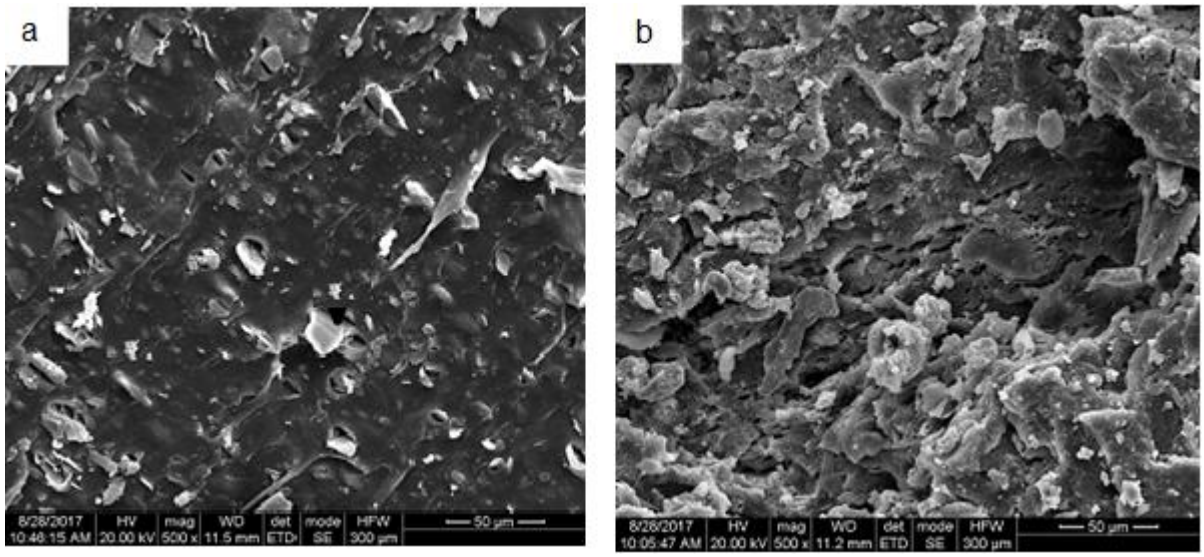

Figure 9. SEM micrograph of rubber specimen with 1% filler (b) before friction test (b) after friction test

3.6 Surface roughness test

Figures 10(a) and (b) show the surface topography of NR/SBR blends without filler for before and friction test on steel grip strut surface in dry condition. The surface roughness, R_a value of specimens before testing is 12.5 µm and R_a value of the same specimen after testing is 47.1 µm. The increase in surface roughness value due to friction test is about 400% due to friction. Figures 10(c) and (d) show the **s**urface topography of NR/SBR blends with 1% filler for before and after friction test. The R_a value of specimen with 1% filler before testing is 9.2 µm which is 25% less when compared to specimen without filler. The R_a value of specimens after testing is 41.1 µm which is 12.5% less when compared to specimen without filler.

It is seen that worn surface topography after friction test in dry condition at 1% surface modified Si_3N_4 filler addition, the surface is less coarse and the peak of asperities obviously decreases when compared to specimen without filler.

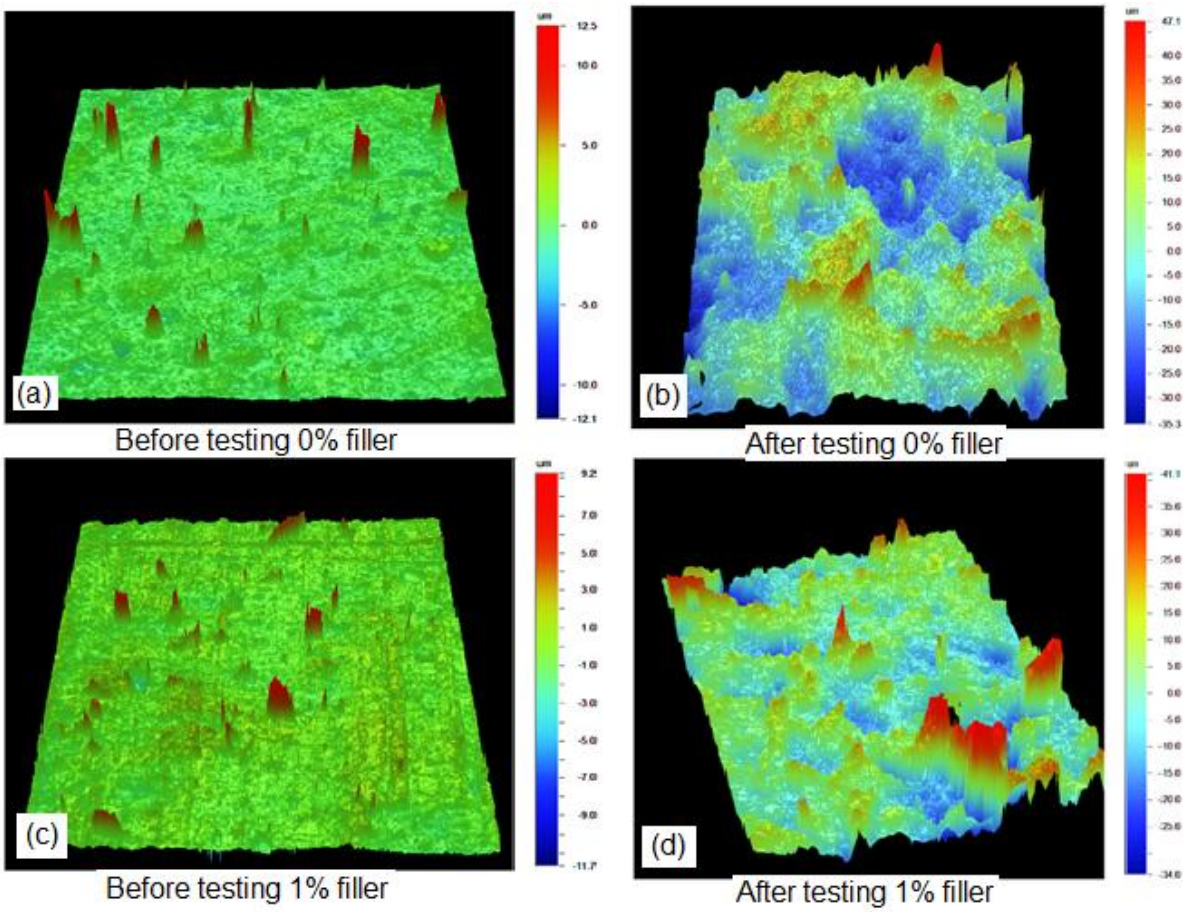

Figure 10. Surface topography of NR/SBR composites before friction test (a) without filler before testing (b) without filler after testing (c) with 1% filler before testing (d) with 1% filler after testing

4. Conclusion

Modified Si_3N_4 and precipitated silica are incorporated into NR/SBR compounds and the specimens are tested to find mechanical and friction behaviour on steel grip plate. The following are observed from this study.

- Dispersion of 1% Si_3N_4 content enhances tensile strength and tensile modulus of NR/SBR rubber blends. The values are decreasing further increase in % of filler dispersion.
- The hardness of rubber increases due to dispersion of filler from 1% to 7%.
- The incorporation of Si_3N_4 particles into rubber composites is having little effect on specific wear rate.
- The static and dynamic coefficients of frictions at dry condition are higher than mud, wet and oil environmental condition between rubber and steel antiskid plate.
- COF value increases for Si_3N_4 filler dispersed rubber in all tested conditions when compared to specimen without filler. The maximum increase in coefficient of friction is about 50% for specimen with 7% filler.

5. References

1. Frank L. Roth, Raymond L. Driscoll, and William L. Holt 1943 Frictional Properties of Rubber: *Rubber Chemistry and Technology*, Vol. 16(1) pp 155-177.
2. M.A. Cruz Gomez, E. A. Gallardo-Herna´ndez 2013 Rubber steel friction in contaminated contacts: *Wear* 302 pp1421- 1425.
3. S Maegawa, F Itoigawa, T Nakamura 2015 Effect of normal load on friction coefficient for sliding contact between rough rubber surface and rigid smooth plane: *Tribology international,* 92 pp 335-343.
4. Dae-Hyun Cho, Bhushan B and Dyess J 2016 Mechanisms of static and kinematic friction of polypropylene polytethylene terapthlate and high density polyethylene pairs during sliding: *Tribology International* 94 pp 165–175.
5. Yan-long Tai, Jia-sheng Qian, Ji-bin Miao, Ru Xia, Yu-chuan Zhang, Zhen-guo Yang 2012 Preparation and characterization of Si3N4/SBR nanocomposites with high performance: *Material and Design* 34 pp522-527.
6. Paveena Tangudom, Sirinthorn Thongsang, Narongrit Sombatsompop 2014 Cure and mechanical properties and abrasive wear behaviour of natural rubber, styrene–butadiene rubber and their blends reinforced with silica hybrid fillers: *Material and Design* 53 pp 856-864.
7. F. Nsib, N. Ayed, Y. Chevalier 2006 Selection of dispersants for the dispersion of carbon black in organic medium: *Prog. Org. Coat*. 55pp 303–310.
8. Z. Demjén, B. Pukánszky, E. Földes, J. Nagy 1997 Interaction of silane coupling agents with CaCO3 :*J. Colloids Interf. Sci*. 190 pp 427–436.
9. S.M.B. Nachtigall, M. Miotto, E.E. Schneider, R.S. Mauler, M.M.C. Forte 2006 Macromolecular coupling agents for flame retardant materials: *Eur. Polym. J.* 49 pp 990-999.
10. A Kohut, A. Voronov,W. Peukert 2007 An effective way to stabilize colloidal particles dispersed in polar and non-polar medium *Langmuir* 23pp 504–508.
11. Xiaodong wang Xinjun wan 2013Surface Modification of Nano-Silicon Nitride with Silane Coupling Agent: *Asian Journal of Chemistry* 25 pp 5589-5592.
12. E Harea, R Stocek, M Machovsky 2017 Study of friction and wear of thermoplastic vulcanizates: the correlation with abraded surfaces topology *IOP Conf. Series: Journal of Physics: Conf. Series* 843 pp 012070.