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Research Article

The Effect of Modified Natural Rubber and Silane on Properties of Silica Filled Natural Rubber Composite

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ABSTRACT

Natural rubber composites reinforced with silica nanoparticles were prepared by incorporating different loadings of coupling agent. The coupling agents, i.e. maleic anhydride grafted natural rubber (NRgMAH), epoxidized natural rubber (ENR) and Dynasylan MTMO were used to improve the properties of the composite. The processability, curing characteristics and mechanical properties were investigated. Results indicate that the presence of NRgMAH, ENR and Dynasylan MTMO improves significantly the processability of the rubber composites. NRgMAH acts retarding effect on natural rubber composite vulcanization, both scorch time and cure time increase with increasing NRgMAH loading, while ENR and Dynasylan MTMO enhance the cure characteristics. Increasing coupling agent content also increases the tensile modulus and shows superior tear resistance and abrasion resistance, but the tensile strength and elongation at break decrease with increasing Dynasylan MTMO loading. The homogenous distribution and interfacial interaction of silica particle and natural rubber matrix were enhanced by the addition of NRgMAH, ENR and Dynasylan MTMO, as exhibited by the fracture surfaces of the composite using a Scanning Electron Microscope (SEM). The presence of coupling agent has reclaimed the compound processing and enhanced the mechanical properties.

Key words: NRgMAH, ENR, Silica, Reinforcement

INTRODUCTION

Although natural rubber (NR) is known to exhibit numerous outstanding properties, reinforcing fillers are necessarily added into NR in most cases in order to gain the appropriate properties for specific applications. Reinforcement gives improvement in properties such as tensile strength, tear strength, abrasion resistance, stiffness and hardness [4,9]. Fillers and curing agents to a large extent control the technical properties of rubber compounds [15]. Among the fillers, silicas offer significant benefits to rubber reinforcement. Silica provides a unique combination of tear strength, abrasion resistance, aging resistance and adhesion properties [5]. Particularly since the introduction of the Energy® tyre by Michelin, silica has become more important as reinforcing filler for the rubber industry. In tire treads, silica yields a lower rolling resistance at equal wear resistance and wet grip than carbon black [6]. The surfaces of silicas possess siloxane and silanol groups. The silanol groups are acidic and interact with the basic accelerators, causing detrimental effects such as long cure times and slow cure rates, and also loss of crosslink density in sulphur curing

rubbers [6]. Moreover, the hydrophilic silanol group results in strong filler–filler interaction by hydrogen bonds. When a large amount of silica is added, the viscosity increases significantly, attributed to the strong interaction between the silica particles [1,21]. Filler dispersion has a significant effect on the properties of rubber composites. Mechanical properties such as tensile strength and tear strength were improved as the quality of the filler dispersion increased [16,12] suggested that the improvement in the properties is largely due to the uniform distribution of SiO₂ nanoparticles and the strong interactions between SiO₂ and polymer matrixes. Silane coupling agent is a bifunctional compound developed commercially to improve the reinforcing efficiency of silica. The silanisation of silica can be carried out in two different ways. Firstly, silica and silane are mixed together in a preliminary mixing stage at an optimum temperature and reaction time [18]. Alternatively, silanisation is carried out in situ [19]; during mixing the silane is added to the rubber together with, or after the silica. Silane coupling agents, e.g. bis (3-triethoxy silylpropyl) tetrasulfide, 3-thiocyanatopropyl triethoxy silane are used to improve the filler dispersion and prevent

adsorption of curatives on the silica surface [7,19]. Maleic anhydride grafted natural rubber (NRgMAH) and epoxidized natural rubber (ENR) are a modified natural rubber. Ismail *et al.* [10] observed that the addition of maleated natural rubber improved the rubber–filler interaction, while some other studies showed that epoxidation products that contain ring-opened structures are generally indoluble and this can be attributed to the formation of ether crosslink [5,14]. In this article, the coupling agents, i.e. NRgMAH, ENR and Dynasytan MTMO were selected to improve the properties of silica filled natural rubber composite and their effect on the processability, curing characteristics, mechanical properties and interfacial interaction between the silicas and rubber matrix were investigated.

Materials And Methods

Materials:

STR 5L grade natural rubber was purchased from Rubber Estate Organization. Ultrasil VN3 grade precipitate silica was purchased from Petch Thai Chemical (T) Ltd. and used as the natural rubber composites reinforcement. Maleic anhydride was purchased from Fluka Chemica, Switzerland. Maleic anhydride grafted natural rubber (NRgMAH) was

prepared prior to compounding by grafting the 8 phr of maleic anhydride onto natural rubber chain using a Banbury mixer at 145 °C and 50 rpm according to a procedure reported by Nakason *et al.* [6]. Epoxidized natural rubber (ENR) with 25% mol epoxidation was obtained from Muang Mai Guthrie PCL (T) Ltd. 3-mercaptopropyl trimethoxysilane (Dynasytan MTMO) was supplied by Evonik Industries AG, Germany. Other compounding ingredients such as zinc oxide, stearic acid, sulfur, 2-mercaptopbenzothiazyl disulfide (MBTS), diphenyl guanidine (DPG) and aromatic oil were all purchased from Bayer (T) Ltd.

Formulation and Mixing Procedures:

The formulation used is shown in Table 1. Compounding was carried out on a laboratory-sized (500 ml) internal mixer. The mixing conditions were set as follows; fill factor at 0.7, initial chamber temperature at 80 °C and rotor speed at 40 rpm. The compounds were thereafter sheets out on a two roll mill. Mooney viscosity (ML 1+4 at 100°C) was measured by using a Montech Mooney viscometer (MV 2020). The composites were compression moulded at 150 °C with force of 10 MPa and cure times, t90.

Table 1: Formulation of the silica filled natural rubber composites

Materials	Part per hundred rubber (phr)		
	1	2	3
STR 5L	100	100	100
Zinc oxide	5.0	5.0	5.0
Stearic acid	1.0	1.0	1.0
Sulfur	2.5	2.5	2.5
MBTS	1.0	1.0	1.0
DPG	0.5	0.5	0.5
Ultrasil VN 3	20.0	20.0	20.0
Aromatic oil	5.0	5.0	5.0
NRgMAH	3, 6, 9, 12	-	-
ENR	-	3, 6, 9, 12	-
Dynasytan MTMO	-	-	0.5, 1, 1.5, 2

Measurement of Curing Characteristics, Mechanical Properties and SEM Micrograph:

The cure characteristics of the mixes were studied using a Tech Pro Oscillating Disk Rheometer (rheo TECH OD⁺) according to ASTM D 2084-07 at 150 °C. Tensile test and tear resistance experiments were conducted on a Testometric Tensometer (AX M350) with a cross head speed of 500 mm/min according to ASTM D 412 and ASTM D 624, respectively. The test for hardness was carried out by using the Shore A Durometer according to ASTM D 2240. The abrasion resistance was determined as the volume loss from the wear test using a Cometech Abrader (QC 615A). The cryogenically fracture under liquid nitrogen surfaces of the composites were investigated with a JEOL JSM-5800 LV (SEM5800) scanning electron microscope. The fracture ends of the

specimens were mounted on aluminium stubs and sputter coated with a thin layer of gold to avoid electrostatic.

Results And Discussion

Compound properties:

The effect of coupling agent loading on mixing behavior is illustrated in Fig. 1. Obviously, the mixing energy of the composite decreases continuously with coupling agent content. Increasing coupling agent loading gives rise of the deformable rubber portion in the compound, as the plasticizing effect. The functional groups, i.e. maleic anhydride group in NRgMAH, epoxy group in ENR and methoxy group in Dynasytan MTMO could react chemically with the silanol groups on silica surface

(Fig. 3), giving rise to the reduction of filler–filler interaction. A greater degree of silica disagglomeration is therefore achieved during mixing, leading to the reduction of compound viscosity (Fig. 2) and mixing energy. It can be observed that, at a similar modified natural rubber loading, NRgMAH provides the rubber compounds with lower mixing energy and Mooney viscosity than ENR. Furthermore, the mixing energy and Mooney

viscosity of the composite with Dynasylan MTMO are extremely lower than composite with modified natural rubber coupling agent. This is due to the lower molecular weight of Dynasylan MTMO, when added into the compound, it could react with the silanol groups on silica surface more thoroughly than modified natural rubber, leading to a greater reduction of filler–filler interaction. [19]

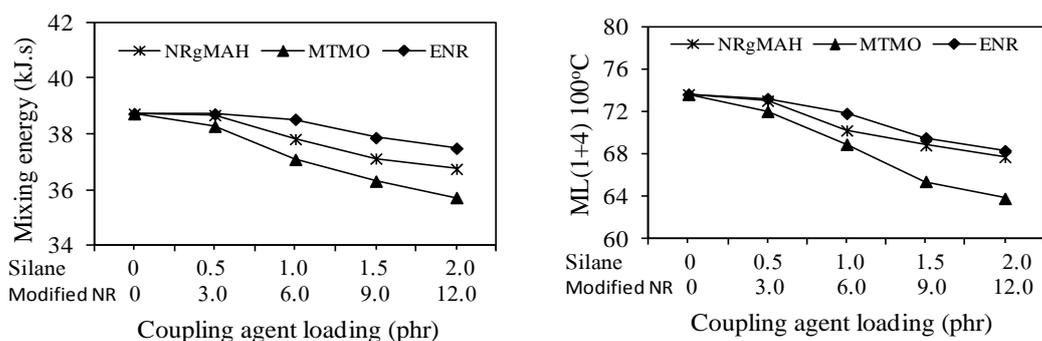


Fig. 1: Effect of coupling agent loading on mixing energy of silica filled NR composite

Fig. 2: Effect of coupling agent loading on Mooney viscosity of silica filled NR composite

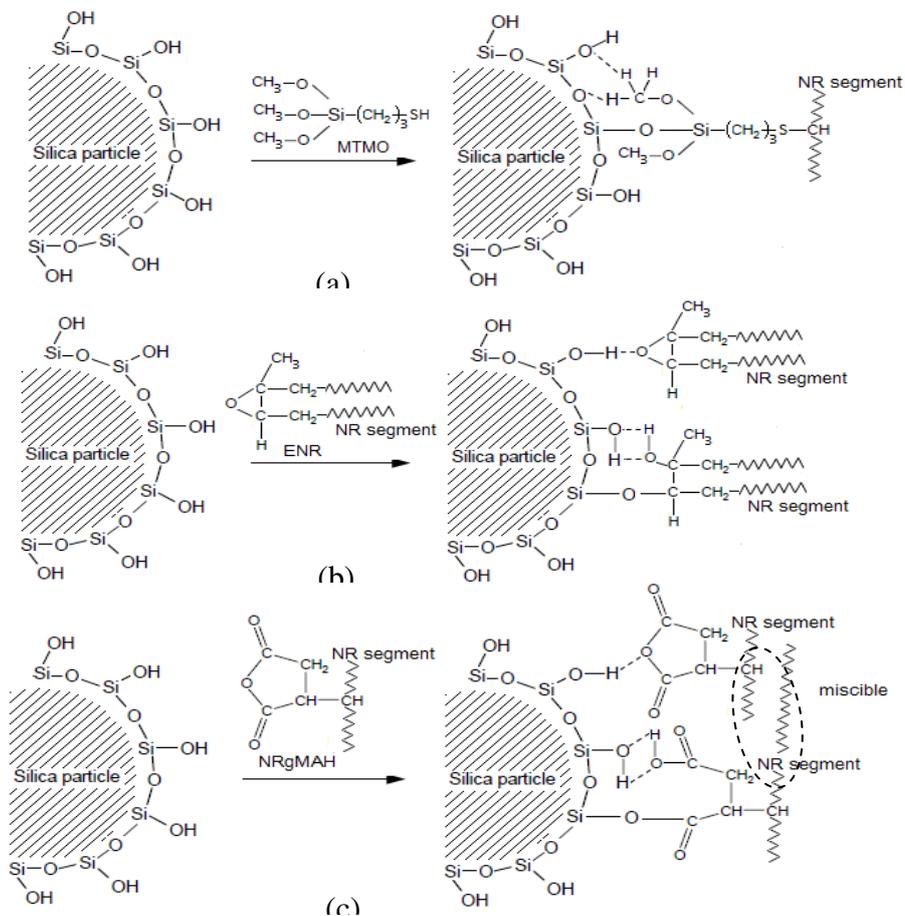


Fig. 3: Bonding of coupling agent to the silica surface; (a) Dynasylan MTMO (b) ENR (c) NRgMAH.

Curing characteristics:

Table 2 shows the results of cure characteristics. It can be seen that ENR and Dynasytan MTMO enhance the cure characteristics, both ENR and Dynasytan MTMO accelerate cure rate for silica filled natural rubber composite. This is due to the coupling agent could react chemically with the silanol groups on silica surface and make the silica surface less chemically reactive. The amounts of accelerators trapped by silica surface are therefore reduced, giving rise to faster cure rate. However, a reaction between the organosilane and the rubber polymer, based on sulphur donation or an interaction of the sulphur moiety in the silane with the rubber leads to premature scorch during mixing and is therefore not desired for composite production [3]. NRgMAH affects the cure characteristics of the composites

differently, shows retarding effect on natural rubber composite vulcanization, both scorch time and cure time slightly increase with increasing NRgMAH loading. This observation might be due to the acidic maleic anhydride groups in NRgMAH. However, Jacob *et al.* [11] has been reported for other filler filled rubber composites that the prolonged cure rate due to the formation of good interaction between filler particles and rubber matrix. In addition of ENR, the composites provide faster cure time than the composites with NRgMAH. An epoxy group in the ENR molecule with a terminal condition provides the double bond of isoprene unit in chain more sensitive and tends to be active group like electron more [20]. However, at high level of ENR (6-12 phr), the increasing of ENR loading slightly rises the scorch time of the composite by the effecting of the acidic epoxy groups in ENR.

Table 2: Scorch time (ts1), cure time (t90), cure rate index (CRI) and maximum torque (MH-ML) of the silica filled NR composites.

Coupling agent	Loading (phr)	cure characteristics			
		ts1 (min)	t90 (min)	CRI (S ⁻¹)	MH-ML (lb.in)
No coupling agent	-	2.20	8.28	16.45	28.10
NRgMAH	3	2.25	8.34	16.42	29.98
	6	2.28	8.45	16.21	28.85
	9	2.36	9.10	14.84	27.99
	12	2.40	9.16	14.79	26.92
ENR	3	1.57	7.09	18.12	22.97
	6	1.49	6.37	20.92	22.49
	9	1.53	6.33	20.83	22.93
	12	1.58	6.53	20.22	23.73
Dynasytan MTMO	0.5	1.54	6.12	21.83	28.48
	1	0.99	5.89	20.41	28.41
	1.5	0.74	5.50	21.01	28.48
	2	0.75	5.41	21.46	28.51

Maximum torque (MH-ML) generally correlates with crosslink density and/or nondeformable solid filler. Table 2 shows that the addition of Dynasytan MTMO slightly increases the torque value of natural rubber composites. Results also reveal that Dynasytan MTMO imparts greater degree of crosslink than modified natural rubber. This is possibly attributed that Dynasytan MTMO contains sulfur atom on its molecule and these sulfur atom can be contributed to the rubber matrix during vulcanization [3]. The composite with modified natural rubber is claimed to have a lower value of maximum torque than those composite with no coupling agent. This indicate that the increasing modified natural rubber loading gives more deformation rubber portion in the compound and higher mobility of the macromolecule chains of the rubber.

Mechanical properties:

Table 3 shows that the stress at 100% and 300% elongation (100%, 300% mod.) rise with the increases in all types of coupling agent loading. However, the tension modulus is found to increase with increasing Dynasytan MTMO loading up to approximately 1.0

phr. Further increase in Dynasytan MTMO loading causes very little change in the modulus of the composites. While, the composites with NRgMAH and ENR show maximum tension modulus at 9 phr of modified natural rubber loading. The results indicate that Dynasytan MTMO and modified natural rubber could enhance the crosslink density of silica filled natural rubber composite. The increased crosslink density is thought to arise mainly from the reduction of adsorbed accelerator on silica surface and the promotion rubber-silica bonding in the presence of coupling agent [1]. The reduction of modulus at high loadings of NRgMAH and ENR is attributed to the flexibility effect of excessive modified natural rubber coupling agent. Hardness property increases with increasing coupling agent loading for Dynasytan MTMO but, for modified natural rubber, both NRgMAH and ENR do not affect the hardness of the composite.

The addition of modified natural rubber coupling agent could enhance the tensile strength of the composite. This indicate that the composite provides good interaction between the functional groups in the coupling agent and the silanol groups on silica surface in rubber matrix, caused the uniformly silica particle distribution which led to reduction in filler-filler

interaction and enhanced tension properties [12]. It can be observed that the composites with Dynasytan MTMO show lower tensile strength than those modified natural

rubber coupling agent composite. This observation might be due to Dynasytan MTMO imparts greater degree of composite crosslink, which could

significantly restrict the flexibility of rubber chains and gives rise to the reduction of molecular crystallization during tension. In addition, very fast cure of Dynasytan MTMO composite does not have enough scorch time for silica dispersion in rubber matrix, lead to more silica aggregates which caused poorer tensile strength [17].

Table 3: Tensile properties and hardness of the silica filled natural rubber composites.

Coupling agent	Loading (phr)	cure characteristics				
		100% Mod. (MPa)	300% mod. (MPa)	TS. (MPa)	EB. (%)	Hardness (Shore A)
No coupling agent	-	1.17	3.20	27.35	750	50.4
NRgMAH	3	1.47	3.44	30.06	763	47.6
	6	1.55	4.52	30.27	775	47.8
	9	1.57	5.53	30.38	800	49.0
	12	1.34	4.21	28.65	825	49.0
ENR	3	1.25	3.37	29.08	700	49.7
	6	1.31	3.93	28.37	700	50.4
	9	1.37	4.20	28.32	725	50.2
	12	1.24	3.26	28.30	750	50.6
Dynasytan MTMO	0.5	2.08	5.59	27.97	680	55.4
	1	2.39	9.92	25.57	615	55.6
	1.5	2.49	10.09	24.79	575	56.0
	2	2.59	10.27	24.02	520	56.2

The elongation at break (EB.) is shown in Table 3. It indicates that the incorporation of NRgMAH into the natural rubber composites increase the elongation at break. However, due to the greater degree of crosslink and also hardness property, the molecular chain slipping leads to lower resistance to break which caused the elongation at break for composite with Dynasytan MTMO is lower than composite with NRgMAH and ENR.

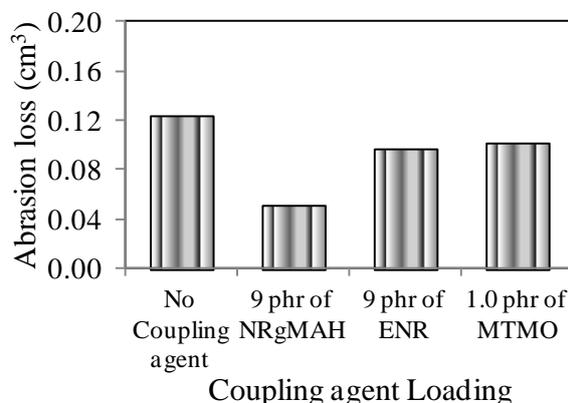
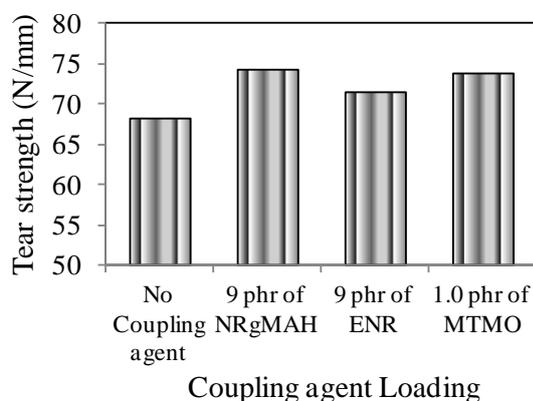


Fig. 4: Effect of coupling agent loading on tear strength of silica filled NR composite

Fig. 5: Effect of coupling agent loading on abrasion loss of silica filled NR composite

Fig. 4 shows that tear strength of the silica filled natural rubber composites. Normally the tear strength was improved by the addition of silica. The silica particles with spherical shape can combine with the rubber chains in three dimensions at the nanometer level, which leads to high tear strengths of the composites (Liu *et al.*, 2008). Furthermore, the tear strength was improved by the addition of coupling agent, both silane and modified natural rubber coupling agent, due to the chemical interaction between functional group in coupling agent and silanol group on silica surface. NRgMAH forms the ester bonding, while ENR and Dynasytan MTMO

show the ether and siloxane linkages, respectively, as shown in fig. 3 [8]. The stable chemical bonding supports more homogenous distribution and better interfacial interaction between silica particle and rubber matrix.

The abrasion resistance of the composites, expressed as abrasion loss, is presented in Fig. 5. Silica also implies the stronger filler–filler interaction in silica reinforced composites, which affects the poorer silica dispersion, thus giving rise to the lower abrasion resistance [1]. However, this report indicated that the abrasion resistance tends to increase by the addition of Dynasytan MTMO silane

and modified natural rubber coupling agent in the composites. This is the effect of the high performance reinforcements of silica in the rubber by the uniformly dispersion and the stronger adhesion of the silica and rubber matrix as mentioned previously.

SEM study:

The fracture surfaces of silica reinforced natural rubber composites are shown in Fig. 6. The dark phase represents the natural rubber matrix and the bright phase corresponds to the silica particles, which are strongly embedded by natural rubber matrix. The composite with no coupling agent in Fig. 4 (a) shows

less uniformly distribution with more large silica aggregates, providing great pull-out of silica particle on the fracture surface. While the scanning electron microscopy fracture surface of the composite with NRgMAH coupling agent in Fig. 4 (b) exhibits the most homogenously distribution of silica particle throughout the natural rubber matrix and shows of a well-developed interfacial interaction between the silica particles and the rubber matrix, leading to the highest properties of almost all mechanical properties such as tensile strength, elongation at break, tear strength and abrasion resistance. Moreover, the composite with NRgMAH coupling agent gives more safety scorch for the composite production.

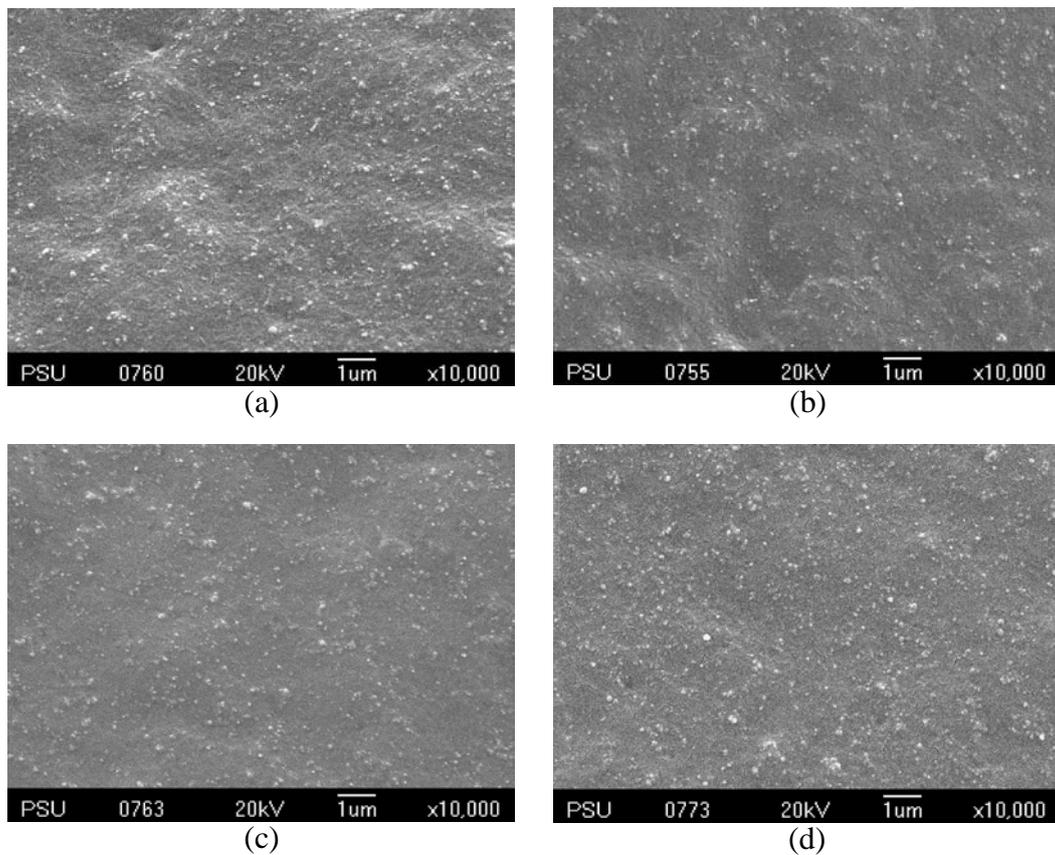


Fig. 6: Scanning electron microscopy fracture surface of 20 phr of silica reinforced natural rubber composites; (a) no coupling agent (b) 9 phr of NRgMAH (c) 9 phr of ENR (d) 1 phr of Dynasylan MTMO (magnification 10000X).

Conclusion:

The presence of modified natural rubber and silane coupling agent in silica filled natural rubber composites improves significantly the processability of the compounds by reducing the mixing energy, the compound viscosity as well as the homogenously distribution of silica particle and rubber-silica interaction. NRgMAH retards cure and gives more safety scorch for the composite production, whereas

ENR and Dynasylan MTMO enhance the cure rate. The addition of all coupling agent, i.e. NRgMAH, ENR and Dynasylan MTMO also increases the tensile modulus and shows superior tear resistance and abrasion resistance. However, the tensile strength decreases with Dynasylan MTMO content. Further the optimized mechanical properties improvement is pronounced at critical coupling agent loading, 9 phr for modified natural rubber and 1.0 phr for Dynasylan MTMO.

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