

Epoxidised Natural Rubber - A Substitute for Silane Coupling Agent in Safe Silica-Filled Natural Rubber Formulations

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Abstract- Natural rubber (NR) vulcanizates prepared using non-regulated nitrosamine generating accelerators such as tertiarybutyl benzothiazolesulfenamide (TBBS) and tetrabenzyl thiuramdisulfide (TBzTD) are reported to be safe and non-carcinogenic. The difficulties during processing of silica-filled NR compounds could be overcome by incorporating silane coupling agent to the silica-rubber mix to improve the interactions between rubber and silica. The work reported in this paper is an attempt to replace the expensive silane coupling agent (Si69) with a modified form of natural rubber, i.e. epoxidised natural rubber (ENR) in safe accelerators incorporated formulation. The silica-filled ENR modified NR vulcanizates show lower optimum cure time compared to silane modified vulcanizate. Silica-filled NR vulcanizates modified with ENR show improved mechanical properties compared to the unmodified silica-filled natural rubber vulcanizate.

Keywords- Non-regulated nitrosamine, Epoxidised natural rubber, Coupling agent, Cure time, Vulcanizate

I. INTRODUCTION

Most of the conventional accelerators used in rubber formulations are derived from secondary amines. The chemicals derived from secondary amines, when exposed in air, form nitrosamines in presence of atmospheric nitrosating agents. Some of the nitrosamines are carcinogenic (regulated) [1-3]. One of the options to eliminate toxic hazards of rubber products is to use nitrosamine safe (non-regulated) chemical ingredients in rubber compounding [4].

Silica is one of the important reinforcing filler used in the rubber industry. Because of the polarity, silica exhibits higher filler-filler interaction and therefore poor rubber-filler interaction. Several modifications of silica filler such as heat treatment, chemical modification of the filler surface groups, grafting of polymers on to the filler surface and use of promoters or coupling agents have been reported to improve the rubber-filler interaction [5, 6]. Silane modification is the most widely practised technique for improving silica-rubber bonding [7, 8]. One of the widely used silane coupling agent is bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) [9]. However, the high cost of silane coupling agent is a

limitation to its widespread acceptance.

Hydroxy functionalised SBR and epoxy functionalised NBR exhibited improved reinforcement with silica as compared to the unmodified rubber [10, 11]. Epoxidised natural rubber (ENR) shows polarity and bifunctionality. ENR may be considered as an alternative to silanes. ENR in small proportions has been used as a reinforcing modifier for silica-filled nitrile rubber (NBR) [12].

This paper discusses the effect of epoxidised natural rubber on the properties of silica-filled safe natural rubber vulcanizates and the feasibility of using ENR as a coupling agent in place of silane in silica-filled NR formulations.

II. EXPERIMENTAL

A. Materials

Natural rubber (ISNR-5) and ENR 25 (containing 25 mol percent of oxirane rings) used in this study were obtained from the Rubber Research Institute of India (Kottayam, Kerala). The antioxidant N-(1,3-Dimethyl butyl)-N'-phenyl-p-phenylenediamine i.e. 6PPD (Mercox 6C), the accelerators TBBS (Mercur TBBS), and TBzTD (MercurTBzTD) were supplied by Merchem Ltd., Kochi, Kerala. Precipitated silica of commercial grade was supplied by Minar Chemicals, Kochi, Diethylene glycol (DEG) was supplied by Merck Limited, Navi Mumbai and the coupling agent used was Si69 i.e. bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT), a product of Degussa AG, Germany. Associated Rubber Chemicals, Kochi supplied the zinc oxide, stearic acid and sulphur used in this study.

B. Compounding and Testing

The formulations employed for the study are shown in Table 1. The compounding of NR was done in a laboratory two-roll mixing mill as per ASTM D 3184.

TABLE I
FORMULATIONS OF THE MIXES

Ingredients	S	S _{silane}	E ₀	E ₁	E ₂	E ₃	E ₄	E ₅
NR (g)	100	100	98.5	98	97	96	95	94
ENR (g)	-	-	1.5	2.0	3.0	4.0	5.0	6.0
ZnO (phr)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid (phr)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
6PPD (phr)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Precipitated silica (phr)	15	15	15	15	15	15	15	15
DEG (phr)	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Si69 (phr)	-	1.5	-	-	-	-	-	-
TBBS (phr)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TBzTD (phr)	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2
Sulphur (phr)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3

The rheographs of the mixes and their cure characteristics were obtained using RPA 2000 Rubber Process Analyzer. The test specimens were prepared by compression moulding in an electrically heated hydraulic press at 150 °C. Tensile and tear strength were measured as per ASTM D 412 and ASTM D 624 respectively using a Shimadzu Universal Testing Machine, at a cross head speed of 500 mm/min. The changes in tensile properties of the samples were determined by keeping the samples in a hot air oven at 70 °C and 100 °C for 24 hours according to ASTM D 572. The Shore A hardness of the samples was determined using Mitutoyo hardmatic hardness tester according to ASTM D 2240. Compression set at constant strain was measured according to ASTM D 395. Rebound resilience was determined by vertical rebound method according to ASTM D 2632. The crosslink density of the vulcanizates was determined by the Flory-Rehner equation using the equilibrium swelling data [13].

Bound rubber content of the master batches and strain-sweep analyses of the uncured compounds were measured in order to assess the rubber-filler interaction. The fluid resistance of the samples were carried out in diesel and lube oil according to the ASTM D 471. Scanning electron microscopy was carried out using scanning electron microscope (JEOL Model JSM – 6390 LV) after sputter coating the surface with gold on the fractured surface of tensile samples to evaluate the distribution of the filler in the NR matrix. The thermal degradation temperature of the NR vulcanizates was determined by the thermogravimetric analysis using TGA Q-50 thermal analyzer (TA Instruments) under nitrogen atmosphere. The samples were heated from room temperature to 800 °C at a heating rate of 20 °C/min. Cytotoxicity of the material was measured from the percentage viability of the cells and by using the method of MTT (3-(4, 5 dimethylthiazol-2-yl)-2, 5-diphenyltetrazoliumbromide) assay [14]. Optical density was read at 540 nm using DMSO (dimethyl sulfoxide) as blank in a microplate reader (ELISASCAN, ERBA). Control samples are the cells (L929 cells) to which polymer solution is not added.

$$\% \text{ viability} = \frac{\text{Optical density of test specimen}}{\text{Optical density of control}} \times 100$$

III. RESULTS AND DISCUSSION

A. Cure characteristics

Cure curves of unmodified silica-filled NR, silane coupling agent modified silica-filled NR and ENR modified silica-filled NR are shown in Fig. 1.

Silane-treated silica-filled NR compound show shorter scorch time and cure time compared to unmodified silica-filled NR compound as shown in the Table 2. In the case of unmodified silica-filled compounds, silanol groups on silica surface can interact with polar materials such as accelerators resulting in long scorch and cure times. In silane-treated compounds the ethoxy groups of silane are hydrolysed to form a hydroxyl group which undergoes condensation reaction with silanol groups on silica surface resulting in less adsorption of accelerator [15 – 18].

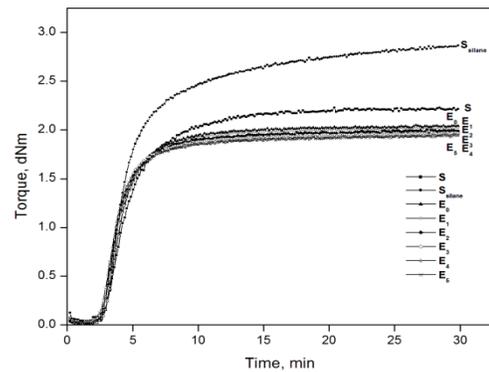


Fig.1 Cure characteristics of the silica-filled NR compounds with and without modifications.

TABLE II
 CURE PROPERTIES OF THE MIXES AT 150 °C

Properties	S	S _{silane}	E ₀	E ₁	E ₂	E ₃	E ₄	E ₅
Scorch time t ₁₀ (min)	3.24	2.79	2.96	2.93	2.85	2.83	2.78	2.71
Optimum cure time t ₉₀ (min)	9.12	9.01	7.58	7.51	7.27	7.11	6.79	6.72
Maximum torque (M _H , dNm)	2.22	2.87	2.04	2.03	2.00	1.97	1.95	1.94
Minimum torque (M _L , dNm)	0.04	0.009	0.013	0.013	0.016	0.016	0.025	0.025

ENR modified compounds show lower optimum cure time as compared to the silane modified NR compound. Optimum cure time decreased as the dosage of ENR was increased. Therefore more crosslinks are formed in shorter time [19]. Improvements noted in the cure behaviour of the ENR modified natural rubber compounds might have resulted from the preferential interaction of the epoxy group with the silanol groups [20]. This may reduce the chances of interaction of the

silanol group with the accelerator and other compounding ingredients. Thus the accelerators and compounding ingredients are available prominently for curing in the ENR modified compounds.

Minimum torque (M_L) observed in the case of ENR modified compounds is lower compared to the unmodified compound but higher than the silane modified compound. This shows that the processability is in the order silane modified compound > ENR modified compounds > unmodified silica-filled NR compound. The minimum torque of the compounds increases with increase in ENR loading. However the maximum torque decreases with increase in the dosage of ENR. The ENR modified NR compounds show lower maximum torque values than silane modified NR compound. Decrease in maximum torque value shows that ENR acts as a plasticizer and improves the processing performance of the compounds.

B. Mechanical properties

The effect of silane coupling agent and ENR on the stress-strain properties of the silica-filled NR vulcanizates was studied. Silane modification improved the tensile strength, as can be seen from the Table 3. Coupling agent, being a crosslinking agent as well [21 – 27], might have contributed to higher crosslink density and improved tensile strength. Silica-filled NR vulcanizates modified with ENR show higher tensile strength as compared to the unmodified silica-filled natural rubber vulcanizate. Incorporation of higher dosage of ENR (4g) resulted in tensile strength comparable to that of silane modified (1.5 phr) silica-filled vulcanizate. Thus slightly higher dosage of epoxidised natural rubber could be a better substitute for the expensive silane coupling agent in silica-filled natural rubber formulations. Because of the polarity and bifunctionality (the oxirane and the unsaturation) of ENR, the interaction of ENR with silica leads to improved rubber-filler interaction [28]. Chemical interaction or chemical crosslinks between the epoxy group and silanol groups has been proposed to be the reason for the unusual reinforcement [29].

On incorporation of the silane coupling agent/ENR the modulus at 300 % elongation shows lower values compared to the vulcanizate containing unmodified silica. This may be due to the mild plasticizing effect imparted by the coupling agent/ENR. Vulcanizates prepared with the coupling agent/ENR shows higher elongation at break as compared to the unmodified silica filled vulcanizate apparently due to the reason cited above.

TABLE III
 PROPERTIES OF THE VULCANIZATES

Properties	S	S _{silane}	E ₀	E ₁	E ₂	E ₃	E ₄	E ₅
Tensile strength (MPa)	20.30	22.77	21.08	22.04	22.46	22.84	22.58	22.36

Modulus at 300% elongation (MPa)	3.19	2.14	1.83	1.87	2.08	2.20	2.20	2.06
Elongation at break (%)	595	945	1033	1025	1012	1021	1031	1029
Tear strength (N/mm)	31.90	35.59	32.35	33.18	33.76	34.85	34.26	34.03
Hardness (Shore A)	35	37	32	32	33	33	34	34
Compression set (%)	23.90	16.28	23.01	22.40	21.65	21.64	22.02	22.55
Rebound resilience (%)	59	65	59	59	60	60	61	62
Crosslink density x10 ⁵ (mol/g rubber hydrocarbon)	4.91	7.79	4.92	4.93	5.06	5.12	5.09	5.01
Swelling index	3.71	3.16	3.83	3.78	3.77	3.75	3.76	3.80
Abrasion loss (cc/h)	10.92	7.94	12.06	11.91	11.75	11.29	11.91	12.09

An improvement in tear strength (Table 3) is observed in both silane-treated and ENR modified silica-filled NR vulcanizates compared to unmodified silica-filled vulcanizate. Tear strength values of the silane modified vulcanizate was higher than that of the ENR modified vulcanizates, which is likely to be due to the rubber-filler covalent bonding achieved through sulphur bridges (in the case of silane modification). Silane incorporation improved the abrasion resistance of silica-filled natural rubber vulcanizate as can be seen in the Table III. Improved tear strength and abrasion resistance are considered as a measure of enhanced filler reinforcement [30]. Silica-filled ENR modified NR vulcanizates show inferior abrasion resistance. This may be due to the higher glass transition temperature of ENR [31–33]. The vulcanizate containing 4g ENR show comparatively high abrasion resistance.

Addition of silane coupling agent to the silica filler increased the crosslink density (Table 3) apparently due to an increase in the interaction between silica and rubber [21]. Crosslink densities of the ENR modified silica-filled vulcanizates are higher compared to that of the unmodified silica-filled vulcanizate. This may be attributed to the fact that ENR can chemically react with both silica and rubber, improve filler-rubber interactions therefore increase crosslink density of the vulcanizates. Silane modified vulcanizate exhibited lower compression set, which can be attributed to the higher network density. Reduction in compression set of the vulcanizates was noted with the incorporation of ENR upto 4 g dosage and then increases.

C. Sorption studies

Swelling studies of the silica-filled NR vulcanizates with (silane and ENR) and without modifications were done in

toluene. Sorption curves of the vulcanizates are shown in Fig. 2. Silane modified silica-filled NR vulcanizate show lower uptake of solvent as compared to the ENR modified and unmodified silica-filled vulcanizate. This may be attributed to the larger crosslinks in the silane modified silica-filled vulcanizate.

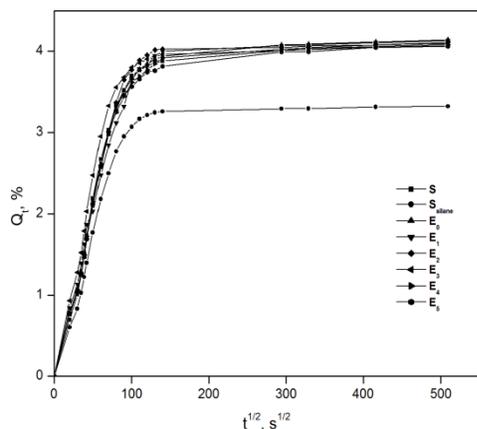


Fig. 2 Q_t vs. $t^{1/2}$ of silane modified, ENR modified and unmodified silica-filled NR vulcanizates

D. Bound rubber content

The bound rubber content (BRC) of the silane modified, ENR modified and unmodified silica-filled masterbatches was measured and shown in Table 4. The silane modification of silica enhanced the bound rubber content, indicating that the modification greatly improved the dispersion of silica and therefore better interaction between silica and natural rubber [21].

Closer values of bound rubber for the ENR modified silica-filled systems and silane modified silica-filled system indicate similar rubber-filler networking status for both. Thus ENR acts as the interface of silica and rubber thus enhancing the rubber-filler interaction. During mixing, a preferential adsorption of ENR over the silica surface might have taken place through the epoxy-silanol interaction or hydrogen bonding [34]. In ENR modified NR, silica would have dispersed well in the rest of the hydrocarbon matrix thus giving the possibility of better rubber-silica binding.

TABLE IV

BOUND RUBBER CONTENTS OF UNCURED MASTERBATCHES

Sample	S	S _{silane}	E ₀	E ₁	E ₂	E ₃	E ₄	E ₅
BRC (%)	30.32	33.78	31.01	31.98	32.08	32.43	33.21	33.32

E. Fluid resistance

The incorporation of silane coupling agent to the silica-filled natural rubber compound enhanced the fluid resistance of the vulcanizates in diesel and lube oil (Table 5). The changes in mass of the ENR modified vulcanizates are smaller compared to unmodified silica-filled vulcanizate, but larger compared to the silane modified vulcanizates. Apparently the volume fraction of absorbing phase is more exposed to oil in the case of ENR modified vulcanizates as evident from the higher value of change in mass as compared to silane modified vulcanizate. The reason for the decrease in change in mass of the vulcanizate after equilibrium swelling with the increase in the dosage of ENR may be due to the increase in the polarity of the vulcanizate.

TABLE V

CHANGE IN MASS (%) OF THE VULCANIZATES

Sample	S	S _{silane}	E ₀	E ₁	E ₂	E ₃	E ₄	E ₅
Increase in mass (%)	Diesel	220	185	208	206	204	203	202
	Lube oil	88	65	85	83	80	74	73

F. Scanning electron microscopy

When the silane coupling agent/ENR was incorporated into the silica-filled NR compound, good distribution of silica filler in the NR was obtained as compared to the SEM photomicrograph of the vulcanizate containing unmodified silica (Fig. 3).

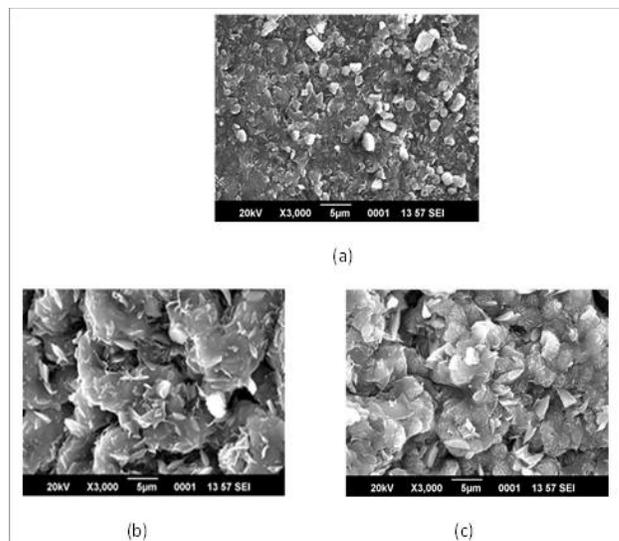


Fig. 3 SEM images of fractured surface of tensile samples of unmodified, silane modified and ENR modified (E₃) silica-filled NR vulcanizates

G. Thermogravimetric analysis

The Figs. 4 and 5 show the degradation behaviour of the silane modified, ENR modified and unmodified silica-filled NR vulcanizates. The results of TGA are summarised in Table 6.

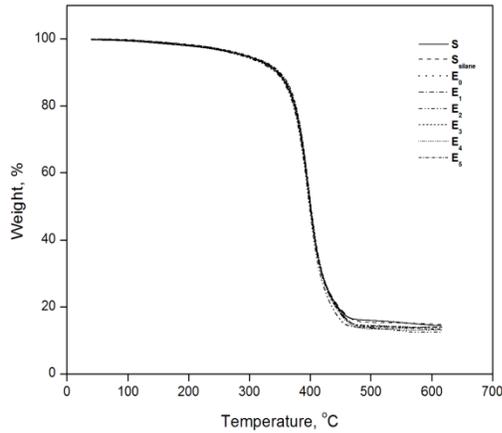


Fig. 4 Thermograms of silane coupled, ENR modified and unmodified silica-filled natural rubber vulcanizates

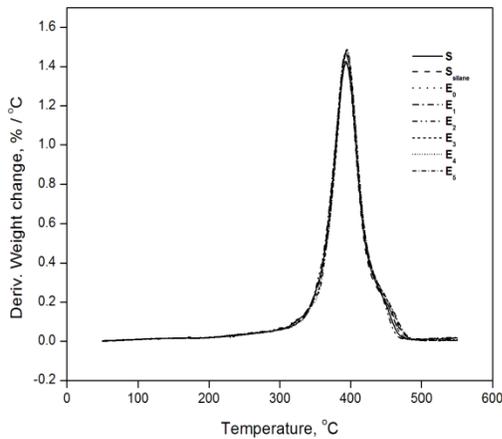


Fig. 5 Derivative thermograms of silane coupled, ENR modified and unmodified silica-filled natural rubber vulcanizates.

The results in the table show that epoxidised natural rubber and silane coupling agent did not contribute much to the thermal stability of silica-filled NR vulcanizates. It is observed that the onset of degradation temperature, temperature of maximum degradation and temperature of 50 % degradation are almost similar for silane modified silica-filled NR vulcanizate and the corresponding dosage of ENR modified silica-filled NR vulcanizate. Further addition of ENR (4g, 5g and 6g) increased marginally the onset of degradation and maximum degradation temperatures of the vulcanizates. The ENR modification of NR contributes to the effective interaction between the filler and the matrix and hence improves the interfacial adhesion. This makes the matrix thermally more stable in the presence of ENR at higher dosages.

TABLE VI

THERMAL DEGRADATION DATA

Sample	T _i (°C)	T ₅₀ (°C)	T _{max} (°C)	Weight loss at 500 °C (%)
S	353	402	394	84.0
S _{silane}	354	400	393	84.6
E ₀	353	400	392	85.6
E ₁	353	400	393	85.6
E ₂	353	401	393	85.6
E ₃	355	401	393	85.9
E ₄	358	401	394	86.6
E ₅	358	401	395	86.2

H. Strain sweep analysis

At very low strains, the complex modulus of the unmodified silica-filled compound is much higher than that of the compounds with silane and ENR modification as shown in Fig. 6, which is attributed to poor dispersion and strong filler-filler interaction of the silica in the NR matrix. With TESPT modification, the Payne effect of the silica-filled compounds is greatly reduced as more silica surface is hydrophobized by TESPT and the silica-silica network is disrupted [35].

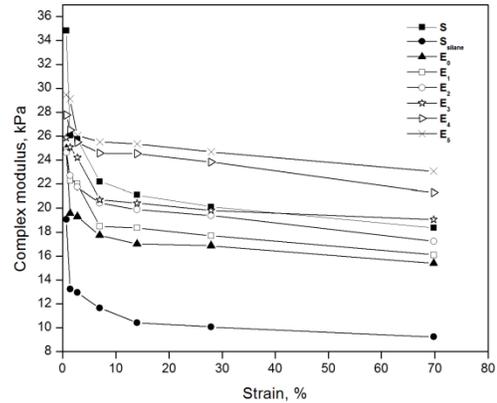


Fig. 6 Dependence of Complex modulus (G^*) on strain amplitude of uncured silane modified, ENR modified and unmodified silica-filled NR compounds

The difference between G^* at very low and high strains is always used as an indication of the Payne effect. The larger Payne effect (a larger difference in complex modulus at 0.7 and 70% strain) suggests the larger degrees of filler-filler interactions [18]. The introduction of TESPT consequently results in more silica-rubber interaction. ENR also has the ability to enhance the interaction between NR and silica, but it is not up to the level imparted by the silane coupling agent. The reduction of filler-filler interaction in the presence of ENR in silica-filled NR compounds can again be attributed to the interactions between the silanol groups of silica and epoxide groups of ENR through hydrogen bonding [36].

I. Dynamic mechanical analysis

Dynamic mechanical properties of the vulcanizates: silica-filled NR, silane modified silica-filled NR and silica-filled ENR modified NR were determined at a temperature range of 40-120 °C. Value of $\tan \delta$ at 60 °C (Table 7) gives information on rolling resistance. High performance rolling materials generally exhibit low $\tan \delta$ at 60 °C [6]. These materials show low rolling resistance.

TABLE VII

Tan δ VALUES OF UNMODIFIED, SILANE MODIFIED AND ENR MODIFIED SILICA-FILLED NR VULCANIZATES AT 60 °C

Sample	$\tan \delta$ at 60 °C
S	0.07
Si ₂	0.05
E ₃	0.06

The lower the $\tan \delta$ at 60 °C, the lower the rolling resistance expected in real performance of the material. It is observed from the table that silane and ENR modified silica-filled NR vulcanizates show lower rolling resistance compared to the unmodified silica-filled NR vulcanizate.

J. Cytotoxicity(MTT assay)

MTT assay is used for getting the percentage viability of cells and is used for finding the cytotoxicity of a material. Phase contrast image for determination of cell morphology of control of MTT assay and confluent cells containing extract of unmodified silica-filled NR vulcanizate, silane modified silica-filled NR vulcanizate and silica-filled ENR modified NR vulcanizate is shown in Fig. 7.

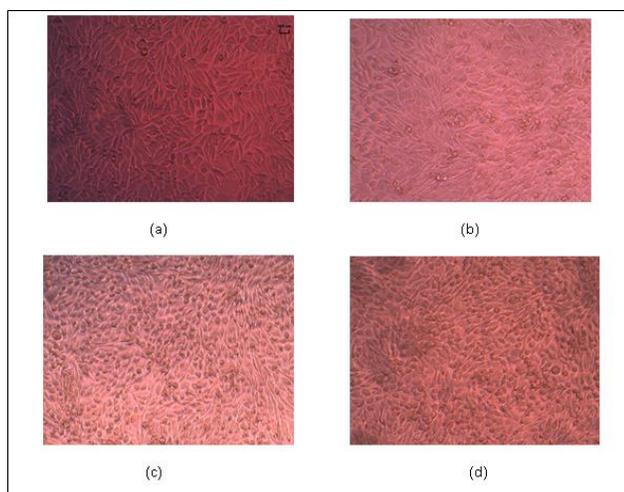


Fig. 7 Phase contrast image (magnification 20 x) for the determination of cell morphology of: (a) Control of the MTT assay, (b) extract of unmodified silica-filled NR vulcanizate, (c) extract of silane modified silica-filled NR vulcanizate and (d) extract of silica-filled ENR modified NR vulcanizate

Control of the MTT assay contains large number of fibroblast cells. The number of viable cells gets reduced in the case of

the confluent cells containing the extract of silane modified, ENR modified and unmodified silica-filled natural rubber vulcanizates after 24 hours incubation.

The samples containing extract of silane modified silica-filled NR vulcanizate, silica-filled ENR modified NR vulcanizate and unmodified silica-filled NR vulcanizate were found to contain 76.51 %, 70.17 % and 81.75 % of viable cells. The samples with less than 60 % viable cells are believed to be carcinogenic (moderately/severely toxic) [37, 38]. It is evident from the MTT assay that ENR modified and silane modified silica-filled NR vulcanizates are mildly cytotoxic (60-80 %) and unmodified silica filled NR vulcanizate is non-cytotoxic. Since the incorporation of silane coupling agent and ENR not produces moderate/severe toxicity (< 60 %) to the cells, the vulcanizates are believed to be safe.

IV. CONCLUSIONS

Silane-treated and ENR modified silica filled NR vulcanizates show shorter scorch time and cure time compared to the unmodified silica-filled vulcanizate. ENR modified vulcanizates show lower optimum cure time as compared to silane modified NR vulcanizates. The silane modification improved the tensile strength, reduced the penetration of solvent through the vulcanizate and contributed to higher crosslink density of the silica-filled vulcanizate. Silica-filled NR vulcanizates modified with ENR show higher tensile strength compared to the unmodified silica-filled natural rubber vulcanizate and comparable tensile strength at slightly higher dosage to that of silane modified silica-filled vulcanizate. Addition of the silane coupling agent and ENR enhanced the bound rubber content and improved the fluid resistance of the vulcanizates. Better distribution of silica filler in the NR was observed in SEM photomicrograph by the incorporation of silane coupling agent and ENR. With TESPT modification, the Payne effect of the silica-filled compounds is greatly reduced. From the strain-sweep analysis of uncured ENR modified compounds better polymer-filler interaction was observed. The thermal stability of the silica-filled vulcanizate shows marginal improvement with the incorporation of higher dosages of ENR. Addition of silane coupling agent and ENR results in low rolling resistance in the safe silica-filled NR vulcanizates. From the MTT assay it is observed that the incorporation of silane coupling agent and ENR produce mild cytotoxicity to the safe silica-filled natural rubber vulcanizates.

REFERENCES

- [1] Iavicoli, I. and Carelli, G., (2006), *J. Occup. Environ. Med.*, **48**, 195-198.
- [2] Fishbein, L., (1979), *Potential Industrial Carcinogens and Mutagens*, Elsevier Scientific Publishing Company, Netherlands.
- [3] Vieira, E.R., Pierozan, N.J. and Lovison, V., (2006), *Braz Arch Biol Technol*, **49**, 73-77.
- [4] Goss Jr., L.C., Monthey, S. and Issel, H.M., (2006), *Rubb. Chem. Technol.*, **79**, 541- 552.

- [5] Dannenberg, E. M., (1975), *Rubber Chem. Technol.*, **48**, 410.
- [6] Kaewsakul, W., *Ph.D. Thesis*, University of Twente, (the Netherlands), (2013).
- [7] Wagner, M. P., (1976), *Rubber Chem. Technol.*, **49**, 703.
- [8] Wang, M. J. and Wolf, S., (1992), *Rubber Chem. Technol.*, **65**, 715.
- [9] Wu, Y. P., Zhao, Q. S., Zhao, S.H. and Zhang, L. Q., (2008), *J. Appl. Polym. Sci.*, **108**, 112.
- [10] Edwards, D.C. and Sato, K., (1979), *Rubber Chem. Technol.*, **52**, 84.
- [11] Edwards, D.C. and Sato, K., (1980), *Rubber Chem. Technol.*, **53**, 66.
- [12] Mariamma, K. G., Varkey, J. K., Thomas, K. T. and Mathew, N. M., (2002), *J. Appl. Polym. Sci.*, **85**, 292.
- [13] Flory, P.J. and Rehner, J., (1943), *J. Chem. Phys.*, **11**, 5120.
- [14] Fotakis, G. and Timbrell, J.A., (2006), *Toxicol Lett.*, **160**, 171.
- [15] Gauthier, S., Aime, J.P., Bouhacina, T., Attias, A.J. and Desbat, B., (1996), *Langmuir*, **12**, 5126.
- [16] Li, Y., Han, B., Wen, S., Lu, Y., Yang, H., Zhang, L. and Liu, L., (2014), *Composites: Part A*, **62**, 52.
- [17] Brinke, J.W.t., Debnath, S.C., Reuvekamp, L.A.E.M. and Noordermeer, J.W.M., (2003), *Compos Sci Technol*, **63**, 1165.
- [18] Katueangnan, K., Tulyapitak, T., Saetung, A., Soontaranon, S. and Nithi-uthai, N., (2016), *Procedia Chemistry*, **19**, 447.
- [19] Sadequl, A. M., Ishiaku, U. S., Ismail, H. and Poh, B. T., (1998), *Eur. Polym. J.*, **34**, 51.
- [20] Xue, G., Koenig, J. L., Ishida, H. and Wheeler, D. D., (1990), *Rubber Chem. Technol.*, **64**, 162.
- [21] Thurn, F. and Wolff, S., (1975), *Kautsch. Gummi. Kunstst.*, **28**, 733.
- [22] Sarkawi, S. S., *Ph.D. Thesis*, University of Twente, (the Netherlands), (2013).
- [23] Brinke, A. ten, *Ph.D Thesis*, University of Twente, (the Netherlands), (2002).
- [24] Reuvekamp, L.A.E.M., *Ph.D. Thesis*, University of Twente, (the Netherlands), (2003).
- [25] Dierkes, W., *Ph.D. Thesis*, University of Twente, (the Netherlands), (2005).
- [26] Mihara, S., *Ph.D Thesis*, University of Twente, (the Netherlands), (2009).
- [27] Noordermeer, J.W.M. and Dierkes, W.K., (2008), *Rubber Technologist's Handbook, Vol.2*, (Eds.: J. White, S.K. De and K. Naskar), Smithers Rapra Technology, Shawbury, UK, pp. 59-88.
- [28] Cataldo, F., (2002), *Macromol. Mater. Eng.*, **287**, 348.
- [29] Varghese, S. and Tripathy, D. K., (1992), *J. Appl. Polym. Sci.*, **44**, 1847.
- [30] Gent, A. N., (1994), *Science and Technology of Rubber*, (Eds: J. E. Mark, B. Erman, F.R. Eirich), Academic Press, San Diego, U.S.A., Ch. 10, P.471.
- [31] Brydson, J. A., (1995), *Speciality rubbers, Rapra review reports-Expert overviews covering the science and technology of rubber and plastics*, Rapra Technology Limited, Shawbury, UK, p.20.
- [32] Groves, S., (1998), *Blends of Natural Rubber*, (Eds: A.J. Tinker, K.P. Jones), Chapman and Hall, London, Ch.10, P.128.
- [33] Chapman, A.V., (2007), *Natural rubber and NR-based polymers: renewable materials with unique properties*, 24th International H.F. Mark-Symposium, 'Advances in the Field of Elastomers & Thermoplastic Elastomers', Vienna, 15-16 November.
- [34] Sarkawi, S. S., Aziz, A. K. C., Rahim, R. A., Ghani, R. A. and Kamaruddin, A. N., (2016), *Polym Polym Compos.*, **24**, 775.
- [35] Saramolee, P., Sahakaro, K., Lopattananon, N., Dierkes, W.K. and Noordermeer, J.W.M, (2016), *J. Elastom Plast.*, **48**, 145.
- [36] Manna, A. J., De, P.P., Tripathy, D. K., De S. K. and Peiffer, D. G., (1999), *J. Appl. Polym. Sci.*, **74**, 389.
- [37] Elizabeth, K. A., *Ph.D. Thesis*, Sree Chitra Tirunal Institute for Medical Sciences and Technology, (Thiruvananthapuram, India), (2005).
- [38] Baek, H. S., Yoo, J. Y., Rah, D. K., Han, D.W., Lee, D. H., Kwon, O. H. and Park, J.C., (2005), *Yonsei Med J.*, **46**, 579.