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PHYSICO-MECHANICAL PROPERTIES OF ELASTOMERS BASED ON NATURAL RUBBER FILLED WITH SILICA AND CLAY

Elastomers based on natural rubber (NR) and silica and clay fillers have been investigated for their physico-mechanical properties. The various mixes were compounded in a Banbury-Pullen laboratory mill and vulcanized using the efficient vulcanization system. The oscillating disc rheometer (ODR) was used for determination of cure characteristics. It was estimated that replacement of silica with clay up to 30 phr (50% replacement) increased the compound cure rate with a reduction in absolute torque level (T_{max}) of the natural rubber mix. Scorch time (Ts2) was observed to be the highest at a 30/30 filler ratio. Hardness and tensile properties of obtained elastomeric materials were studied. The results show a decrease in parameters as the replacement of silica with natural clay progresses. There was improvement in elongation at break with the increase of clay content. The replacement of silica filler with clay reduced the abrasion properties (mg loss/1000 rev.)

Key words: silica; clay; rubber; processing safety; physico-mechanical properties.

Clays are derived from natural deposits and are essentially hydrated aluminium silicates, containing certain groups of hydrous magnesium, iron, sodium, calcium, potassium, and other ions [1]. They are inexpensive natural minerals and have been used as non-black filler for rubber and plastic to improve processability by reducing nerve in improving shaping operations and ensuring dimensional stability in unvulcanized stocks [2,3] for many years. It has also recently been used in foundry sand moulds where it was reported to substantially improve mechanical properties [4]. The consumption of nonblack fillers in the rubber industry is known to be in millions of tons per year [5]. Silica, on the other hand, is prominently used as filler in many rubber wares due to its appreciable ability to reinforce the elastomers while maintaining excellent abrasion resistance. But, its high cost and heat build-up problems which cause deterioration of material properties have been of concern to its users [6-9]. In this study the clay and silica were used as fillers in natural rubber compounds. The aim of the project was to determine the influence of filler mass ratio, silica/clay ratio on curing and mechanical properties of elastomers based on natural rubber.

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EXPERIMENTAL

Natural rubber (NR) was obtained from the Rubber Research Institute of Nigeria (RRIN) plantations situated at Iyanomo, near Benin City, Nigeria. The clay was collected form a deposit in Edo Central Senatorial district of Nigeria. Air dried (49±5 °C), pulverized and sieved through mesh size 300 μm. X-ray diffraction (XRD) recorded from monochromatic X--rays (MD 10 mini diffractometer), with Ni-filter CuKα radiation and automatic slit analyzed using Bragg--Wulf equation ($\lambda = 2d\sin\theta$), where λ is the X-ray wavelength, d is the interlayer spacing, and θ is the angle of diffraction in combination with the International Center for Diffraction Data (ICDD) identification chart showed a mineral complex comprising of chondrodite, $Mg_3Fe_{½}{\cdot}SiO_4{\cdot}H_2O$, titanian, $TiO_4{\cdot}SiO_4{\cdot}H_2O$ and kaesutite, $NaCa_2MgFe)_4TiSi_6Al_2O_{22}(OH)_2$, with a 1:1 tetrahedral lattice [5]. Some physico-chemical properties of the clay sample are given in Table 1. Formulations of five types of compounds are given in Table 2. The compounding ingredients (zinc oxide, stearic acid, paraffin oil, silica, etc.) were purchased from Berk Chemicals UK. Silica (vulkasil S) having a

particle size around 30 nm, and density 2.00 g cm^{-3} was used in the experiments.

Table 1. Physicochemical characteristic of clay

Particle size distribution (PSA)[a]	Content, mass%
Clay	83
Sand	10
Silt	7
Colour	Grayish-brown
Density of clay, gcc^{-3}	2.62
Density of silica, gcc^{-3}	2.00
SiO_2	38.48
Al_2O_3	12.46
Fe_2O_3	6.18
TiO_2	1.85
MgO	14.67
CaO	12.05
Na_2O	1.42
K_2O	9.57
Loss on ignition	13.5
pH	7.43

[a]According to the USDA [22]

Mixing

Mixing of rubber compounds was carried out in a laboratory two roll mill (Banbury-Pullen, model, 35100). The mill opening was set at 1.4 mm, and the initial temperature of the mill was set at 80±5 °C. The mixing involved a two stage operation. In the first step an initial banding of natural rubber on the front roll of a two roll-mill, followed by ¾ cuts on both sides of the band, followed by adding the half content of fillers, then zinc oxide, stearic acid, paraffin oil and wax, allowed to mix properly for 5 min. This was followed by the incorporation of the remaining ingredients and 6PPD for a further 3.5 min. In the final step the addition of accelerator and vulcanizing agents (CBS and sulphur) for 2.0 min was done after the stock was allowed to cool to 70 °C.

Cure behavior determination and sample preparation

The aptitude to vulcanization of rubber compounds was determined on Alpha Oscillating Disc Rheometer (ODR 2000) using a 1° rotor oscillating amplitude and frequency 50 Hz [10]. The cure rate index (CRI) [11] and other parameters of the cure were estimated from obtained rheographs. The elastomeric samples were obtained by compression moulding at 140 °C using electric heated hydraulically operated press for various times extrapolated from the rheographs.

Mechanical properties characterization

Hardness

The hardness tests of the rubber vulcanizates were carried out in accordance to BS 903 (ISO 7619), with an international rubber hardness tester. Specimens with a thickness of 6mm were tested at room temperature. The reported values are based on the average of five measurements [12].

Tensile properties

Dumbbell-shaped samples were cut from the molded sheets, according to BS 903, Part A2 (DIN 53504). Tensile properties: M100, M200 and tensile strength (TS) were determined at room temperature on Zwick/Roell testing machine Z005 with crosshead speed of 200 mm/min [13].

Abrasion resistance test

The abrasion test was carried out in accordance to BS 903, Part A9, consisting of a trial run, a running-

Table 2. Formulation for investigating clay/silica filled NR rubber compounds (adopted model formulation from Malaysian Natural Rubber Producers Research Association (MRPRA) Technical bulletin sheet D 105 D117, for manufacture of general mechanical goods, which include variety of products like hose, conveyor belts, rubber linings, gasket seals, rubber rolls, rubberized fabrics etc.)

Component	Phr	Phr	Phr	Phr	Phr
1. Natural Rubber	100	100	100	100	100
2. Paraffin oil	10	10	10	10	10
3. Clay	0	20	30	40	60
4. Silica[a]	60	40	30	20	0
5. Zinc Oxide	10	10	10	10	10
6. Stearic acid	2	2	2	2	2
7. 6PPD[b]	1.5	1.5	1.5	1.5	1.5
8. Wax	1.5	1.5	1.5	1.5	1.5
9. CBS[c]	0.6	0.6	0.6	0.6	0.6
10. Sulphur	2.8	2.8	2.8	2.8	2.8

[a]Silica (vulkasil S); particle size: ≈ 30 nm; [b]*N*-(1,3-dimethylbutyl)-*N*-phenyl-*p*-phenylenediamine; [c]*N*-cyclohexyl-2-benzothiazole sulfenamide. (All chemicals were purchased from Berk chemicals UK, Ltd.)

-in period and five test runs. Absolute value of abrasion loss was the mean value determined from the five test runs expressed as milligrams per 1000 revolutions of the abrasive wheel [14].

RESULTS AND DISCUSSION

The rheological properties during cross-linking of the natural rubber filled with mix compositions of silica and clay are shown in Figure 1 and all estimated data are given in Table 3. It has been stated that ODR is a convenient technique for the functional evaluation of fillers for their reinforcing potentials [15-17]. The silica filled compound had the highest minimum torque (*ML* = 22.23 d N m), *ML* for other compounds silica/clay loading, were at 40/20 phr (40% replacement loading); 13.98 d N m, 30/30 phr (50% replacement loading); 9.42 d N m, 20/40 phr (60% replacement loading); 7.89 d N m, and 0/60 phr (100% replacement loading); 3.91 d N m, respectively. Since *ML* is a measure of effective viscosity of unvulcanized mix, the results show that the stiffness as well as the viscosity of the uncured compound is reduced as the clay content increases. This effect correlates the hydrodynamic equation [15]:

$$\eta_f = \eta_u(1 + 2.5c + 14.1c^2) \quad (1)$$

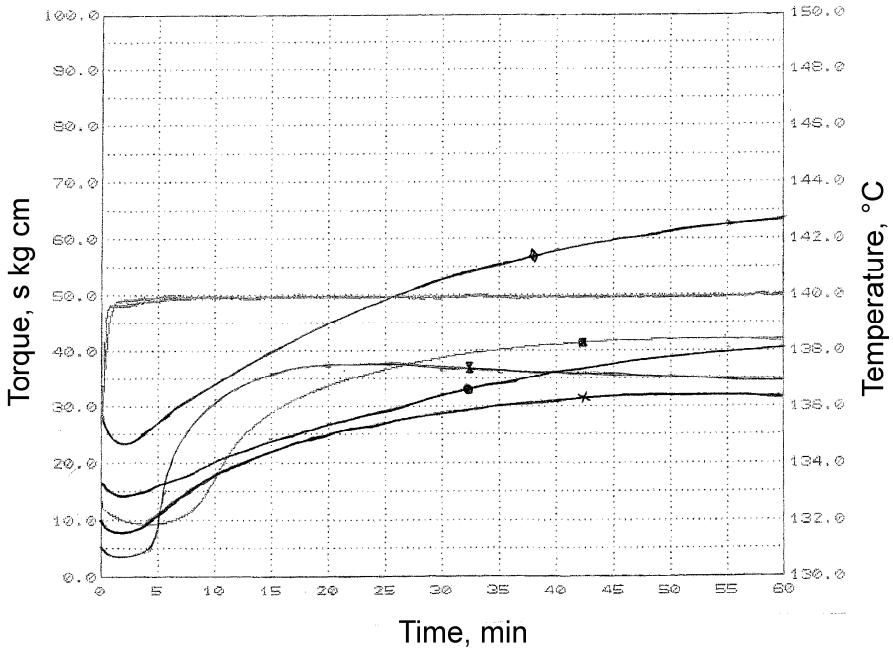


Figure 1. Rheographs at 140 °C (arc. 1°) of varying filler mix compositions in phr; ♦ - silica/clay 60/0, ● - silica/clay 40/20, ■ - silica/clay 30/30, x *- silica/clay 20/40,* ⁎ *- silica/clay 0/60.*

Table 3. Cure characteristics of natural clay /silica filled NR (compound mix: rubber, NR (100), paraffin oil 10, Stearic acid 2.0) rubber compounds; ML - minimum torque; MH - maximum torque; CRI - cure rate index, 100/(T_{90} - T_{s2}); t_{s1} - time to 1 unit rise above ML; t_{s2} - time to 2 unit rise above ML; t_{s10} - time to 10 units rise above ML; t_{90} - time to maximum cross linking

Cure properties	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5
Clay	0	20	30	40	60
Silica	60	40	30	20	0
t_{s1} / min	3.19	3.05	6.53	3.44	3.55
t_{s2} / min	3.50	3.51	7.49	4.18	4.13
t_{10} / min	4.48	4.28	8.33	12.30	6.21
t_{50} / min	16.53	21.21	13.03	12.30	6.21
t_{90} / min	41.46	48.02	30.19	34.25	12.14
Absolute torque level (T90+ML), T_{max}	63.69	62.0	36.61	42.14	16.05
CRI	2.63	2.25	4.41	3.33	12.48
ML / kg cm	22.23	13.98	9.42	7.89	3.91
MH / kg cm	62.74	41.34	42.23	32.57	37.46
(*MH* - *ML*) / kg cm	40.51	27.36	32.81	24.68	33.55

where η_f and η_u are the viscosities of the filled and unfilled compounds, and c is the volume fraction of the fillers. From Eq. (1) it is obvious that viscosity is expected to increase with increase in filler loading (volume fraction). However, viscosity is also dependent on the silica/clay interactions and between the elastomer network and fillers.

Scorch times (t_{s2} in Table 3) for samples with various filler ratio of silica and clay (60/0, 40/20, 30/ /30, 20/40 and 0/60) were 3.50, 3.51, 7.49, 4.18 and 4.13 min, respectively. The highest value was observed at 30/30 phr (50% replacement loading). This is a valuable assessment to the compounding recipe as it gives compounds processing safety [18]. This scorch retarding effect can be observed as the clay fraction increases in the mix formulation. Some acids substances like phthalic anhydride (at 0.5-2.0 phr), other been *N*-nitrosodiphnylamine (at 1-5 phr) have been used as retarders [19] in NR mix. Silica is known to exhibit a cure retarding effect when incorporated as filler in mixes cured using the efficient vulcanization system [20]. The extent of vulcanization is measured by maximum torque (MH). A high rheometric torque, which is a measure of crosslinking degree, was observed for the control mix (60 phr silica) without clay. Replacement of silica with clay up to 50% replacement, *i.e.* 30/30 phr increased the cure rate of natural rubber as well as their MH.

The vulcanizate properties of NR filled with mix blends of silica and clay used in this investigation are shown in Figures 2-7. The all-silica, 0% clay (control mix) exhibited the characteristic reinforcing property of silica fillers. In general, there was an observed decrease in tensile properties as the clay gradually replaced silica in compounds. Hardness (Figure 1) and tensile stress properties (Figures 3-5) which included M100, M200, and tensile strength (TS) followed the same sequence of reduction. There was marked reduction in hardness (from 24-54%) as replacement progressed through 40/20, 30/30, 20/40, and 0/60 phr of silica/clay in the filler mix. The M100 showed a reduction from 11 to 74%, while M200 showed a reduction from 20 to 86.4% and tensile strength (TS) indicated a reduction from 12.3 to 78.7% as the clay increased in the mix, respectively. Particle sizes of fillers play significant role in coupling of filler to polymer. As the particle size of fillers in a polymer compound decreases, its resilience and strength decreases while the abrasion is increased [21]. This also by extension corroborates the effect on the abrasion in mg loss/1000 revolutions, Figure 7, as the clay in the filler mix increases. However, there was improved extension in the mixes as the clay in the formulation increases. As it can be seen from Figure 6 elongation at break were 190, 223, 238, 245 and 350% for the 60/0 phr (100% silica loading), 40/20 phr (40% replacement loading), 30/30 phr (50% replacement loading), 20/40 phr (60% replacement loading) and 0/60phr (100% replacement loading), respectively.

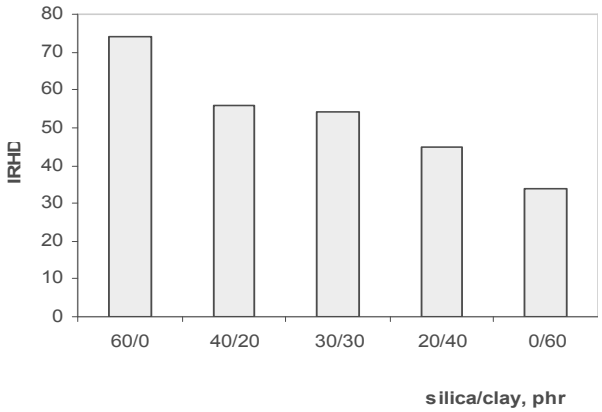


Figure 2. Comparative values for hardness of NR vulcanizates filled with different ratio mix of silica and clay.

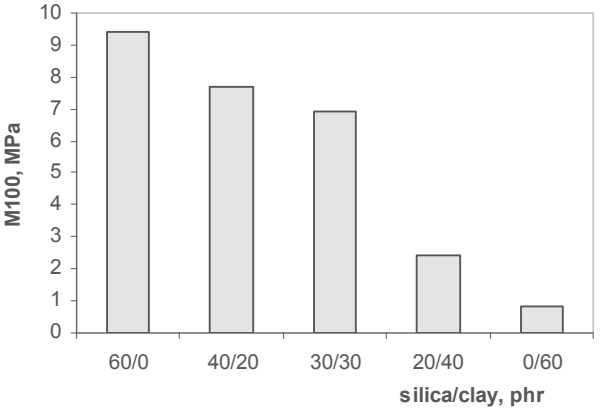


Figure 3. Comparative values for M100 of NR vulcanizate filled with different ratio mix of silica and clay.

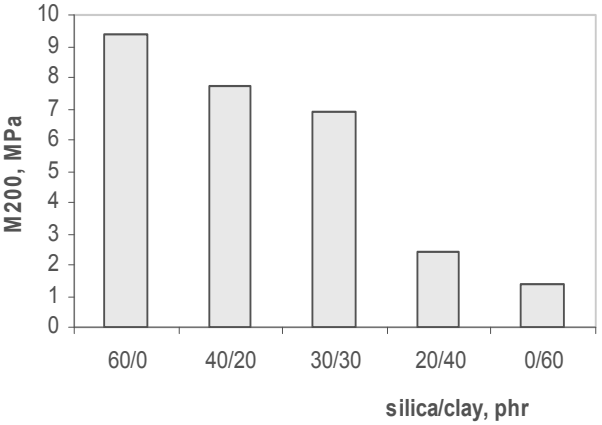


Figure 4. Comparative values for M200 of NR vulcanizate filled with different ratio mix of silica and clay.

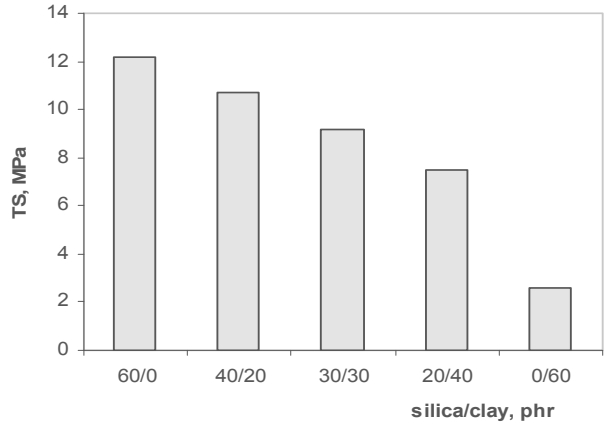


Figure 5. Comparative values for tensile strength, TS of NR vulcanizates filled with different ratio mix of silica and clay.

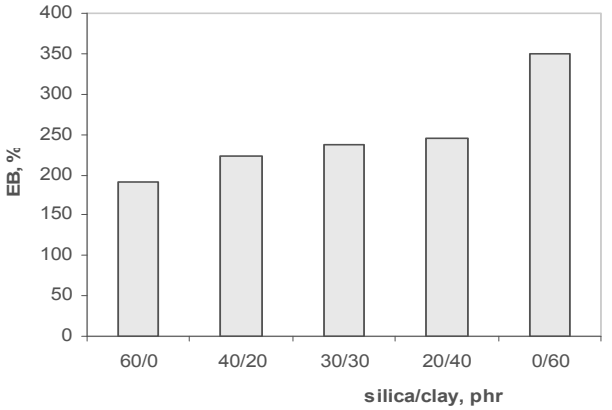


Figure 6. Comparative values for elongation at Break EB (%) of NR vulcanizates filled with different ratio mix of silica and clay.

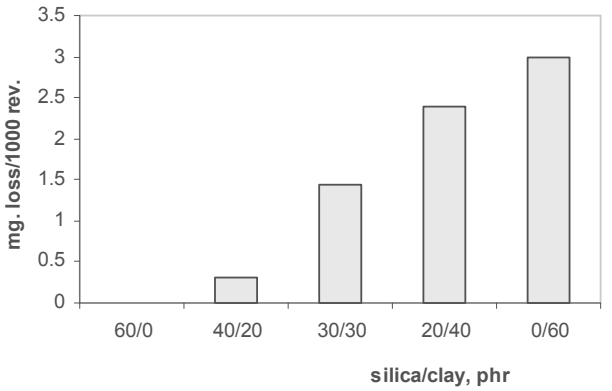


Figure 7. Comparative values for abrasion (mg loss/1000 rev.) of NR vulcanizate filled with different ratio mix of silica and clay.

CONCLUSION

In this study, elastomeric materials reinforced with silica and clay mixes were prepared by changing filler ratio in natural rubber compound formulations. For the five filler mixes studied, the filler ratio 30/30 phr (50% clay replacement) exhibited the optimal scorch time (7.49 min), a condition indicative for good processing safety. Silica fillers are used in a lot of rubber articles such as hose, cables, footwear uppers, mechanical goods and therefore the use of clay particles together with silica may find acceptability in rubber industry in areas requiring processing safety.

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NAUČNI RAD

FIZIČKO-MEHANIČKA SVOJSTVA MEŠAVINA PRIRODNOG KAUČUKA, SILICIJUM-DIOKSIDA I PRIRODNE GLINE

Ispitivane su fizičko-mehanička svojstva elastomera baziranim na prirodnom kaučuku i puniocima tipa silicijum dioksida i gline. U laboratoriji Banbury-Pullen pripemljene su različite mešavine koje su podvrgnute vulkanizaciji. Karakterizacija vulkanizata je vršena pomoću oscilujućog disk reometra (ODR). Utvrđeno je da zamena silicijum dioksida glinom do 30 phr (50% zamene) povećava brzinu vulkanizacije mešavine uz smanjenje stepena obrtnog momenta (Tmax) prirodne gume. Vreme sušenja (Ts2) je najveće pri odnosu punilaca 30/30. Proučavane su, takođe, tvrdoća i sila zatezanja dobijenih elastomera. Rezultati pokazuju smanjenje navedenih parametara zamenom silicijum-dioksida prirodnom glinom. Postoji izvesno poboljšanje u prekidnom istezanju sa povećanjem količine gline. Zamena silicijumovog punioca prirodnom glinom smanjuje abrazivne osobine (mg gubitaka/1000 rev.).

Ključne reči: silicijum-dioksid; glina; guma; bezbedna obrada; fizičko-mehaničke karakteristike.