

Influence of Clay, Silicate and Carbon Black on the Environmental Resistance Properties of Hard Rubber

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The effects of clay, silicate, and carbon black on the environmental resistance properties of hard rubber were investigated in this study. A laboratory electrolytic cleaning tank immersion test was conducted to evaluate the environmental resistance ability of all compositions. The experimental results showed that carbon black had the best hardness and resistivity stability after the immersion test. The optimum carbon black content in clay/carbon black-filled hard rubber sample is 45 phr when total filler content is either 105 or 120 phr. The silicate/carbon black-filled hard rubber samples in this study cannot pass the electrolytic cleaning tank immersion test.

Keywords: Hard rubber, Electrolytic cleaning, Carbon black, Resistivity

1. INTRODUCTION

Hard rubber, also called ebonite, is one kind of rubber with a glass transition temperature (T_g) higher than room temperature; it is prepared by long-time curing with a much higher content of sulfur than those used in common rubbery products. Hard rubber possesses high resistance to chemicals, good electrical insulating properties, excellent strength properties, and the ability to be machined easily, which leads to wide applications, such as pipe lines, storage tanks, reaction vessels, rollers, and pump linings⁽¹⁾. In the steel cold rolling process, hard rubber linings have been used successfully in the electrolytic cleaning tank corrosion-resistant linings on account of its excellent chemical and temperature resistance⁽²⁾.

The nature of the rubber and the mechanical and chemical properties of its vulcanizates are the important factors that affect the efficiency of the rubber lining. When used as an electrolytic cleaning tank lining in the steel plant, the insulation property is another important property that must be considered. By far the best known hard rubber is that produced from NR (natural rubber), although hard rubber can easily be produced from both SBR (styrene-butadiene rubber) and NBR (nitrile-butadiene rubber)⁽³⁾.

Although natural rubber exhibits numerous outstanding properties, such as high mechanical strength,

excellent elasticity, good abrasion resistance, good low temperature resistance, and good electrical insulation⁽⁴⁾, reinforcement fillers are necessarily added into NR in most cases in order to gain the appropriate properties for some specific applications. A wide variety of particulate fillers are used in the rubber industry for various purposes, of which the most important are reinforcement, the reduction in materials costs and improvements in processing⁽⁵⁾. The most common fillers in the rubber industry are CB(carbon black), mineral fillers (such as calcium carbonate, silica, clay, talc, and baryte), and synthetic fillers (precipitated calcium carbonate, metal oxides, precipitated silica, silicates)⁽⁶⁾.

In the 1960's, there were intensive investigations into hard rubber regarding the effective vulcanization process. Meltzer studied the influence of fillers and degree of vulcanization on the mechanical properties of hard styrene-butadiene rubber (SBR) – butyl rubber. T_g is found increasing with the degree of vulcanization⁽⁷⁾. Meltzer also reported the fraction of sulfur atoms effective in crosslinking is 0.04–0.07 and 0.10–0.13 in hard rubber for natural rubber and SBR, respectively⁽⁸⁻⁹⁾. For cis-polybutadiene rubber, the fraction turns from 0.06 to 0.17 and for trans-polybutadiene rubber it turns from 0.07 to 0.16⁽¹⁰⁾. Bhaumik et al. developed a method to determine the reaction heat during the curing by differential thermal analysis(DTA); heat evolution was found first in samples containing about 7% sulfur

and thereon the amount of heat evolved shows a nearly linearly increase up to 30% sulfur⁽¹¹⁻¹⁴⁾.

Recent studies on natural rubber blends have showed great interest in the synergistic effect of carbon black⁽¹⁵⁾, silica⁽¹⁶⁻¹⁷⁾, clay⁽¹⁸⁻²⁰⁾, carbon nanofiber⁽²¹⁾, and mica⁽²²⁾ on the curing characteristics and chemical resistance, as well as on the physical properties of the filled natural rubber. These research efforts are briefly reviewed below.

Rattanasom et al. studied the mechanical properties, heat ageing resistance, cut growth behavior and morphology of natural rubber which had been prepared by a partial replacement of the calcined clay with different amounts of various types of carbon black. At similar hardness, the compounds containing both clay and carbon black give the better tensile strength, edge-cut tensile strength, tear strength and thermal ageing resistance compared to the control⁽¹⁵⁾. Sung-Seen Choi investigated the influence of the modification of silica on the retraction behaviors of natural rubber vulcanizates reinforced with silica and carbon black. The vulcanizates containing the silane coupling agent recovered faster than those without the silane coupling agent⁽¹⁶⁾. Rattanasom et al. examined the mechanical properties of natural rubber reinforced with silica/carbon black hybrid filler at various ratios in order to determine the optimum silica/carbon black ratio. The results revealed that the vulcanizates containing 20 and 30 phr of silica in hybrid filler exhibit the better overall mechanical properties⁽¹⁷⁾. Rattanasom et al. also measured the mechanical properties at similar hardness levels of natural rubber vulcanizates filled with various reinforcement fillers. The results showed that higher amounts of carbon black and silica are needed to achieve the same hardness value as a natural rubber vulcanizate containing montmorillonite clay. At equal loading of fillers, clay-filled vulcanizate exhibits higher modulus, hardness, tensile strength and compression set. For the vulcanizates having the same hardness value, a carbon black-filled vulcanizate gives the better overall mechanical properties⁽¹⁸⁾.

Liangliang Qu et al. studied the synergistic reinforcement of nanoclay and carbon black in natural rubber. A synergistic effect in reinforcement between nanoclay and carbon black was proven by the marked enhancement in tensile strength from 11.4MPa for neat natural rubber to 28.2MPa for natural rubber nanocomposite with 5wt% nanoclay and 20wt% carbon black⁽¹⁹⁾. Jia et al. found that the mechanical properties of natural rubber filled with both clay and carbon black were greatly superior than those of either natural rubber/clay nanocomposites or natural rubber/carbon black nanocomposites⁽²⁰⁾.

Bhattacharya et al. investigated ternary nanocomposites obtained from consolidation of NR/nanoclay

and NR/carbon nanofiber (CNF) nanocomposites with different loadings and grades. It was observed that the mechanical and dynamic mechanical properties of these nanocomposites were much better than those of either NR/clay or NR/CNF nanocomposites or of the NR/CB control microcomposite⁽²¹⁾. Daniele F. Castro et al. studied the effect of the mixing procedure and mica addition on the mechanical and dynamic mechanical properties. The results showed that the mechanical properties are sequence-dependent. It was also observed that an addition of mica improves the mechanical properties⁽²²⁾.

Apart from the above intensive studies of various fillers, there has been no report on the influence of the fillers in hard rubber on its environmental resistance properties, such as the chemical resistance and the insulation properties. Since the effects of fillers are not the same for all rubbers, different physical properties have their optimum value associated with different optimum filler loadings. Moreover, rubber materials reinforced by only one kind of filler cannot satisfy the increasingly complicated industrial applications which usually demand materials that possess various outstanding properties⁽¹⁹⁾.

The main purpose of this study was to obtain a better hard rubber compound that can be used in the severe corrosion environment of the electrolytic cleaning process as electrolytic cleaning tank rubber linings. In this study, the influence of clay (Windsor clay), silicate (Sillitin N85) and carbon black (Medium Thermal carbon black, N990) on the physical and resistivity properties of hard rubber were investigated. The effects of the type and the ratio of fillers on various environmental resistance properties were systematically studied and the results presented. The ratio of carbon black in co-filler filled hard rubber vulcanizate that gave better overall environmental resistance properties is also reported.

2. EXPERIMENT

2.1 Materials

NR (Natural rubber, similar to RSS3) was obtained from Oak Union Trading Co., Ltd. Clay (Windsor Clay) was available from the Kentucky Tennessee Clay Company. Silicate (Sillitin N85) was available from Hoffmann Minerals GmbH. Carbon Black (Medium Thermal carbon black, N990) was available from Cancarb Ltd. S6H (Trade name 'Pliolite') was available from Eliokem Inc. Milbar D45 was supplied by Asian Mineral Resources Co., Ltd. 318M (Trade name 'Bayferrox') was available from Lanxess Corp. ZnO was supplied by Chi Fung Chemical Industrial Co., Ltd. Accelerant TMTD was obtained from the Sovmer Chemical Company. Sulfur was supplied by Suan

Huang Co., Ltd. SA (Stearic Acid) was commercially available. Electrolytic cleaning agent (VR6393) was supplied by Henkel Taiwan Ltd.

2.2 Formulations and vulcanization

The rubber recipes used in this study are shown in Table 1. The chemical compositions of the main components of the materials and accelerants used in this study are shown in Table 2. It should be noted that the samples in Table 1 can be divided into three categories. The first three samples are single filler-filled vulcanizates. N112 to N117 are clay/carbon black or silicate/carbon black co-filler-filled vulcanizates with total filler contents of 120 phr and where the amount of carbon black ranges from 45 to 60 phr. N124 to N130 are clay/carbon black co-filler-filled vulcanizates with total filler contents of 105 phr and where the amount of carbon black ranges from 15 to 105 phr.

Natural rubber was mixed with additives by Brabender Plasticorder (Model PLE-330, mixing chamber Model W50-EHT, chamber volume 50cm³, chamber

temperature 70°C, mixing speed 20rpm, mixing time 7 minutes) and then the compound was cured at 150°C for 2 hours in an electrically heated platen press.

2.3 Laboratory Electrolytic Cleaning Tank Immersion Test

The vulcanized hard rubber samples were submerged in a laboratory electrolytic cleaning tank for 28 days. The volume of the cleaning tank was 30L(W 40cm x D 20cm x H 37.5cm). The electrolytic cleaning agent in the cleaning tank was Henkel VR6393 with total alkali content being 3.0±0.5%. The electrolytic current density was 1.89A/dm². The temperature of the electrolytic cleaning agent solution was 85°C. The sample size for the immersion test was 9cm(L) x 9cm(W) x 0.5cm(t).

The samples were washed by tap water and air-dried at room temperature after submersion. The weight, density, hardness, and resistivity were then measured. The sample weight was measured with 0.1 mg accuracy. The weight variations of the samples

Table 1 The recipes in this study

Content(phr)	N70	N73	N86	N112	N113	N114	N115	N116	N117	N124	N125	N126	N127	N128	N129	N130
NR(Natural rubber)	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Clay (Windsor clay)	90			60	75	90				90	75	60	45	30	15	
Silicate (Sillitin N85)		90					60	75	90							
Carbon black(N990)			90	60	45	30	60	45	30	15	30	45	60	75	90	105
S6H	40	40	40													
Milbar D45				15	15	15	15	15	15	15	15	15	15	15	15	15
318M				15	15	15	15	15	15	15	15	15	15	15	15	15
SA	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
ZnO	5	5	5	3	3	3	3	3	3	3	3	3	3	3	3	3
Accelerant TMTD	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Sulfur	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45
Total amount	288	288	288	306	306	306	306	306	306	291	291	291	291	291	291	291

Table 2 The chemical compositions of main components of the materials and accelerants used

Materials and accelerants	Chemical composition of main components (typical value)
Windsor clay	SiO ₂ 45.21%, Al ₂ O ₃ 37.75%, Fe ₂ O ₃ 1.01%, TiO ₂ 1.97%
Sillitin N85	SiO ₂ 84%, Al ₂ O ₃ 10%, Fe ₂ O ₃ < 1%
S6H	Styrene butadiene resin (Styrene/Butadiene 82.5%/17.5%)
Milbar D45	Barium sulphate (BaSO ₄)
318M	Iron oxide (Fe ₂ O ₃ 85~95%)
SA	Stearic acid
ZnO	Zinc oxide (min. 99.5%)
Accelerant TMTD	Tetramethylthiuram disulfide

were calculated as follows:

$$\begin{aligned} \text{Weight variation} &= W\% \\ &= (W_2 - W_1) / W_1 \times 100 \dots\dots\dots (1) \end{aligned}$$

Where W_1 is the initial weight of the sample and W_2 is the weight of the sample after being submerged in the electrolytic cleaning agent VR6393 solution. The volume of the sample was calculated from dividing the weight by the density. The variations of volume (V%), and hardness (H%) were also calculated using Equation (1).

2.4 Characterization

Cure Characteristics

The cure characteristics, which are the scorch time (t_{s2}), cure time (t_{90}), minimum torque (M_L), and maximum torque (M_{H1}) of the hard rubber sample were determined at 150°C for 2 hours with a moving die rheometer (MD 3000A, GOTECH) in according to ASTM D5289. About 6g of rubber sample were tested with a $\pm 1^\circ$ oscillation arc.

Thermogravimetric (TG) analysis

Thermal degradation analysis of the natural hard rubber samples was carried out using a Perkin-Elmer Pyris Diamond thermogravimetric analyzer. The weight of the sample was about 10mg. The weight change of the sample was investigated throughout the entire heating process. A two step heating procedure was conducted in this study. In the first step, the temperature of samples was heated from 30°C to 600°C, at a heating rate of 20°C/min in a nitrogen atmosphere, and held at 600°C for 3min. In the second step, the temperature of the samples was heated from 600°C to 850°C, at a

heating rate of 20°C/min in an air atmosphere, and held at 850°C for 5min. The first derivative of the thermogravimetric curve was calculated using the built-in software.

Hardness

The hardness shore test was carried out using a Teclock Shore D durometer (GS-702N, Type D) according to ASTM D2240.

Density measurement

The density of all rubber samples was calculated via Archimedes's principle with the following equation:

$$\rho = \rho_1 \times (W_a / (W_a - W_b)) \dots\dots\dots (2)$$

where ρ is the density of the rubber sample; ρ_1 is the density of the buoyant (water); and W_a and W_b are the sample weight in air and in the buoyant, respectively.

Resistivity measurement

The resistivity of the sample was measured by a Hioki Super Megohmmeter SM-8220 with SME 8310 Plate Sample Measurement Electrode. The sample size was 9cm (L) x 9cm (W) x 0.5cm (t), the same as the immersion test sample. The volume resistivity (ρ_v , ohm-cm) and the surface resistivity (ρ_s , ohm) of the sample were calculated as follows:

$$\text{Volume resistivity}(\rho_v) = (19.6 / t) \times R_v \dots\dots (3)$$

$$\text{Surface resistivity}(\rho_s) = 18.8 \times R_s \dots\dots\dots (4)$$

where t (cm) was the thickness of the sample; R_v (ohm) was the volume resistance measured; R_s (ohm) was the surface resistance measurement.

3. RESULTS AND DISCUSSION

Table 3 Curing characteristics of Windsor clay-, N85- and N990-filled hard rubbers

Content(phr)	Windsor clay	Sillitin N85	N990	ML(dN-m)	MH(dN-m)	ts2(min)	t90(min)
N70	90			1.9	128.7	1.1	62.0
N73		90		2.2	141.5	1.3	69.2
N86			90	2.3	142.9	1.2	60.6
N112	60		60	3.1	175.2	1.0	45.8
N113	75		45	3.9	171.0	0.7	59.5
N114	90		30	4.1	149.2	0.7	47.4
N115		60	60	2.6	144.2	1.0	45.0
N116		75	45	5.8	192.8	0.8	62.7
N117		90	30	4.2	199.3	1.0	63.5
N124	90		15	3.5	128.2	0.7	52.2
N125	75		30	3.4	153.6	0.7	52.7
N126	60		45	3.7	156.4	0.8	52.7
N127	45		60	3.4	161.5	0.9	51.8
N128	30		75	3.6	166.5	0.8	45.1
N129	15		90	3.4	169.5	0.9	63.3
N130	0		105	3.4	195.4	0.8	61.9

3.1 Curing characteristics

Table 3 shows the curing characteristics of all compositions. It can be seen that the type and ratio of filler have no significant effect on M_L (minimum torque), t_{s2} (scorch time) and t_{90} (optimum cure time).

Figure 1 presents the maximum torque (M_H) of hard rubber compounds filled with clay/carbon black and silicate/carbon black (total filler content is 120phr) at various filler ratios. It was interesting to find out that the maximum torque increased when the carbon black content increased in the clay/carbon black-filled hard rubber compound but decreased when carbon black content increased in the silicate/carbon black-filled hard rubber compound.

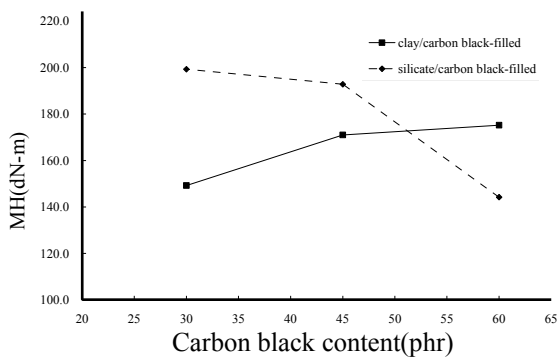


Fig.1. Maximum torque (M_H) of hard rubber compounds filled with clay/carbon black and silicate/carbon black (total filler content 120phr) at various filler contents.

Figure 2 presents the maximum torque of hard rubber compounds filled with clay/carbon black (total filler content is 105phr) at various filler ratios. It is easily seen that the maximum torque increased when the

carbon black content increased in the clay/carbon black-filled hard rubber compound. It is apparent that this result is consistent with former results when total filler content is 120phr. The actual mechanism of reinforcement with carbon black is not yet fully understood and needs further investigation.

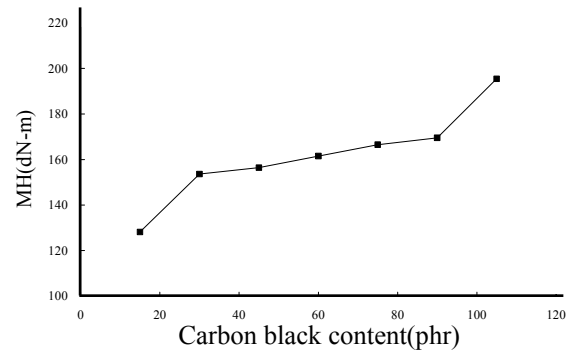


Fig.2. Maximum torque (M_H) of hard rubber compounds filled with clay/carbon black (total filler content 105phr) at various filler contents.

In addition, the maximum torque values of all the samples in this study are much higher than those of soft rubber (M_H is normally 10~20dN-m for soft rubber). High maximum torque means an excessive high level of curatives⁽²³⁾.

According to Table 1, the optimum curing time (t_{90}) ranges from 45 to 70min. In order to achieve 90% of the maximum torque, the curing time of all compositions is 120min in this study.

3.2 Thermal degradation analysis

Figure 3 demonstrates the thermogravimetric deg-

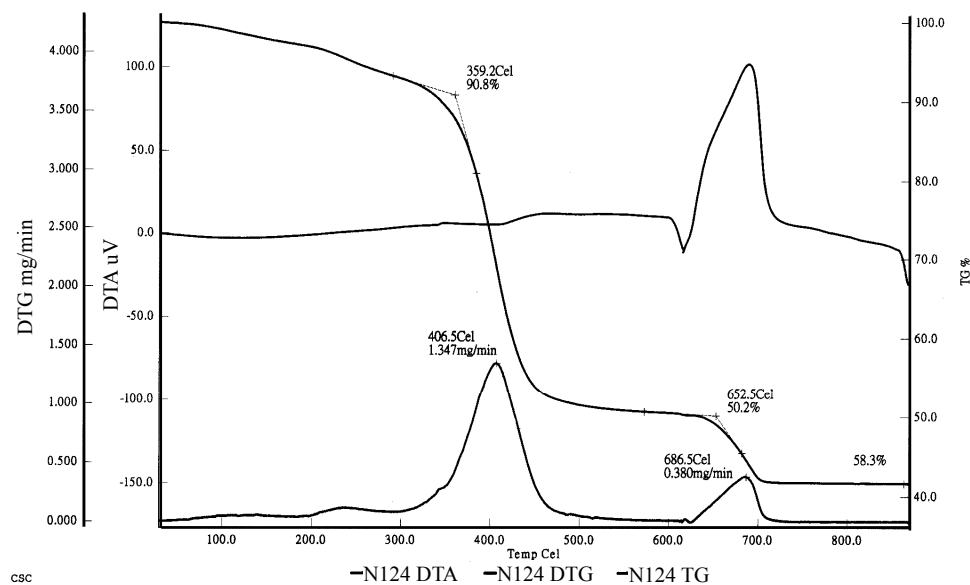


Fig.3. Thermogravimetric degradation of N124 in the temperature range of 30~850°C.

radation of N124 in the temperature range of 30–850°C. For all compositions in this study, the degradation starts at about 300°C. The temperature at the maximum rate of decomposition (T_{max}) of all compositions are listed in Table 4 and T_{max} is perfectly valid for polymer identification⁽²⁴⁾. The experimental results show that T_{max} of all compositions ranges only from 392.5 to 412.9°C. This indicates that the thermal stability of all compositions is nearly the same, which also implies that the extent of curing reaction of all compositions might be rather close.

3.3 Effect of Filler Type

Table 5 shows the variations of the physical properties and resistivity of clay-, silicate-, and carbon black-filled hard rubber samples before and after immersion test. It is apparent that carbon black had the lowest variation values of physical properties and the highest resistivity after the immersion test in comparison with the other two fillers. This finding is consistent with the previous work done by N. Rattanasom et al.⁽¹⁶⁾ and might be due to the better dispersion of carbon black in hard rubber blends. It is seen from the above

discussion that carbon black had the best hardness and resistivity stability after the immersion test.

Meanwhile, the weight variation of silicate-filled hard rubber is negative after the immersion test. This indicates that the silicate filler is easily dissolved out during the immersion test. The dissolved silicate filler may further contaminate the surface of the steel plate passing through the electrolytic cleaning tank. Therefore, the weight variation of hard rubber sample after immersion test must be positive.

3.4 Effect of Carbon Black Content

Variations of physical properties and resistivity of clay/carbon black- and silicate/carbon black-filled hard rubber samples before and after immersion test are given in Table 6. The total filler content is 120phr. The variations of weight and volume of the clay/carbon black-filled hard rubber samples increased after the immersion test when the carbon black content was decreased. In contrast, the resistivity of the clay/carbon black-filled hard rubber samples decreased after the immersion test when the carbon black content was decreased.

Table 4 The temperature at maximum rate of decomposition (T_{max}) of all compositions

Content (phr)	Windsor clay	Sillitin N85	N990	The temperature at maximum rate of decomposition (T_{max} °C)
N70	90			411.2
N73		90		409.2
N86			90	412.9
N112	60		60	392.5
N113	75		45	405.1
N114	90		30	399.6
N115		60	60	403.2
N116		75	45	401.1
N117		90	30	406.4
N124	90		15	406.5
N125	75		30	401.2
N126	60		45	404.3
N127	45		60	403.1
N128	30		75	400.6
N129	15		90	401.2
N130	0		105	402.0

Table 5 Variations of physical properties and resistivity of Clay-, Silicate-, and Carbon Black-filled hard rubber samples before and after immersion test

Content (phr)	Windsor clay	Sillitin N85	N990	W%	V%	H%	Volume resistivity (ohm-cm)		Surface resistivity (ohm)	
							Before test	After test	Before test	After test
N70	90			4.61	-9.09	-7.69	4.21E+13	5.49E+07	4.21E+13	5.49E+07
N73		90		-0.06	-3.36	-7.41	2.46E+15	6.76E+07	2.46E+15	6.76E+07
N86			90	1.40	-2.09	0.13	1.81E+15	2.69E+13	1.81E+15	2.69E+13

The variation of weight turned negative when the carbon black ratio reached 50%. This result suggests that the upper limit of carbon black content in clay/carbon black-filled hard rubber is between 45phr and 60phr when the total filler content is 120phr. In this study, the optimum carbon black content in clay/CB-filled hard rubber samples is 45phr when the total filler content is 120phr.

Furthermore, the variations of weight of all the silicate/carbon black-filled hard rubber samples are negative. It is clear from the results that the silicate/carbon black-filled hard rubber samples in this study cannot pass the electrolytic cleaning tank immersion test.

Table 7 shows the variations of physical properties and the resistivity of clay/carbon black-filled hard rubber samples before and after the immersion test. The total filler content in the vulcanizate is 105phr and the carbon black content ranges from 15 to 105phr.

The variations of weight and volume of clay/carbon black-filled hard rubber sample decreased after the immersion test when carbon black content was increased. In contrast, the resistivity of clay/carbon

black-filled hard rubber samples increased after the immersion test when the carbon black content was increased. It is apparent that this result is consistent with the former results when the total filler content was 120phr.

The variation of weight is negative when the carbon black content is 60phr. This result suggests that the upper limit of carbon black content in clay/carbon black-filled hard rubber is between 45phr and 60phr when the total filler content is 105phr. The carbon black content in clay/CB-filled hard rubber samples with total filler content 105phr given the best environmental resistance properties is 45phr.

4. CONCLUSIONS

The optimum carbon black content in clay/carbon black-filled hard rubber samples is 45phr when total filler content is either 105 or 120phr. Carbon black had the best hardness and resistivity stability after the immersion test. Silicate filler is easily dissolved out during the immersion test. The silicate/carbon black-filled hard rubber samples in this study cannot pass the electrolytic cleaning tank immersion test.

Table 6 Variations of physical properties and resistivity of Clay/Carbon Black- and Silicate/Carbon Black-filled hard rubber samples (Total Filler Content 120phr) before and after immersion test

Content (phr)	Windsor clay	Sillitin N85	N990	N990 Ratio %	W%	V%	H%	Volume resistivity (ohm-cm)		Surface resistivity (ohm)	
								Before test	After test	Before test	After test
N112	60		60	50.0	-0.79	-3.76	-9.30	2.24E+13	1.42E+10	2.43E+13	1.84E+10
N113	75		45	37.5	2.40	-2.63	-12.94	5.28E+12	8.99E+07	4.61E+12	2.71E+08
N114	90		30	25.0	7.48	6.45	-14.94	6.81E+12	BDL	3.06E+12	1.07E+07
N115		60	60	50.0	-0.01	-0.05	-8.05	6.38E+13	1.38E+14	1.10E+13	3.99E+13
N116		75	45	37.5	-0.36	-2.62	-4.76	1.14E+13	3.12E+10	3.10E+09	2.41E+07
N117		90	30	25.0	-1.09	0.17	-4.76	5.36E+11	2.45E+09	4.72E+10	6.05E+08

BDL : Below Detection Limit

Table 7 Variations of physical properties and resistivity of Clay/Carbon Black-filled hard rubber samples (Total Filler Content 105phr) before and after Immersion test

Content (phr)	Windsor clay	N990	N990 Ratio %	W%	V%	H%	Volume resistivity (ohm-cm)		Surface resistivity (ohm)	
							Before test	After test	Before test	After test
N124	90	15	14.3	4.26	2.65	-10.98	2.09E+13	1.19E+08	1.25E+13	BDL
N125	75	30	28.6	3.09	1.20	-6.10	9.25E+13	2.18E+08	4.36E+12	2.28E+07
N126	60	45	42.9	0.39	-1.30	-4.88	1.68E+13	1.90E+09	1.86E+13	2.78E+08
N127	45	60	57.1	-1.37	-0.45	-3.61	4.51E+14	4.11E+13	8.99E+12	9.33E+12
N128	30	75	71.4	-0.52	0.38	-1.20	2.09E+13	5.89E+13	1.41E+13	1.97E+13
N129	15	90	85.7	0.03	0.69	-1.22	2.48E+11	8.69E+12	2.97E+10	3.27E+13
N130	0	105	100.0	-0.27	0.22	-1.23	2.15E+09	6.63E+10	4.78E+08	4.31E+10

BDL : Below Detection Limit

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