MODIFIED CLAY AS A FILLER IN RUBBER COMPOUNDING

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ABSTRACT

Elastomer formulations have changed continuously in order to achieve optimum cost-performance characteristics. The surface modification of low cost mineral fillers had an impact on the rubber industry, because it made possible to convert non reinforcing mineral fillers into reinforcing ones and displace expensive carbon black fillers from rubber compound. Therefore low cost mineral filler such as china clay has been upgraded by surface modification to obtain creditable performance as reinforcing filler in rubber industry.

Also this modified filler has improved the quality of rubber compound through better dispersion of ingredients added to the mix.

But primary advantage of the modification has been related to the interfacial adhesion between rubber and filler, since the modificator, acting as a surfactant provides the bond formation across modificator-clay interface as well as rubber-modificator interface.

INTRODUCTION

Mineral fillers today mainly fulfil the same purpose as they did at the start of this century, mainly to lower rubber compound cost due to its diluent effect.

Surface modification of clay minerals has recently experienced significant interest from rubber technologists. A result of this renewed interest is associated with the real perspective of partial or complete displacement of expensive carbon black fillers from rubber compounds with much cheaper mineral ones without any deteriorating in the performance/properties.

Surface modification techniques generally consist of surface treatment, where the composition or mechanical properties of the existing surfaces are altered or the deposition of coatings where a different material is deposited to create a new surface
Surface treatment is regarded as a chemical treatment, if the composition changes by chemical reactions, that can be originated by ion implantation or deposition. [1]

Major intensity in the development of modification technologies is focused on the production of low cost fillers with improved reinforcing properties similar to properties of traditional carbon black fillers.

The relative positions of rubber fillers in terms of filler usage are shown below;

Filler		Usage %
Carbon black		44
Whiting		17
Clay		15
ZnO		4.4
TiO_2 + and Baryta		2.3
Talc		1.2
Miscellaneous	}	
Non-Black fillers	}	8.3
		48.2% Non-Black fillers

In order to convert a mineral filler in to reinforcing one, a filler must comply with two main following requirements;

1. Develop a large interface between the filler particles and polymeric substance.
2. Posses a surface with high degree of activity.

Therefore the main aim of our investigation was to fulfil the above mentioned requirements with regard to clay.

EXPERIMENTAL

The high grade china clay selected for our investigation was obtained from Borelesgamuwa
Initially clay was calcinated for 8 hours at 900°C to remove the organic substances present in the clay. After the calcination the clay was ball milled for 8 hours to convert the two-layer structure to a booklet structure. Then 0.1 M ammonium acetate solution was added to china clay. The last was wetted well and two components were intermixed thoroughly. The mixture was allowed to stand 12 hours and filtered. The filter cake was washed with a small amount of ethyl alcohol at ambient temperature.

To ensure absorption of ammonium ions by the clay and to control required amount of ammonium ions, Nessler's solution was used. The series of complex investigations were conducted using a number of physico-chemical analyses. The amount of bound rubber was calculated on the basis of solubility of the rubber compound in toluene. The formulation used is given in Table 1

The Natural Rubber, filler (modified and unmodified) and other additives were mixed in two stages. Primary mixing was done by using a laboratory internal mixture. Secondary mixing was done on a laboratory size two -roll mill (16"x18").To find out the effect of bound rubber, master batches were prepared and tested after 24 hours of preparation. It was reported by several authors that after keeping the specimen of compounded rubber at ambient temperature for a long time, the content of the bond rubber increased.

All experiments on uncured compounds were performed with a simple mixture of filler and rubber.

The bound rubber was measured by extracting rubber with toluene at ambient temperature for four days, weighing the residue and calculating the percentage of insoluble polymer.

All curing characteristics were measured using a Moony viscometer and a Monsanto Rheometer. Vulcanised samples for physical and mechanical testing were prepared by compression moulding in an electric press.

RESULTS AND DISCUSSION

The curing characteristics of the rubber compounds filled with modified and unmodified china clay are given in Table 2. Obtained results showed that effect of modification manifested in decreasing the cure time and consequently in increasing the cure rate. Compound B, filled with modified china clay required shorter period to become fully vulcanized as compared to compound A, filled with unmodified china clay, while other curing parameters were fairly similar.

Such effect of modification is considered as a positive one, in terms of capital investments and can be explained as follows.

In clay minerals, the oxygen and hydroxyl valencies at the planer surfaces of the structure are completely satisfied. However, there are aluminium, silicon, oxygen and hydroxyl ions at the edges that are not so satisfied, because the lattice is capable of extension indefinitely in the "ab" plane [Fig 1] .These unsatisfied valencies or “broken bonds”, are satisfied in practice by external ions that do not form part of the structure, but merely act as counter -ions, preserving electrical neutrality. These counter-ions, particularly the cations, are capable of being exchanged for other ions. However in disordered kaolinites, additional balancing cations are present because of the lattice substitutions. These additional cations probably account for greater part of the action exchange that occurs with disordered kaolinites [3]

Organic electrolyte (i.e. ammonium acetate), that is ionised in aqueous solution, may also replace other cations on clay surfaces, as shown below;

$R.\ NH_3 + Ca - clay \rightarrow R.\ NH_3\ Clay + Ca^{+2}$.

Since the amine is absorbed with NH_3^+ group close to the surface, the alkyl group R projecting outwards the surface presented to the suspending medium is effectively an "Organic" surface that is hydrophobic one.[Fig 2] Thus, association energy of the composite clay particles is drastically reduced.while solvation energy of clay particles by organic medium increases in other words amine clay having now organophobic surface properties is highly compatible with organic rubber matrix.

The concept of surface activity refers to inter reaction between filler particles and polymer leading to formation of various type of adhesion bonds across their interface. Partial insolubility of polymer in a filled elastomer is due to adsorption of the macromolecules on to the surface of reinforcing fillers.[4] But we presume, that effect of amine modification on physical and mechanical properties due to ;

(1) Increasing in the adhesion between rubber and filler by improvement their interfacial interaction. [Fig.2]

(2) Improvement of quality of the rubber compound by better dispersion of filler particles in rubber matrix.

Fundamental thermodynamic equation of the adhesion work shows, that

$W = \gamma_{\text{filler-air}} + \gamma_{\text{Rubber-air}} - \gamma_{\text{Rubber-filler}}$.

Where	W	=	Adhesion work
	$\gamma_{\text{Fill-Air}}$	=	Surface energy of filler - air interface
	$\gamma_{\text{Rubber-Air}}$	=	Surface energy of rubber -air interface
	$\gamma_{\text{Rubber-Fill}}$	=	Surface energy between rubber -filler interface

the adhesion can be increased by minimising (decreasing) surface energy at rubber-filler interface.

Therefore any treatment of filler with an agent, which can act as surfactant, decreasing interfacial energy, will improve its adhesion to rubber [5]

After modification the inorganic surface of the filler is transformed into "organic" hydrophobic or "rubber philic" one. So the closer nature of contact surfaces, lower their interfacial energy ($\gamma_{\text{Rubber - filler}} \rightarrow 0$) and higher adhesion values are to be expected.

The adhesion of macromolecules to filler surface proceeds through adhesion of structural units on the filler surface where attractions are formed and these attractions are sufficiently permanent to resist the swelling action of a solvent [3].
Our experimental data on swelling test confirmed this assumption.

Practical results namely in bound rubber content, tensile strength, abrasion resistance, swelling test and fatigue resistance quite clearly indicated that part of the rubber molecule was strongly adhered to the surface of the filler. [Table3] The larger the surface area of the filler, the larger the number of structural units which are strongly adhered to the surface in this way. The content of bound rubber was higher for the new product than the content of bound rubber for the unmodified clay mineral again indicating a high interaction.

Discussion of dispersion quality would be incomplete without evidence from microscopy analysis. Fig. 3 and Fig. 4 indicate typical micrographs of both compounds. From these, it appears that the particle distribution of new product was more uniform than that of the unmodified clay.

Also we assumed, cation exchange is not a one to one replacement. Therefore neutrality of the clay particle is disturbed [2]. This result is present of a net charge. Due to this the particles are repelled and the dispersion is increased.

Also maximum reinforcing effect is realised by complete wetting of all clay particles with rubber that can be considered as a high viscosity liquid phase. So no agglomeration of filler particles must be in rubber matrix. After the modification of clay mineral by ammonium acetate, the solvating energy of hydrophobic filler particles in organic medium is increased, while association energy is drastically reduced. [5]. Therefore created conditions induce deflocculation of filler particles that provides their better dispersion in rubber matrix.

The next important point is the rate of cure. [Table.2] We can not also ignore the possibility of chemical interaction of alkyl amine groups with elementary sulphur or with mercapto benzo-thiazole accelerator or with both. Most likely product of this reaction was responsible for the acceleration of vulcanization.

Also amine liberated from the modified clay mineral and present in the reaction system is capable of further reaction with sulphur compounds as well as the sulphur molecules. Some papers report that both alkyl and aryl amines accelerate the reaction of hydrocarbon with sulphur [6].

CONCLUSION

The active development of modification of the functions of clay was devoted to match carbon black /silica fillers in its reinforcing capability.

However, new development promises to improve physico-mechnical properties of clay more closer to reinforcing properties of carbon black/silica. Also, the. properties contributed by low-cost extended filler (clay) can be modified and compound is given greater control over all performance properties. It provides a desirable balance between dynamic and mechanical properties too.

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Curing Characteristics

A - compound with unmodified china clay
B -. Compound with modified china clay

Table 1

	compound A	compound B
Minimum Torque N/m	28	24
Minimum Torque N/m	3.5	3.5
Scorch Time Min	3.5	3.5
Curing Time Min	12.0	7.0
Cure rate Min^{-1}	11.8	28.8

Physical and Mechanical Properties

Table 2

Properties	Units	Compound A	Compound B
Hardness	IRHD	53-54	54-55
50% Modulus	mPa	3.67	3.00
300% Modulus	mPa	7.45	8.00
Tensile Strength	mPa	17.15	25.93
Elongation at Break	%	600	750
Resilience (Lupke)	%	58-60	62-64
Fatigue Resistance	cycles	29829	181487
Abrasion Resistance(DIN)	g	.19	0.013
Swelling in Toluene	%	287	194
Bound Rubber	%	1.98	12.56

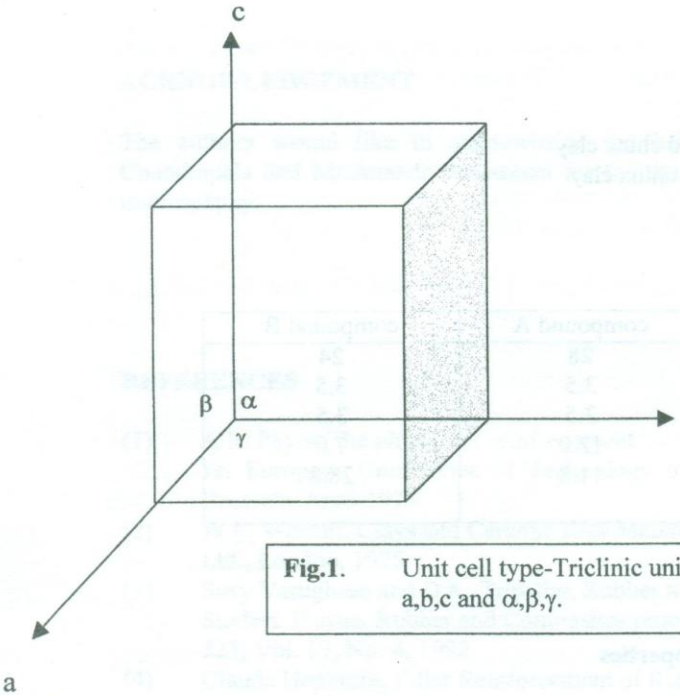

Fig.1. Unit cell type-Triclinic unit cell dimensions a,b,c and α,β,γ.

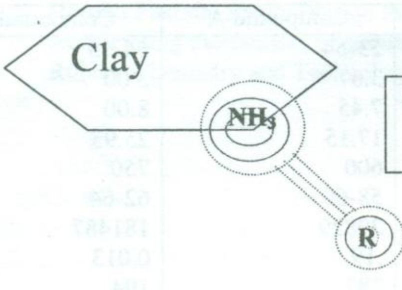

Fig. 2 A schematic diagram of the possible interaction between rubber and modified filler.

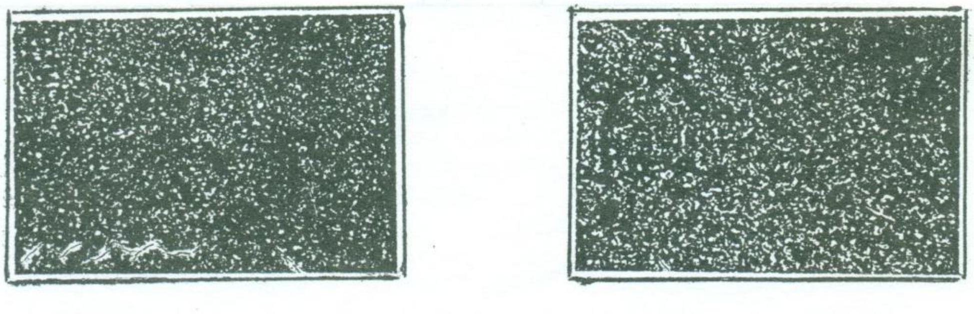

Fig3-Micrgrphs of polymer-filler blends consisting of (a) modified (b) unmodified fillers