Natural Rubber Research, 21 (1&2): 125-129, 2008

SHORT SCIENTIFIC COMMUNICATION

PERFORMANCE OF SURFACE MODIFIED CLAYS IN NATURAL RUBBER COMPOUNDS

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Varghese, L., Madhusoodanan, K.N., Thomas, K.T. and Mathew, N.M. (2008). Performance of surface modified clays in natural rubber compounds. *Natural Rubber Research*, 21 (1 & 2):125-129.

Natural rubber compounds containing different modified clays were evaluated for their processing and technological properties. The amino and mercapto silane modified compounds had higher modulus and abrasion resistance and lower compression set. Flex cracking resistance was more when mercapto silane modified filler was used and hence this was rated as superior modification for clay to be used in natural rubber compounds.

Key words: Fillers, Natural rubber compounds, Modified clay.

Fillers are incorporated into polymers for reinforcement, abrasion resistance, electrical resistance, improved processability or cost reduction. Mineral fillers like carbonates, clays, silicas and talc are used in rubber industry to extend and/or reinforce elastomers. Kaolin clay, a hydrated aluminium silicate, is one such mineral abundant in India. It has the finest particle size range among all naturally occurring minerals (Stoy and Washabaugh, 1987). Clays have been used as filler in compounding of rubbers as an extender and the relatively inferior properties of the resulting vulcanizates are accepted in consideration of lower cost and processability. Clay has been the predominant non-black filler of choice in the inner and white sidewall compounds. Clay has also been used in rubber lubricant and tyre sealant formulations (Waddel, 1996). The surface properties of clays cause difficulties in their use as a reinforcing agent, particularly in hydrocarbon rubbers (Dannenberg, 1975). The filler surface is highly polar and hydrophilic as a result of its polysiloxane structure and the presence of numerous silanol groups. The large quantity of adsorbed moisture in clay adds to the difficulty in rapid wetting and dispersion in rubber. Physical moisture content is almost impossible to control due to the strong desiccant nature and the release of moisture during mixing with rubber at elevated temperature. Compounding recipes are developed using glycols, which decrease their influence on the vulcanization reactions by hydrogen bonding and blocking of the hydroxyl groups. Altering the surface nature of the clays by other techniques like heat treatment, coating or surface modification can enhance their performance in elastomers. By modification, the clay particles can be made to disperse individually in the polymer matrix and thus improve the dispersion level and processability. Recent advances in the chemistry and processing of clay has led to the

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development of surface modified clay fillers which perform like highly reinforcing fillers (Lackey *et al.*, 1997). In the present study the efficiency of various modifier treatments were monitored by physical tests on their compounds and vulcanizates with natural rubber.

The modified clays supplied by M/s. English India Clays, Thiruvanthapuram (India) *viz.*, calcined, stearic acid coated, TEA coated, vinyl modified, aminosilane modified and mercapto silane modified clays were used for the study. Commercial clay was used as a control. Other chemicals used were of commercial grade.

The compounds (Table 1) were prepared in a laboratory size two roll mixing mill (150 x 300 mm) as per ASTM D3182 (1989). The cure characteristics were determined using a Rheometer R 100 at 150°C. The test specimens were moulded at 150°C in an electrically heated hydraulic press. For thicker samples extra time was given so as to get the same extent of cure for all the samples. The mechanical properties of the vulcanizations were determined according to the relevant ASTM standards.

Table 1. **Formulation**

Ingredient	Parts by weight
Natural rubber	100
Zinc oxide	5
Stearic acid	1.5
*Clay	70
Naphthenic oil	7
MBTS**	1.3
TMT***	0.2
Sulphur	1.5

* Clay type A-G (as shown in Table 2)
** Dibenzthiazyl disulphide
*** Tetramethyl thiuram disulphide

Processing properties of the compounds prepared with different clays are given in Table 2. The maximum torque increased for all the samples. The optimum cure time and scorch time of the compounds containing modified clays were observed to be higher except for the amino silane modified one. Water molecules present can enhance the nucleophilic nature of the accelerator species during vulcanization, thus increasing the rate of reaction with sulphur. In the samples containing modified clays the lower levels of silanols and adsorbed water may have led to slower reaction and longer cure times (Wagner, 1976). For the amino silane modified sample, the cure and scorch times were less because of the involvement of the amino groups in the cross linking reaction

Table 2. **Processing properties of the compounds**

Compound	Clay type	Maximum torque (dN.m)	Cure time (min)	Scorch time (min)
A	Control (untreated)	55	6.0	29.5
B	Calcined	59	8.0	53.5
C	Stearic acid coated	60	9.5	50.0
D	TEA coated	58	9.0	42.0
E	Vinyl modified	58	9.0	54.5
F	Amino modified	59	4.0	14.2
G	Mercapto modified	59	7.5	36.8

Table 3. **Technological properties of vulcanizates**

Compound	Clay type	Hardness (Shore A)	Resilience (%)	Heat build up (△T)°C	Tear strength (N/mm)	Flex cracking (kilocycles)	
						Initiation	Failure
A	Control (untreated)	42	62.4	17.0	27.8	5.7	29.9
B	Calcined	43	61.1	17.0	28.0	2.0	10.2
C	Stearic acid coated	44	61.7	17.0	27.6	3.7	10.7
D	TEA coated	44	58.3	18.0	29.2	3.7	12.2
E	Vinyl modified	43	61.8	17.0	28.4	3.7	10.2
F	Amino modified	50	59.7	18.0	40.5	5.0	18.7
G	Mercapto modified	49	61.7	17.0	41.7	15.0	29.0

(Hoffman, 1967). The primary amino group reacts with the sulphur component, adds to the polymer chain and function at the filler surface to neutralize active acidic sites, which normally reduce the efficiency of the curative system.

The technological properties of the different clay filled vulcanizates are shown in Table 3. High hardness was observed for the amino and mercapto modified samples, as pendant amino groups were available for the subsequent cross linking reaction. Heat buildup and resilience values were comparable for all the compounds. Flex crack resistance was improved only by the mercapto silane modification. Improvement in abrasion resistance (Fig. 1) was observed for the amino and mercapto silane modified samples, indicating that the mercapto modification is more effective. Abrasion resistance is the result of two major factors, rupture energy and hysteresis. For mercapto silane modified sample the abrasion resistance is increased due to the dominant effect of increased rupture energy over the low hysteresis property (Dannenberg, 1975). Improvement in tear strength for amino and mercapto modified samples also indicate better filler-to-polymer bonding. The surface modifiers (stearic acid

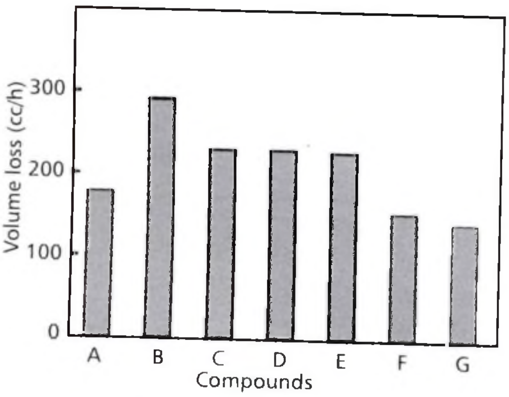

Fig. 1. Abrasion resistance

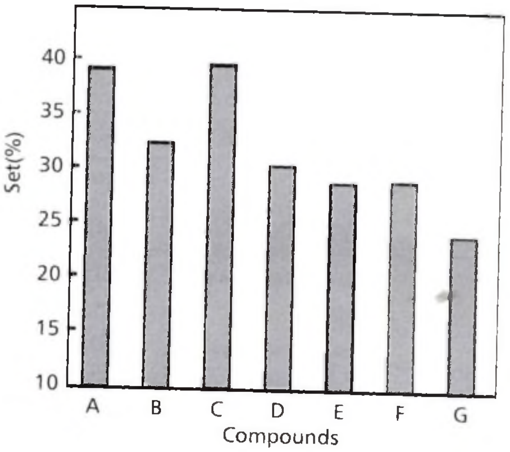

Fig. 2. Compression set

or TEA) aid in processing, compounding and wetting but do not necessarily form strong bonds and hence resistance to these types of failure is not much improved. Vinyl silanes also gave poor surface interaction response with respect to abrasion resistance although they are reported to be effective in EPDM compounds (Ranney *et al.,* 1971). Compression set resistance (Fig. 2) was improved by all the treatments except stearic acid coating and the mercapto silane modified sample was the most effective.

Tensile and ageing properties of the compounds are given in Table 4. Improvement in modulus was observed for the vinyl, mercapto and amino silane modified samples. Increase in modulus is due to increased bonding of the modified sample, thus restricting the polymer movement (Grillo, 1971). Less vacuole formation at clay-rubber interfaces and improved bonding were reported by Rodriguez (1967) by comparing the volume change upon elongation of the modified and control samples. Tensile strength is not greatly affected since the rupture strength of the polymer-polymer linkages remains unchanged. Elongation at break is reduced, consistent with reduced polymer mobility due to increased filler to polymer bonding. This effect is also evident in the higher shore A hardness and reduced compression set. After ageing the retention in elongation at break was higher for all the treatments. Aged tensile strength and modulus were higher for the amino and mercapto silence modified samples.

Processing and technological properties of the natural rubber vulcanizates containing modified clays have been compared with those of vulcanizates from ordinary china clay. Vulcanizates filled with amino or mercapto silane modified clays showed improvements in modulus, compression set resistance and abrasion resistance. The tensile properties of the amino and mercapto silane-modifed samples after ageing were also higher. However, flex cracking resistance improved only for the mercapto modified sample. Hence, mercapto silane modification was found to be the most effective for natural rubber. The silane reacts with surface silanol groups of silica by hydrolysis

Table 4. **Tensile and ageing properties of vulcanizates**

Compound	Clay type	Before ageing			Per cent retention after ageing (100°C, 48h)		
		Tensile strength (MPa)	300 % Modulus (MPa)	EB (%)	Tensile strength	300 % Modulus	EB
A	Control (untreated)	21.0	5.1	869	59	102	68
B	Calcined	21.0	5.1	629	59	102	82
C	Stearic acid coated	20.7	4.7	626	62	102	85
D	TEA coated	22.0	4.2	669	69	102	85
E	Vinyl modified	21.0	5.9	598	65	102	80
F	Amino modified	21.1	6.9	683	83	124	80
G	Mercapto modified	22.0	5.8	744	86	115	89

of its methoxy groups followed by condensation with the olefinic double bonds in the elastomer chains during vulcanization by means of the mercapto functionality. The relative reactivity of the organofunctional group thus plays a critical role in better performance of the modified clay fillers.

The authors are grateful to the R&D Centre of English India Clays, Thiruvananthapuram for supplying the modified clay samples for evaluation.

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