

SBR-mica-silica compositions and their physico-mechanical behaviour

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Summary

Brazilian muscovite mica was used as filler in vulcanized compositions of styrene-butadiene rubber (SBR) in partial replacement of silica. Physico-mechanical properties of the compositions, such as tensile and tear strength, 100% modulus, elongation at break, hardness, abrasion loss and resilience have been studied. The investigations have shown that it is possible to partially replace silica for mica, without remarkable changes in some properties. Relationships between mechanical behaviour and structure have been examined under scanning electron microscopy (SEM) on the fracture surface of the compositions.

Introduction

The chief ingredients in rubber compositions are sulfur, accelerators, pigments, antioxidants and fillers. Sulfur and accelerators are used in the vulcanization process. Antioxidants protect rubber against chemical changes and effects of heat, sunlight and air. Fillers make rubber stronger and are of great importance from the practical point of view.

Carbon black is unquestionably the most universal reinforcing filler, both with regard to the diversity of its physico-chemical characteristics, as well as to the level of performance which its use authorizes. However, there is a general trend to replace carbon black by white mineral fillers, like silica. Silica, which has some properties weaker than those of carbon black, has had for a long time its use restricted. But now, on account of a better knowledge of reinforcement phenomena, it is more and more used in technical goods (1).

The greatest problem of silica (2), mainly precipitated ones, is its price, sometimes forbidding its use in some compositions, which therefore must be compounded with other minerals, like clays, chalks or carbonates, usually conferring inferior technological performance.

As mica is a well known class of low cost mineral profuse in Brasil, predominantly potassium aluminium silicates which may also contain various proportions of magnesium, iron, lithium or fluorine, depending upon the particular source and variety and as it has been used, traditionally, as a filler in phenolic and epoxy resins (3) and more recently in a variety of thermoplastics, although studies on its use in rubber are still rare (4-6), we feel that it can successfully be used as a filler in elastomeric compositions.

This work studies the possibility of partial replacement of an active filler as precipitated silica for mica in vulcanising composition of styrene butadiene rubber (SBR).

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Experimental

Materials

The products used in this work were : SBR-1502, a styrene butadiene rubber, containing 21.5 % styrene, manufactured by Petroflex Industria e Comércio S. A., Brasil; muscovite mica supplied by Araguaia Metais Nobres, Goiás, Brasil; dibenzothiazyl disulfide (MBTS), tetraethyl thiuram disulphide (TMTD) and sulphur from National Bureau of Standards (NBS); di-*o*-tolylguanidine (DOTG) and silica supplied by Bayer do Brasil S.A. and Rhodia S.A., respectively. Other compounding ingredients such as polyethylene glycol 4000, zinc oxide and stearic acid were of reagent grade. Mica used in this work has the physico-chemical characteristics shown in Table 1.

Table 1. Physico-chemical characteristics of mica

Chemical analysis	(%)
SiO ₂	41.80
Al ₂ O ₃	35.40
K ₂ O	12.20
Fe ₂ O ₃	1.50
Na ₂ O	0.33
MgO	0.21
H ₂ O	4.40
Physical properties	
Surface area (m ² /g) (BET, N ₂)	2.00
Specific gravity (g/cm ³)	2.83
pH	4.86
Average particle size (μm)	17.00

Preparation of mixes, rheometry and preparation of test samples

Mixes formulations are given in Table 2. Mixing was carried out on a two-roll mill at a friction ratio of 1.4:1 and 50 °C, according to ASTM D 3191.

Mica was dried at 120 °C for 1hr (7) and silica at 105 °C for four hours (8), immediately before use.

Optimum cure time at 150 °C was obtained from a Monsanto Rheometer TM-100 (Figure 1). Mixes were vulcanized in an electrically heated press at 150 °C and 4,1 MPa. Vulcanizates were conditioned for 24 h before testing. All properties were measured along the grain direction.

Physico-mechanical testing of the samples

Stress-strain data were obtained from an EMIC dynamometer (model MEM 2000) using an ASTM C type dumbbell specimen, according to ASTM D 412. Other physico-mechanical tests were : tear strength (ASTM D 624), abrasion resistance (ASTM D 1044), hardness (ASTM D 2240), resilience (ASTM D 2632) and density (ASTM D 792).

Scanning electron microscopy studies

SEM observations of tensile failure surfaces were done in a direction transverse to the grain direction, using a JEOL JSM-5300 model scanning electron microscope. Fracture surfaces of the test samples were carefully cut from the failure test pieces without touching the surfaces. These specimens were sputter coated with gold within 72 hr of testing. The tilt was kept at 0° in all cases.

Table 2. Formulation

Components	(phr)
SBR-1502	100.00
Zinc oxide	3.00
Stearic acid	1.00
MBTS ^a	1.50
DOTG ^b	1.00
TMTD ^c	0.15
Sulphur	2.10
Polyethylene glycol 4000	2.50
Filler	variable

a dibenzothiazyl disulfide

b di-o-tolylguanidine

c tetraethyl thiuram disulfide

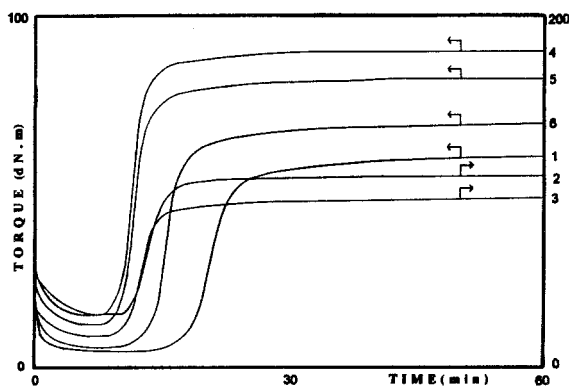


Figure 1 : Rheographs of mica-silica-SBR compositions at 150 °C.

- (1) 0 - 0 - 100;
- (2) 0 - 40 - 100;
- (3) 10 - 30 - 100;
- (4) 20 - 20 - 100;
- (5) 30 - 10 - 100;
- (6) 40 - 0 - 100.

Results and Discussion

The rheometer curves shown in Figure 1 indicate that mica has quite a marked effect on the cure behaviour. Curve 2, which corresponds to a composition with 40 phr of silica presents the highest values in both initial viscosity and final torque level. Subsequent compositions show progressive decrease in these values. These results suggest that, as more mica is incorporated the crosslink density diminishes.

Physico-mechanical properties for the SBR compositions with a total filler content kept constant at 40 phr, are summarized in Table 3.

Table 3 : Physico-mechanical properties of vulcanizates

Properties	Filler loading : mica/silica					
	0/0	0/40	10/30	20/20	30/10	40/0
Tensile strength (MPa)	1.75	12.20	8.79	5.40	3.52	2.18
100% Modulus (MPa)	1.10	2.53	2.04	1.67	1.61	1.63
Elongation at break (%)	225	450	440	370	320	250
Tear strength (kN/m)	8.77	40.67	33.64	26.60	20.05	15.29
Hardness (Shore A)	43	70	63	60	57	54
Abrasion loss (g/1000 cycles)	0.03	0.16	0.17	0.23	0.25	0.29
Resilience (%)	60	43	45	50	51	51

Modulus, tensile and tear strength data for mica-silica-SBR formulations show a maximum value with pure silica as filler and decrease in the presence of mica. These properties are substantially affected by changes in crosslink density (9). Tensile and tear strength increase with crosslink density up to some intermediate crosslink density value and then decrease with further crosslink formation. On the other hand, modulus increases continuously as crosslink reactions progress. These behaviours are in good agreement with data obtained by rheometry, since the composition 0-40-100:mica-silica-SBR seems to have the highest crosslink density.

Elongation at break and abrasion loss show better results when 10 phr of mica and 30 phr of silica were used, as well as when silica was used alone. However, as the mica content is increased beyond this apparently ideal value of 10 phr, a decrease in these properties is observed.

Mica causes a moderate increase in resilience when added to SBR composition and a pronounced decrease in hardness.

These behaviours can be explained considering that the physico-mechanical properties of the vulcanizates depend on the filler characteristics as well as on polymer properties, chemical composition, operational conditions and adhesion degree (10).

The most important filler characteristics are size, shape, specific surface area and a combination of size distribution and shape, i.e. particles packing ratio. The fillers used in this work presented very different primary characteristics, as can be seen in Tables 1 and 4, and Figure 2. A higher surface area, associated with the smaller diameter of silica compared to mica, added to a high-energy surface because of the siloxane and silanol groups (1), leads to a better interaction between silica and the polymer. Hence, we may expect better mechanical properties for the compositions in which the proportion of silica is higher than that of mica.

Table 4 : Physical characteristics of silica

Surface area (m ² /g) (BET,N ₂)	170.0
pH	6.5
Average particle size (Å)	0.013

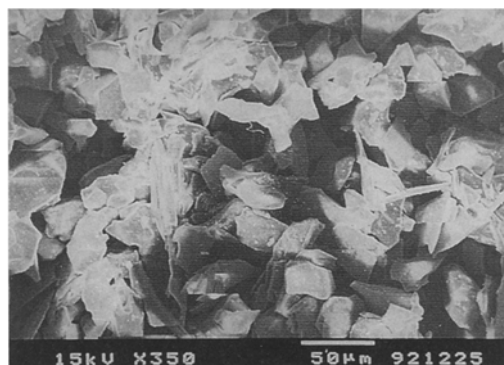


Figure 2 : Electron micrograph of mica.

The polymer-filler interaction, i.e., the adhesion degree at the interface of the two components exerts a considerable influence on the mechanical properties of the vulcanizates (10). Informations about the nature of this adhesion and relations between mechanical properties and structure can be obtained by scanning electron microscopy on fracture surface of the compositions (5,6,11,12).

Figure 3 shows the tensile fractograph of mica-silica filled compositions. The tensile fractograph of SBR gum vulcanizate (Figure 3 (a)) shows brittle fracture (5). The failure pattern changes in the presence of filler, the presence of debonded mica particles (Figure 3 (f)) indicates poor polymer-filler interaction (4,5), whereas in the silica-SBR

composition (Figure 3 (b)), straight fracture path and rough failure surface show higher polymer-filler interaction which results in good mechanical performance (12).

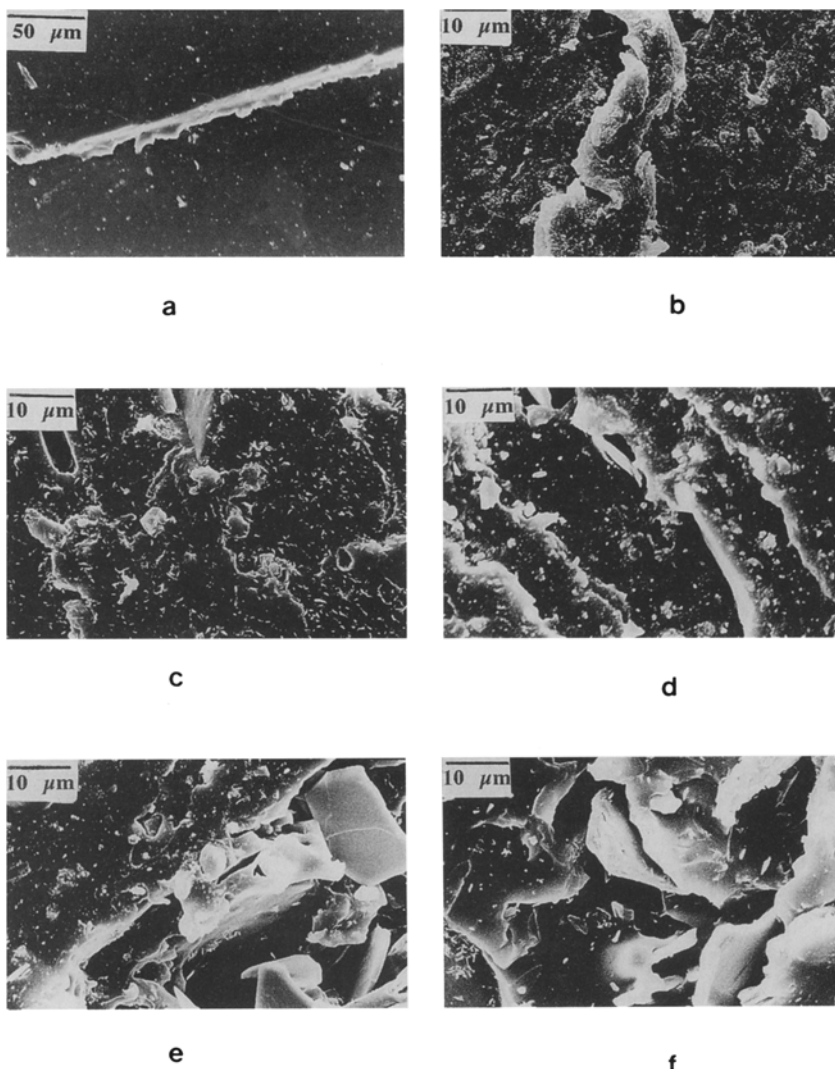


Figure 3 : Scanning electron micrographs of the tensile fracture surface of the mica-silica-SBR compositions. (a)0-0-100; (b)0-40-100; (c)10-30-100; (d)20-20-100; (e)30-10-100; (f)40-0-100.

As the mica loading increases (at the expense of silica), the straight fracture path decreases and a great number of debonded mica particles appears in the SEM fractograph of the tensile fracture surface, which supports the tensile properties (Table 3).

Figure 4 shows some pits which appear on the fracture surface of mica-silica-SBR compositions. These pictures show the poor polymer-filler interaction in the mica-SBR composition (Figure 4 (d)) and the enhancement of the pits size as more mica was incorporated, which corroborate with the mechanical behaviour (10).

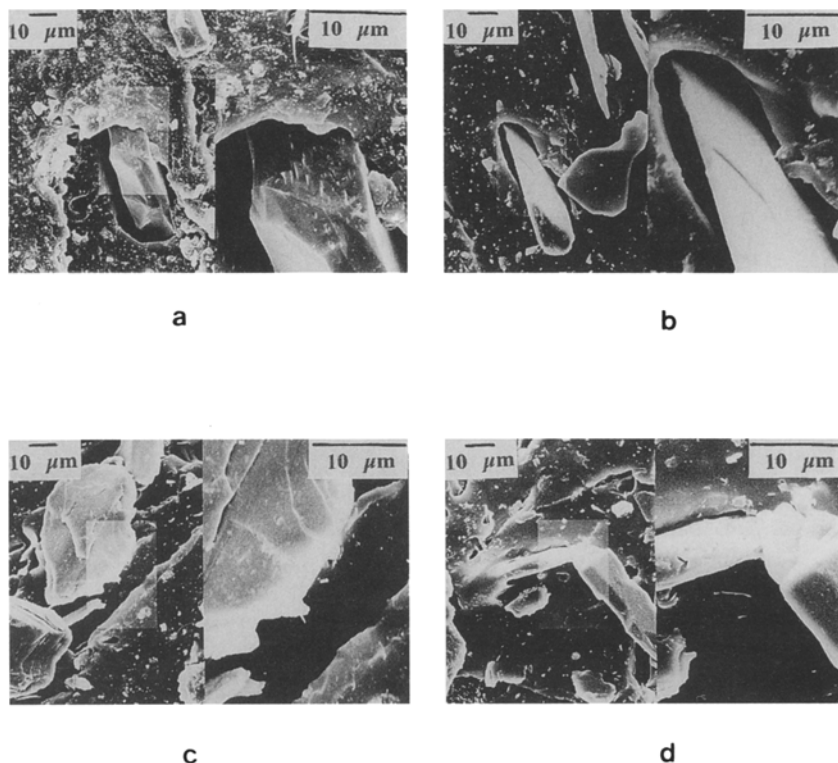


Figure 4 : Scanning electron micrographs of the tensile fracture surface of the mica-silica-SBR compositions. (a)10-30-100; (b)20-20-100; (c)30-10-100; (d)40-0-100.

Conclusions

Mica has a marked effect on crosslink density as could be shown by both curing characteristics and physico-mechanical properties.

This study has shown that mica can be a cheap, low active filler and that it can be recommended to partially replace precipitated silica in the SBR formulation used.

The tensile properties are supported by scanning electron microscopy observations of the tensile fracture surfaces.

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