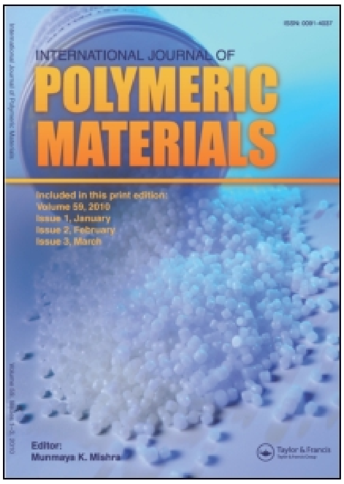

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Rheology and Processability of Natural Rubber Composites with Mica

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Rheology and Processability of Natural Rubber Composites with Mica

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This work is concerned with the influence of mica in natural rubber compounds on properties such as Mooney viscosity, processability and rheological behavior. The amount of this filler was varied from 0 to 40 phr and the stabilized and totalized torques, specific and mechanical energies were determined in a HAAKE torque rheometer. The elastic torque (S′) and complex dynamic viscosity (η^*) were measured on a rubber processing analyzer (RPA). The results show that mica influences processability and rheological properties, by acting as a processing agent in natural rubber composites.

Keywords: mica, Mooney viscosity, natural rubber, processability, RPA

INTRODUCTION

The use of fillers in rubber is almost as old as the use of rubber itself. As soon as rubber-mixing machinery was developed, a variety of fillers, such as ground whiting, barytes, clay, silica or carbon black were

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added to cheapen the products and/or to improve the mechanical properties [1].

The performance of a rubber, as far as fabrication of the final article is concerned, may depend upon breakdown, mixing, rheological behavior, fracture and friction properties. Each of these factors may need to be considered in an overall measure of processability, so it would seem unlikely that an adequate but simple, quick test could be devised no matter how much the industry may desire it. The task of developing a simple but reliable method of characterizing rheological properties, perhaps the most important behavior aspect during the fabrication stages, is in itself a difficult one [2].

In this work, muscovite mica, which is a plate-like crystalline aluminum silicate, was used as filler in natural rubber (NR) composites due to its excellent mechanical, electrical and thermal properties as well as low cost and abundance in Brazil [3]. The amount of mica used ranged from 0 to 40 phr.

EXPERIMENTAL

Materials

Natural rubber (NR) with Mooney viscosity of 82 ML $(1+4)$ at 100°C and muscovite mica with density of $2.78\,g/cm^3$, average particle size of $54.77\,\mu m$ and superficial area $3.7864\,m^2/g$, were supplied respectively by Sociedade Michelin de Participações, Indústria e Comércio Ltda. and by Brasilminas Indústria e Comércio Ltda. The additives used were zinc oxide (ZnO – Uniroyal Química S.A.), stearic acid (NBS 372i US – National Bureau of Standards), N-t-butyl-2-benzothiazol sulfenamide (TBBS – Flexsys Indústria e Comércio Ltda.), Pentaerythritol-tetrakis-[3-(3′,5′-di-tertbutyl-4′-hydroxyphenyl) propionate] (Irganox 1010 – Ciba Geigy Química S.A.) and Sulphur (S – Carlo Erba do Brasil S.A.)

Composites Formulation

The formulation in phr (parts per hundred resin), used in this work followed ASTM D 3184: NR (100), ZnO (5.0), stearic acid (2.0), TBBS (0.7), Irganox 1010 (1.0), S (2.25), mica (0–40).

Processability of Composites

Processing of the mixtures, according to ASTM D 3184, was performed on a Rheomix 600 Haake rheometer under the following conditions:

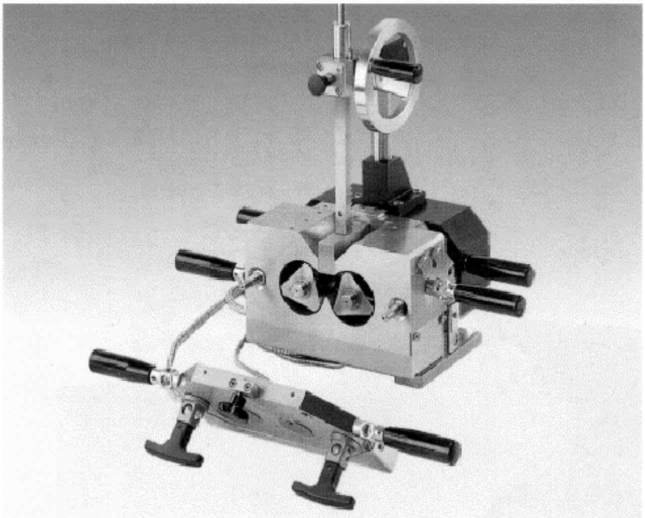

FIGURE 1 Rheomix 600 Haake.

rotor cam, temperature 60°C, rotation rate 60 rpm, time 12 min. The equipment is shown in Figure 1.

On a graph of torque vs. time the following parameters were measured: total torque (TTQ), given by the integral under the curve, and stabilized torque (TQ), the equilibrium torque, which indicates that homogenation has been achieved and is also indicative of the melt viscosity.

The energy required to process the mixtures can be calculated from the power, given by P, which is the energy consumed, dE, during time, dt.

$$P = \frac{dE}{dt} \tag{1}$$

The power consumption during rotation is:

$$P = wM \tag{2}$$

where M is torque and w is the angular velocity. Combining Eqs. (1) and (2):

$$\frac{dE}{dt} = wM \quad \text{or} \quad dE = wMdt \tag{3}$$

As w is constant, integration of Eq. (3) gives the following where E_M is Mechanical Energy:

$$E_M = w \int Mdt \tag{4}$$

The $\int Mdt$ integral corresponds to the area under the torque curve. The angular velocity is calculated as $w = 2\pi f$, where the rotational frequency f is equal to the number of revolutions per unit time, thus equal to the rotational speed, N. Equation (4) leads to Eq. (5):

$$E_M = 2\pi N \int Mdt \tag{5}$$

If the mechanical energy is divided by the weight (m) of the sample (in grams) in the mixer, the specific energy E_{sp} can be obtained [4–7]:

$$E_{sp} = (2\pi N/m) \int Mdt \tag{6}$$

Compounding

The composites were prepared on a two-roll mill (Berstorff), under the following experimental conditions: temperature 25°C, mixing time 20 min and friction ratio 1:1.25.

Rheology of Composites

Rheology of uncured compositions was investigated in the rubber processing analyzer (RPA-2000—Alpha Technologies, USA) with frequency sweep test at 100°C and 28% strain.

The viscosity of all compositions as well as of raw natural rubber was measured by using Mooney viscometer (MV2000—Alpha Technologies) at 100°C according to ASTM D 1646.

RESULTS AND DISCUSSION

Table 1 shows the processability results obtained from Haake rheometer. The stabilized torque (TQ) (melt viscosity), total torque (TTQ) and mechanical energy (E_M) show a little increase with the addition of mica, as a consequence of the mineral characteristic of this filler. This behavior is indicative of a weak rubber-filler interaction. As

TABLE 1 Processability Results from Haake Rheometer

Composites NR/Mica (phr)	Stabilized torque TQ (J)	Total torque TTQ (J × min)	Mechanical energy (kJ)	Specific energy (J/g)
100/0	17.19	241.35	90.94	1545
100/5	17.71	242.45	91.36	1509
100/10	17.84	245.18	91.83	1487
100/20	17.71	252.79	95.25	1461
100/30	18.01	253.77	95.62	1405
100/40	18.75	252.86	95.28	1347

mica is a plate-like material it seems that its crystalline form makes processability easier, thus acting as a processing agent. This would explain the decrease in the specific energy (E_{sp}) with the increase in the filler content, illustrated in Figure 2, where the stabilized torque results are also shown. It seems that the influence of mica in these NR composites starts to appear at 20 phr content.

In this work the complex dynamic viscosity (η^*) of all NR/Mica compositions was determined during the linear regime of elastic deformation. To know this limit, the elastic torque (S′) was measured as a function of deformation, at 100°C and 1 Hz (Figure 3).

It can be seen in Figure 3, for all compositions, inflexion points appearing in the range 70 to 210% strain (1 degree arc = ±14% strain), as an indicative of the borderline between linear and nonlinear

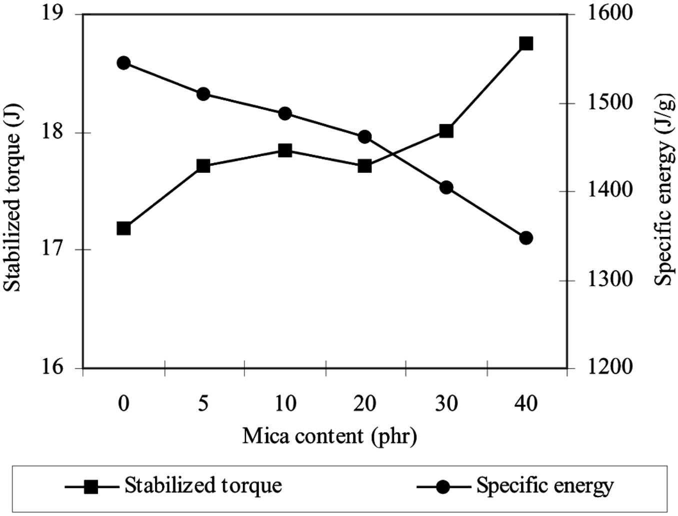

FIGURE 2 Stabilized torque and specific energy of NR/Mica composites.

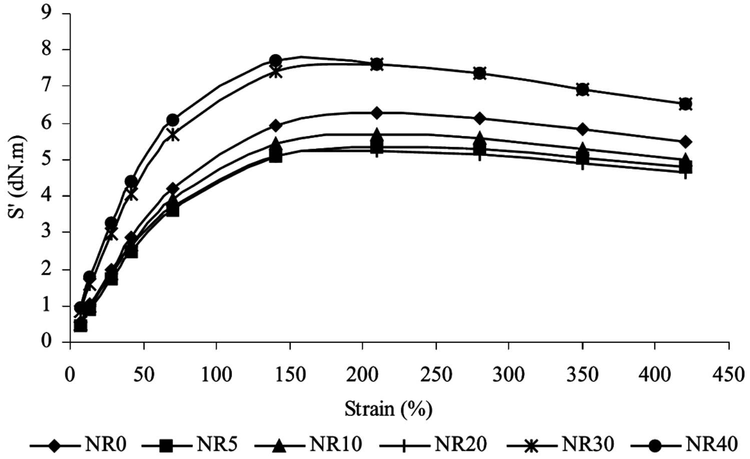

FIGURE 3 Elastic torque of NR/Mica composites.

regimes [8,9]. From Figure 3 it is also possible to see that the elastic torque (S′) is higher than the value for the unfilled composite only for the compounds with 30 and 40 phr of mica which can be related with the filler loading necessary to improve the mechanical properties.

Cox and Merz [10] published the following empirical relationship between capillary rheometer viscosity η_{app}, measured under conditions of steady shear rate, and complex dynamic viscosity η^*, which is measured by sinusoidal deformation (and constantly changing shear rate) with a dynamic mechanical rheological tester. This relationship is given by Eq. (7).

$$\eta_{\text{app}}(\dot{\gamma}) = \eta^*(\omega) \tag{7}$$

Where: η_{app} is the apparent (uncorrected) capillary viscosity, at a steady shear rate of $\dot{\gamma}$ (in sec^{-1}); η^* is the complex dynamic viscosity, measured at an oscillatory frequency of ω (in radians per second).

In the present work the complex dynamic viscosity (η^*) was obtained in the RPA equipment, in frequency sweep, the temperature being kept constant at 100°C and the strain in the linear regime (at 28% or 2°).

Figure 4 shows the log plots of RPA complex dynamic viscosity (η^*) vs. shear rate (from changes in frequency, in radians/second). The results characterize the rubber as a pseudoplastic material in which the viscosity decreases with the increase of shear rate [11]. The curves in Figure 4 have the same profile, non-Newtonian in character and independent of the presence of filler or its content.

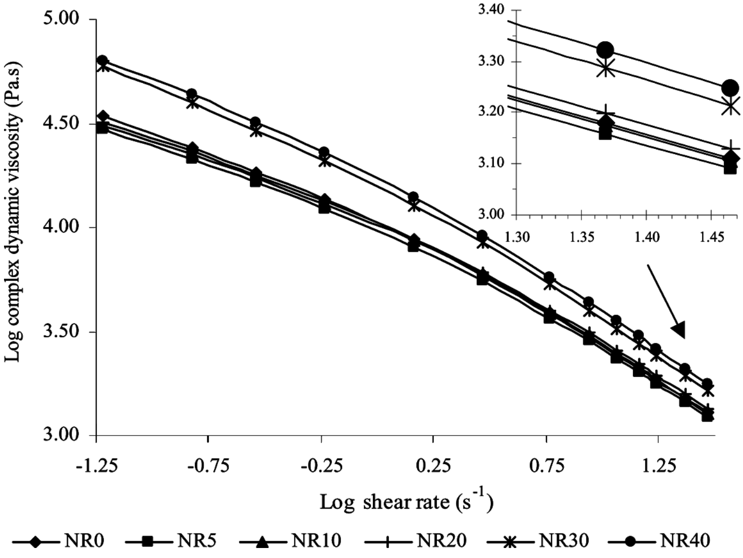

FIGURE 4 Complex dynamic viscosity as a function of shear rate (100°C, 1 Hz).

For the compositions with less than 20 phr of mica, the curves lie below that with no filler, indicating that at these low levels mica acts as a processing agent. However at higher loading the non-Newtonian behavior becomes more evident, especially at low shear rates. Also, only mica loading in excess of 10 phr gave rise to a complex dynamic

TABLE 2 Complex Dynamic Viscosity as a Function of the Shear Rate

	Complex dynamic viscosity × 10^3(Pa · s)					
Shear rate (s^{-1})	NR0	NR5	NR10	NR20	NR30	NR40
0.06	34.22	29.87	30.66	31.91	59.22	63.21
0.15	24.43	21.46	22.65	23.28	39.59	43.43
0.29	18.41	16.46	17.46	17.84	29.27	32.10
0.58	13.60	12.28	13.03	13.32	20.87	22.93
1.46	8.74	8.05	8.56	8.76	12.70	13.98
2.92	5.98	5.55	5.88	6.07	8.41	9.20
5.84	3.91	3.66	3.85	4.01	5.31	5.80
8.74	3.00	2.84	2.96	3.10	4.00	4.36
11.68	2.47	2.34	2.42	2.56	3.25	3.54
14.60	2.13	2.01	2.09	2.20	2.77	3.00
17.53	1.86	1.77	1.83	1.94	2.41	2.61
23.38	1.51	1.44	1.50	1.58	1.94	2.10
29.22	1.29	1.23	1.28	1.35	1.63	1.77

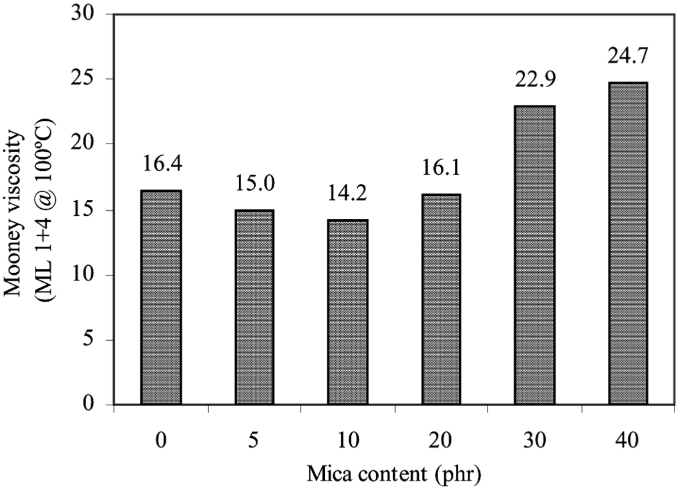

FIGURE 5 Mooney viscosity of composites.

viscosity value higher than that for the unfilled compound at shear rates up to $1.46\,s^{-1}$ (Table 2).

The Mooney viscosity (shown in Figure 5) was also determined at 100°C for all composites and the results corroborate the complex dynamic viscosity (η^*) data obtained from RPA. Considering the range investigated, 20 phr of mica seems to be the upper limit for this filler to be considered as a processing agent.

CONCLUSIONS

Mica filler has characteristics that entitle it as a processing aid for material rubber compositions. This can be seen from the results of Mooney viscosity, the energy necessary for processing the NR-mica compounds, determined in the Haake torque rheometer, and the rheology, studied in the rubber processing analyzer. However, to function as a processing agent in natural rubber compounds, the content of mica must be kept below 20 phr.

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