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Organo-montmorillonite as substitute of carbon black in natural rubber compounds

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Abstract

The use of octadecylamine modified montmorillonite as substitute of carbon black in natural rubber (NR) compounds is studied. Rubber with 10 parts per hundred resin (phr) of pristine (clay) and octadecylamine modified montmorillonite (organoclay) were compared with 10 and 40 phr carbon black as filler. The modified silicate is analysed by X-ray, FTIR and thermogravimetric analysis. Vulcametric curves show that the organoclay and carbon black accelerate the vulcanization reaction and, furthermore, give rise to a marked increase in the torque, indicating a higher degree of crosslinking as was also confirmed by swelling measurements and DSC. The vulcanisation rate and torque value of the organoclay compound are sensibly higher than the carbon black compound even at high contents (40 phr). Mechanical characterization shows the strong reinforcing effect of both fillers up to 350% in the strength in relation to NR. The mechanical properties of NR with 10 phr organoclay are comparable to the compound with 40 phr carbon black. Moreover, the organoclay improves the strength of the NR without hardly any reduction in the elasticity of the material.

Keywords: Organomontmorillonite; Nanocomposite; Natural rubber

1. Introduction

The reinforcement of rubbers is expressed by enhancement of the modulus, failure properties (tensile and tear strength), and abrasion resistance of the vulcanizates. The main aim for filler addition is to improve certain properties and cheapen the compound. Among several fillers, carbon black is the most important reinforcing agent used in the rubber industry. Because of its origin from petroleum, carbon black causes pollution and gives the rubber a black colour. In the last two decades, research was focused on the development of other reinforcing agents to replace carbon black in rubber compounds. Sepiolite, kaolin and precipitated silica were commonly used as reinforcing agents. However, their reinforcing properties are lower than those of carbon black. Because of their inorganic nature, these mineral fillers are not compatible with polymer matrices. Since the Toyota group [1–4] introduced polyamide organoclay nanocomposites, polymer layered nanocomposites have focused the attention of researchers [5–7]. Nanocomposites exhibit physical and chemical properties very different from their bulk counterparts [8,9], because of the nanometer scale dispersion of reinforcement agents and the high surface-to-volume ratio [10].

Clays and clay minerals such as montmorillonite, saponite, hectorite, etc, were widely used as filler for rubber and plastic for many years, for saving polymer consumption and reducing the cost [11–14]. The clay minerals are composed of silicate layers 1 nm thick and 200–300 nm in the lateral dimensions [15]. The internal and external cations can be exchanged by other inorganic or by organic ions [16], for example quaternary alkyl ammonium ions. Organophilic modification makes the silicate compatible with the polymer. These entering guest molecules can either simply increase the distances between the still-parallel layers in an intercalation process or randomly entirely disperse the separate layers in an exfoliation.

Organoclays have been mainly tested with engineering plastics, but, up to now there are only a few studies on rubber–clay nanocomposites. Okada et al. [17] showed for acrylonitrile–butadiene rubber (NBR), that only 10 phr organoclay were necessary to achieve tensile strength comparable to compounds loaded with 40 phr carbon

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black. Usuki et al. [18], prepared ethylene–propylene-diene (EPDM)–clay hybrids by a vulcanisation process using several vulcanisation accelerators. The authors showed that the silicate was exfoliated and uniformly dispersed in EPDM. In addition, the gas permeability of the EPDM–clay hybrid decreased 30% as compared with pristine EPDM.

The aim of this study is to evaluate the properties of NR nanocompounds prepared with an alkylammonium modified montmorillonite in comparison with carbon black compounds.

2. Experimental part

2.1. Materials

Natural rubber was kindly supplied by Malasyam Rubber under the trade name CV 60 (Mooney viscosity, ML(1 + 4) 100 °C 60). Na^+-activated montmorillonite with cation exchange capacity (CEC) value of 70 mequiv./100 g) was provided by Tolsa S.A. (Spain). In order to increase the interlayer spacing, the clay has been treated in our laboratories with octadecylamine. Carbon black was kindly supplied by Cabot, S.A. under the trade name Spheron 6400 (DBP 100 cc/100 g).

2.2. Organoclay preparation

Na^+-activated montmorillonite (20 g) was dispersed into 1000 ml of hot water (80 °C) with continuous stirring. Octadecylamine (7.7 g, 28 mmol) and conc. hydrochloric acid (2.9 ml) were dissolved into 500 ml of hot water (80 °C). Then this solution was poured into the hot clay water dispersion under vigorous stirring for 50 min to flocculate the clay. The precipitate was collected on a filter, washed three times with 500 ml of hot water (80 °C), and dried to yield the organoclay.

2.3. NR nanocomposites preparation

Rubber compounds were prepared in an open two-roll mill at room temperature. The rotors operated at a speed ratio of 1:1.4. The vulcanization ingredients were added to the elastomer previously to the incorporation of the filler and, finally, sulphur was added. The recipe of the compounds are described in Table 1. Vulcanizing conditions (temperature and time) were previously determined by a Monsanto Moving Die Rheometer MDR 2000E. Rubber compounds were vulcanized at 150 °C in a thermofluid heated press. The vulcanization time of the sheets corresponds with optimum cure time (t_{97}) derived from the curing curves of the MDR 2000E. Specimens were mechanically cut out from the vulcanized plaques.

Table 1
Recipes of the rubber compounds

Natural rubber	100	100	100	100	100
Zinc oxide	5	5	5	5	5
Stearic acid	1	1	1	1	1
Sulphur	2.5	2.5	2.5	2.5	2.5
MBTS[a]	1	1	1	1	1
PBN[b]	1	1	1	1	1
Unmodified clay	–	10	–	–	–
Organoclay	–	–	10	–	–
Carbon black	–	–	–	10	40

[a] Benzothiazyl disulfide.

[b] Phenyl beta naphtyl amine.

2.4. Characterization

FTIR spectra were recorded on a Perkin–Elmer System Spectrum One Fourier-transform infrared spectrophotometer.

The XRD patterns were recorded by a Philips diffractometer (Cu Kα, 40 kV, 25 mA). Bragg's law, defined as $\lambda = 2d \sin \theta$, was used to compute the crystallographic spacing (d) for the unmodified and organically modified montmorillonite.

The number of active network chain segments per unit of volume (crosslinking density) was determined on the basis of the rapid solvent-swelling measurements (toluene and n-heptane during 72 h at 30 °C) by application of the Flory–Rhener equation [19].

DSC measurements were carried out on a Mettler Toledo differential scanning calorimetric model DSC 822. Isothermal curing was performed at 160 °C. The weight of the samples was 15–20 mg. The heat of vulcanisation was determined by integrating the area under the exothermal calorimetric signal.

Tensile stress–strain properties were measured according to ISO 37-1977, with type 2 test specimens. Compression set measurements were performed according to ISO 815-1972 during 24 h at 70 °C with 25% compression. Tear strength was measured following the ISO 816-1983. Rebound resilience measurements were carried out on a Schob pendulum according to ISO 4662-1978. Shore hardness was measured by using a Bareiss Rockwell tester according to ASTM D-2240. Abrasion measurements were performed according to ISO 4649-1985.

3. Results and discussion

3.1. Organoclay characterization

Fig. 1 shows the X-ray diffraction patterns of the clay (a) and the organoclay (b). The clay shows a diffraction peak at $2\theta = 7°$ which is assigned to the interlayer platelet spacing (001 diffraction peak) with a spacing of 12.6 Å. In the organoclay a displacement of the peak to lower angles

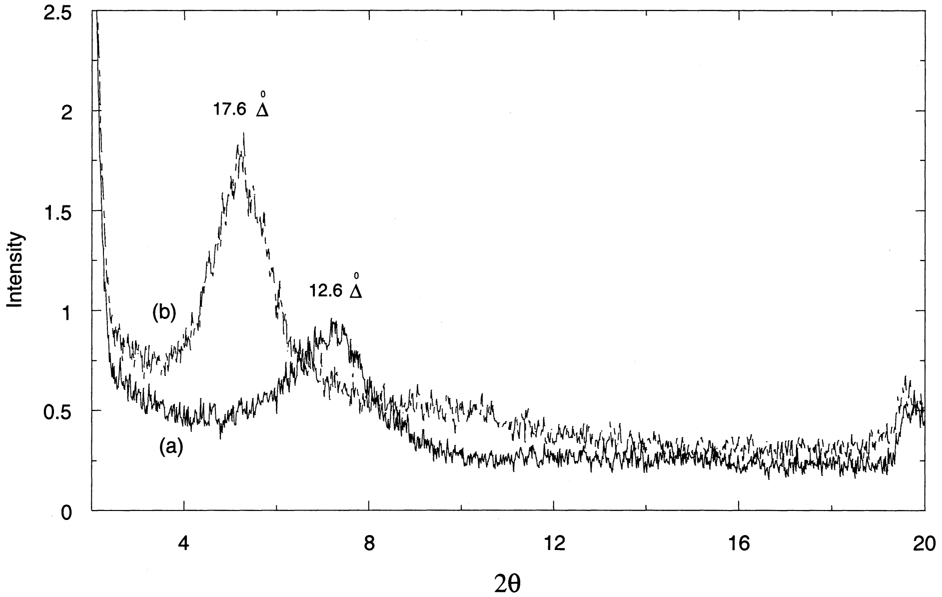

Fig. 1. XRD patterns of clay (a) and organoclay (b).

($2\theta = 5°$) is observed. In this case, the interlayer distance have increased to 17.6 Å.

Fig. 2 shows the FTIR of unmodified and organically modified clay. The infrared spectrum of the unmodified clay presents two peaks which corresponds to the Si–O stretching (969 cm^{-1}) and interlayer water deformation (1633 cm^{-1}) vibrations. The organoclay presents three new peaks in the FTIR spectrum. Bands at 2918 and 2850 cm^{-1} are attributed to the C–H asymmetric and symmetric stretching vibrations of octadecylamine, respectively. The band at 1467 cm^{-1} is assigned to the ammonium salt.

The thermal decomposition expressed in terms of weight loss as a function of temperature for both pristine and the organically modified clay is graphically shown in Fig. 3. The total weight loss of the clay is about 6%, which corresponds to the surface and interlayer adsorbed water, as well as the water resulting from the structural OH groups of the clay. However, the decomposition of the organoclay starts to 150 °C since the absorbed water has disappeared due to the organophilic character of the modified clay and the total weight loss is about 32%. This weight loss is attributed to the interlayer and structural water and the octadecylamine introduced into the montmorillonite galleries. The shape of the TGA curve could be attributed to the liberation of the octadecylamine in two steps, the first one due to the octadecylamine molecules which are in the

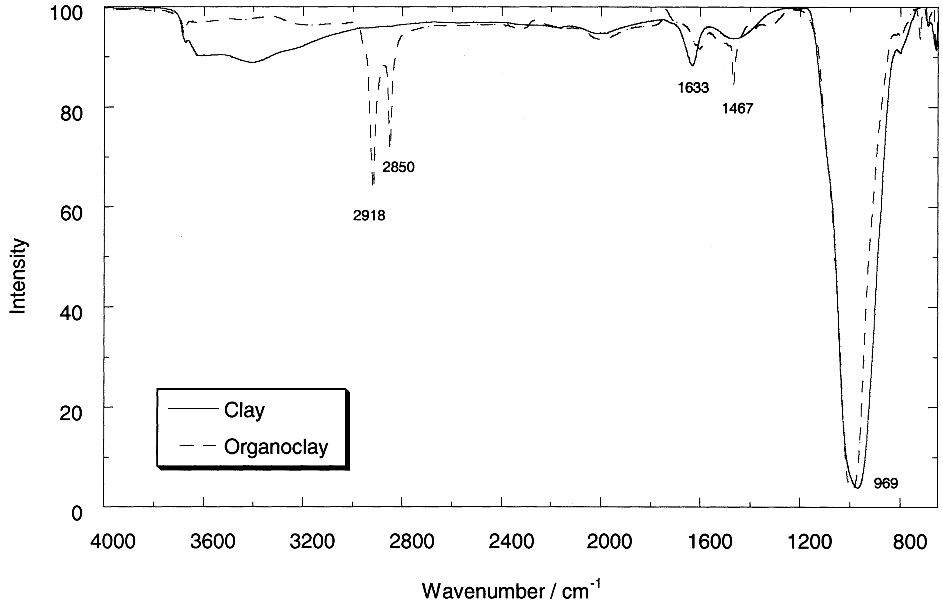

Fig. 2. FTIR spectra of clay (a) and organoclay (b).

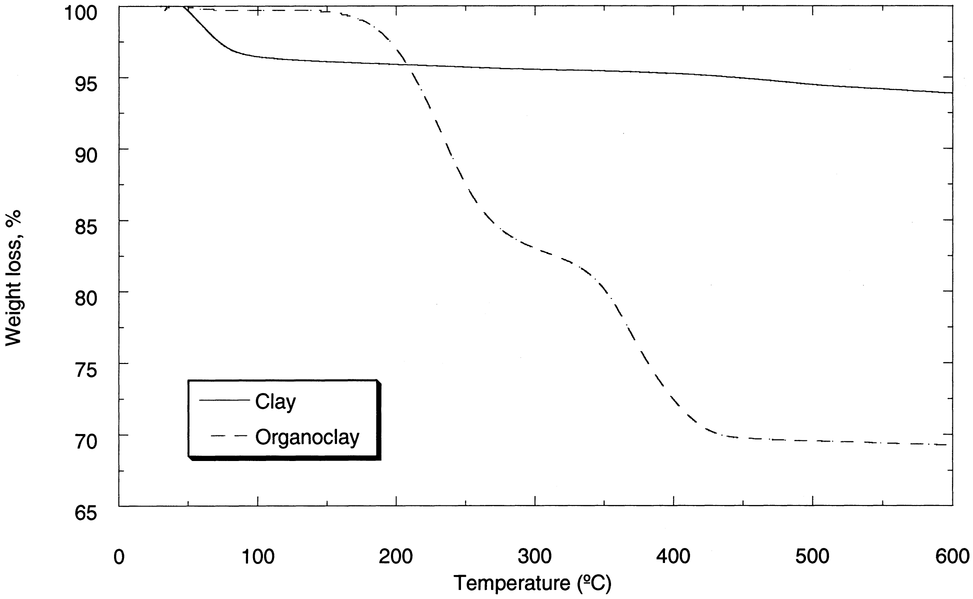

Fig. 3. TGA thermograms of clay (a) and organoclay (b).

extremes of the galleries and the second one to those that are in the interior of the galleries.

These results confirm that the octadecylammonium ions have been incorporated into the galleries of the silicate.

3.2. Characterization of NR–organoclay compounds

Fig. 4 shows the XRD patterns of NR-compounds filled with unmodified (a) and organically modified (b) montmorillonite. The first one shows a peak about $2\theta = 7°$ which corresponds to the interlayer spacing of the silicate. According to these results, the formation of a conventional composite at a microscopic scale, where the polymer is not intercalated into the silicate galleries, can be assumed. However, in the case of the NR–organoclay nanocomposite, this peak disappeared due to the higher layer spacing by insertion of the elastomer into the galleries of the organophilic montmorillonite. In other words, the elastomer chains are confined within the layered silicate.

3.3. Vulcanisation characteristics of compounds

The curing behaviour of the composites was analysed at 150 and 160 °C on a Monsanto oscillating disc curemeter. The scorch time, t_{97} (time for 97% cure) and the torque value, ΔS, (measured as the difference between maximum and minimum torque), are summarized in Table 2. Unmodified clay hardly varies the cure characteristics of

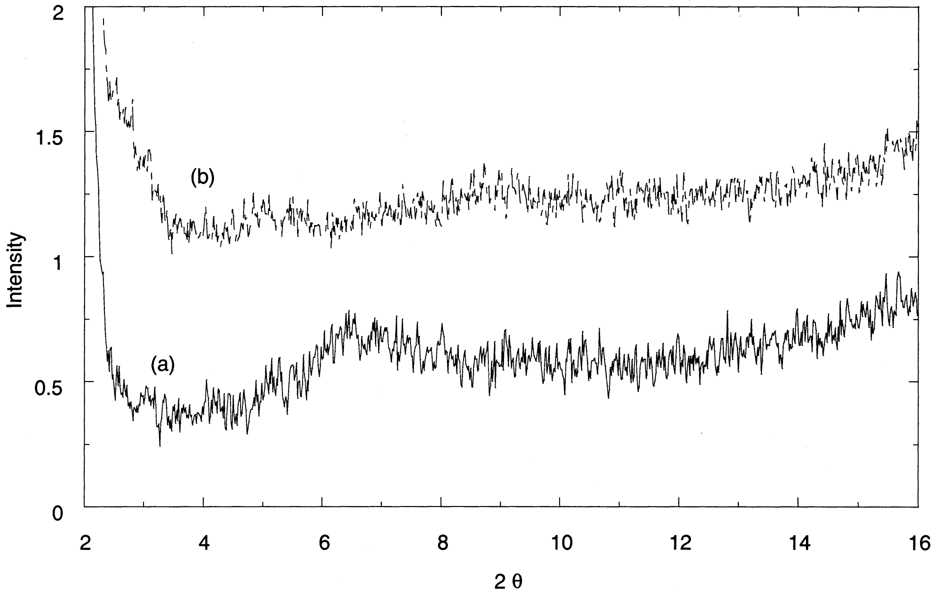

Fig. 4. XRD patterns of NR–clay (a) and NR–organoclay (b) composites.

Table 2
Curing characteristics of the studied compounds

Compound	Curing temperature (°C)	Scorch time (min)	t_{97} (min)	S_{max} (dN m)	S_{min} (dN m)	$\Delta S = S_{max} - S_{min}$ (dN m)
NR	150	8.00	19.97	4.78	0.31	4.46
	160	4.10	9.48	4.59	0.29	4.30
NR–unmodified clay (10 phr)	150	6.50	17.74	3.17	0.07	3.10
	160	3.20	9.10	2.91	0.06	2.85
NR–organoclay (10 phr)	150	1.30	4.09	9.04	0.06	8.98
	160	0.60	2.34	8.77	0.06	8.71
NR–carbon black (10 phr)	150	6.10	16.64	5.02	0.09	4.93
	160	3.10	7.76	3.99	0.08	3.91
NR–carbon black (40 phr)	150	4.10	14.66	6.56	0.05	6.51
	160	2.20	6.80	5.17	0.05	5.12

the rubber, probably due to a poor compatibility between the unmodified clay and hydrophobic polymer. However, the optimum cure time, denoted as t_{97}, was sharply reduced in presence of the organoclay. Thus, the organoclay behaves as an effective accelerant agent for NR vulcanisation. This effect is attributed to the ammonium groups of the organic cations. In fact, amine groups facilitate the curing reaction of SBR and natural rubber stocks [20]. The optimum cure time, t_{97}, also gradually decreases when the carbon black content in the composites increased but to a smaller extent.

The torque value ($\Delta S = S_{max} - S_{min}$) increases in the presence of both fillers, and the organoclay is more effective. The nanocomposite with 10 phr of organoclay shows higher torque values than the counterpart with 40 phr of carbon black. Assuming that the torque value derived from Monsanto Curemeter, is related to the crosslinking density, the nanocomposites with the organoclay have a higher number of crosslinks than carbon black nanocomposites.

3.4. Determination of crosslinking density

The crosslinking density was determined by solvent-swelling measurements (toluene and n-heptane at 30 °C) by application of Flory–Rhener equation [19]:

$$-[Ln(1 - \Phi_r) + \Phi_r + \chi\Phi_r^2] = V_0 n\left[\Phi_r^{1/3} - \frac{\Phi_r}{2}\right]$$

where Φ_r is the volume fraction of polymer in the swollen mass, V_0 is the molar volume of the solvent (106.2 for toluene and 143.0 for n-heptane), and χ is the Flory–Huggins polymer–solvent interaction term. The values of χ are 0.393 and 0.460 for toluene and n-heptane, respectively. The volume fraction of polymer, Φ_r, is calculated by the expression:

$$\Phi_r = \frac{W_i - W_w}{(W_i - W_w) + \left(\dfrac{W_S - W_i}{\rho_s}\right)}$$

where W_i, W_s and W_w are the weights of the rubber samples in air, swollen state and immersed in water, respectively, and ρ_s is the solvent density (0.87 for toluene and 0.71 for n-heptane). In the case of the composites, the volume fraction of the filler is obtained from:

$$\Phi_f = (W_i - W_w) - \frac{W_i - a}{b\rho_f}$$

where a is the phr of filler in the formulation, b the total weight of the compound and ρ_f is the filler density (2.05 g cm^{-3} for clay and 1.80 g cm^{-3} for carbon black). The results are reported in Table 3. The crosslinking density of the pure NR is reduced by the addition of montmorillonite, probably due to the incompatibility between both phases. The crosslinking density increases when organoclay and carbon black are added. The density of crosslinking of the organoclay nanocomposite is higher than the carbon black composite even at high contents (40%) of this one. These results agree with the Monsanto measurements, indicating the good compatibility between the organoclay and the elastomer.

A further evidence of an enhanced crosslinking in the presence of the organoclay was obtained by the DSC (Fig. 5). The heat of reaction involved during the vulcanization under isothermal conditions increased in presence of both fillers, but this effect is more pronounced for the organoclay (Table 3). This change in the heat of vulcanization can be only explained in terms of a higher degree of curing in presence of the fillers. It is noteworthy that the nanocomposite with low organoclay amounts (10 phr) shows a higher degree of crosslinking than with high carbon black contents (40 phr).

3.5. Mechanical properties

The mechanical properties of the composites are reported in Table 4. The tensile properties are given in terms of the modulus at different strains (100, 300 and 500%), the strength and elongation at break. The low reinforcing effect of unmodified montmorillonite is evident. A poor compatibility between the clay and the matrix (formation of a conventional composite at micro scale) is expected. A marked increase of the mechanical properties is observed for the organoclay as filler. Increments of above 350% in the strength are obtained. The effect of the organoclay on the

Table 3
Crosslinking density measurements and curing enthalpy

Compound	ϕ_r		n		ΔH_c (J/g)
	Toluene	*n*-Heptane	Toluene	*n*-Heptane	
NR	0.161946	0.22315	8.97×10^{-5}	9.23×10^{-5}	9.20
NR–unmodified clay	0.127181	0.18144	3.98×10^{-5}	3.93×10^{-5}	11.41
NR–organoclay	0.209615	0.27165	1.61×10^{-4}	1.56×10^{-4}	19.61
NR–carbon black (10%)	0.176050	0.2340	1.08×10^{-4}	1.04×10^{-4}	12.75
NR–carbon black (40%)	0.187225	0.24716	1.24×10^{-4}	1.19×10^{-4}	16.55

stiffness is more evident when measured at higher strains (increments of 191, 224 and 274% on the modulus are observed at 100, 300 and 500% elongations, respectively). In fact, the reinforcing effect of a filler is more noticeable at high elongations when it is perfectly dispersed in the matrix since the breakage depends on the amount of weak spots or inhomogeneities in the vulcanized rubber [21]. Improved hardness and abrasion resistance are also in concordance with tensile results. It is important to note that the elastic characteristics of the NR are maintained in presence of the organoclay as deduced from the rebound resilience and compression set measurements.

When comparing the organoclay with carbon black as fillers for NR, it is observed that at similar filler contents the reinforcing effect of the organoclay is more noticeable. As deduced from Table 4, it is necessary to add 40 phr carbon black to obtain similar mechanical properties as the composite with 10 phr organoclay. However, high contents of carbon black gives rise to a marked loss in the elastic behaviour of the NR composite.

4. Conclusions

The possibility of substituting carbon black by white fillers as reinforcements of natural rubber has been investigated. In particular, an octadecylamine-modified montmorillonite is object of analysis.

The organoclay gives rise to a higher degree of crosslinking as compared to the counterpart with carbon black, which is reflected in a considerable increase in the mechanical properties of the elastomer. In fact, the organoclay behaves as an effective reinforcing agent for natural rubber, showing a stronger reinforcing effect than carbon black while retaining the elasticity of the elastomer. Only 10 phr of the organoclay are enough to obtain a similar mechanical behaviour as the compound with 40 phr of carbon black.

From the above results it can be assumed that the organic treatment of the silicate increases the interlayer spacing which allow the dispersion of silicate layers into the matrix at a nanoscale level and improves the filler-matrix compatibility.

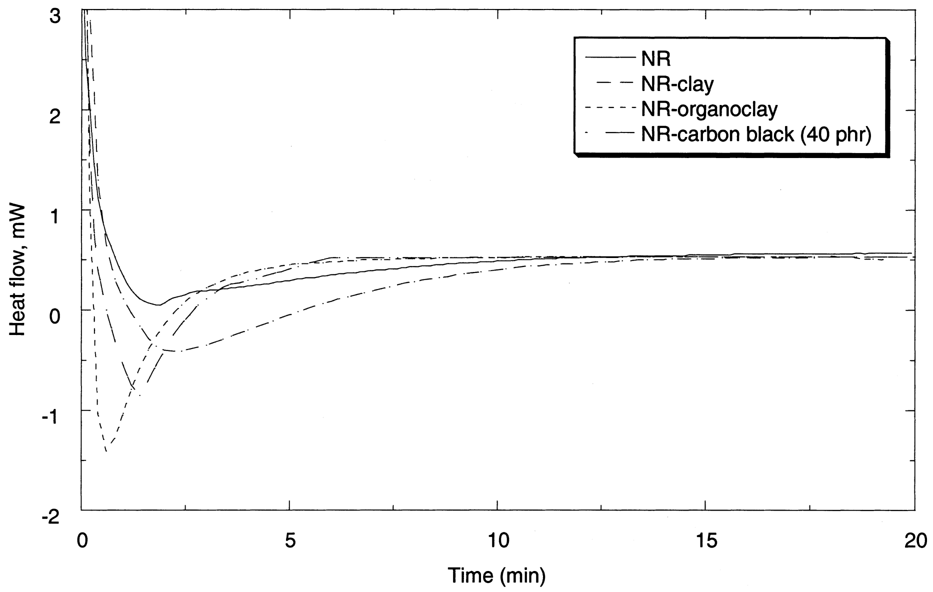

Fig. 5. Isothermal DSC thermograms of NR and its composites, at 160 °C.

Table 4
Mechanical properties of the studied compounds

	NR	NR–unmodified clay (10 phr)	NR–organoclay (10 phr)	NR–carbon black (10 phr)	NR–carbon black (40 phr)
Modulus 100% (MPa)	0.59	0.53	1.72	0.83	1.60
Modulus 300% (MPa)	1.33	1.38	4.31	2.53	5.52
Modulus 500% (MPa)	2.60	2.90	9.73	-	-
Maximum strength (MPa)	4.25	3.60	15.0	4.93	10.3
Elongation at break (%)	>700	555	>700	464	434
Hardness (shore A)	28.8	20.7	43.5	30.5	38.3
Rebound resilience (%)	63.0	58.0	62.5	58.5	50.5
Compression set (%)	17.5	27.9	22.4	28.7	42.8
Abrasion loss (mm^3)	286.2	-	217.5	282.0	199.3
Density (g/cm^3)	0.975	1.030	1.004	1.014	1.081

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