Vulcanization Kinetics of Natural Rubber–Organoclay Nanocomposites

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ABSTRACT: The effect of the incorporation of a bentonite on the vulcanization kinetics of natural rubber was investigated by means of both cure-meter testing and differential scanning calorimetry (DSC) under dynamic and isothermal conditions. The vulcanization curves showed that the modified clay behaved as an effective vulcanizing agent, accelerating the vulcanization reaction of the elastomer. A marked decrease in the induction time and optimum cure time of the elastomer were observed in the presence of the organoclay. Although the octadecylamine itself accelerated the vulcanization process, the octadecylamine-modified clay gave rise to a further noticeable increase in the vulcanization rate, which could be attributed to a synergetic effect between the filler and the amine. Moreover, in the presence of the organoclay, a dramatic increase in the torque value was obtained because of the formation of a higher number of crosslinks, which could be attributed to the confinement of the elastomer chains within the silicate galleries and, consequently, to better interactions between the filler and the rubber. However, no significant changes were observed in the unmodified clay composite. These results were in concordance with those obtained by DSC. In addition, the activation energy of the vulcanization process was also calculated by means of both techniques. A clear decrease in the activation energy was observed when the organoclay was added to the nanocomposite, which indicated that the layered silicate favored the processing of the elastomer. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1–15, 2003

Key words: rubber; clay; nanocomposites; vulcanization kinetics

INTRODUCTION

Clay is a cheap natural raw material that has been widely used for many years as a filler for rubber and plastic to reduce polymer consumption and cost.[1,2] Clay is composed of silicate layers that are 1 nm thick in planar structure and 200–300 nm in the lateral dimension.[3] Because of the agglomeration of these particles and their low surface activity, their reinforcing effect is poor. However, the Toyota research group[4,5] demonstrated a new way to improve the reinforcing ability of clay, which revolutionized the composite materials world. These authors demonstrated the ability of layered silicate to disperse into polymer matrices at nanoscale level. The polymer can be intercalated into the silicate galleries. In other words, the polymer is nanoscopically confined into the silicate layers to form clay–polymer nanocomposites. Cations such as Na^+, Ca^+, and K^+ exist in the interlayer galleries and can be substituted by organic alkyl ammonium cations to produce organophilic clays, generally known as organoclays. Organophilic modification results in compatibility between the filler and polymer. Recent interest in polymer–clay nanocomposites has arisen because of the dramatic improvement in thermal and mechanical properties than can be obtained by the addition of just a small fraction of clay (< 5 wt %) to a polymer matrix. Many articles on clay–polymer intercalated nanocomposites[6–8] can be found in the literature. Until now, organoclays have been mainly used with engineering plastics, such as polypropylene,[9] polyamide 6,[10] polyamide 12,[11] polystyrene,[7] polyurethane,[12] epoxy resins,[13] and poly(ethylene terephthalate).[14] Because of their structure, these nanocomposites exhibit unique properties, such as high stiffness, impact strength, and heat distortion temperature and an improved gas barrier action.[5,15,16] However, the procedure of preparing polymer–clay nanocomposites has only been successfully applied to polar polymers but not to nonpolar ones, such as the majority of elastomers. In fact, there have been very few studies on clay–rubber nanocomposites. Okada et al.[17] showed for acrylonitrile–butadiene rubbers that only 10 phr of organoclay was enough to achieve a similar tensile strength to that obtained with 40 phr of carbon black. One of the effects of these nanoparticles could be the reduction of gas permeability, so its use as a tire innerliner was proposed.

It is well known that vulcanizate properties strongly depend on the vulcanization reaction. However, until now, no studies on the vulcanization behavior of rubber–clay nanocomposites have been reported in the literature.

Vulcanization, which involves a huge amount of energy to convert an unformed plastic material to an elastic end product, is one of the most important process in the rubber industry. For the analysis, optimization, and control of processes involving rubber vulcanization, it is useful to perform a complete thermal and rheological characterization of the material during the curing reactions. Usually, induction, curing, and overcure periods can be found along the vulcanization process. Curing kinetics are analyzed with differential scanning calorimetry (DSC) and oscillating-disc cure-meter testing.

The main goal of this study was to evaluate the effect of the incorporation of unmodified and organically modified Na^+–bentonite on the vulcanization kinetics of natural rubber (NR). The effect of the octadecylamine itself (in the absence of clay) was also studied.

Background

DSC is a major achievement in the field of analytical tools for the determination of the energy required during rubber vulcanization. Analysis through DSC is based on the assumption that the heat of reaction is only due to a single curing reaction and is proportional to the extent of the reaction, whereas cure-meter measurements are based on the assumption that the crosslinking density is proportional to the stiffness of the rubber. Therefore, the degree of curing (α) can be calculated from the heat-flow peak of a DSC curve or from the dynamic viscoelastic properties obtained in cure-meter testing.[18] Thus, α can be easily defined by the following equations. For DSC

$$\alpha = \Delta H_t / \Delta H_\infty \qquad (1)$$

For the cure-meter test

$$\alpha = (F_t - F_0)/(F_\infty - F_0) \qquad (2)$$

where ΔH_t is the accumulated heat evolved to time t, ΔH_∞ is the total amount of heat generated during the reaction, and F_0, F_t, and F_∞ are the torque values at time zero, at curing time t, and at the end of the vulcanization process.

It is assumed that the equation describing the thermal behavior of an elastomer during the vulcanization process is obtained by the appraisal at each instant of a thermal balance, where the diffusion of heat and source terms originated from the exothermic reaction occurring during the vulcanization phenomenon are taken into account. A typical cure curve is shown in Figure 1. Three regions are clearly observed. The first region is the scorch delay or induction period, during which the most of the accelerator reactions occur. The second period is due to the curing reaction, during which the network structure is formed. In the last period, the network matures by overcuring reversion, equilibrium or additional but slower crosslinking, depending on the nature of the compound. In our case, NR tended to give reactions of overcuring reversion because of the degradation of polysulfide bonds.

The dynamics of the reaction, after the induction time (t_i) has elapsed, are modeled by means of a differential equation with regard to time, where the influence of the temperature and vulcanization rate are separated,[19] as in many other classical chemical reactions. Thus, the equation governing the vulcanization rate may be written as follows:

$$d\alpha/dt = K(T)f(\alpha) \qquad (3)$$

where t is the time, T is the temperature, and K is the kinetic constant. The function $K(T)$ is described by the Arrhenius expression:

$$K(T) = K_0 \exp(-E_a/RT) \qquad (4)$$

where K_0 is the preexponential factor, E_a is the activation energy, and R is the universal gas constant. From eqs. (3) and (4), the following relationship can be deduced:

$$d\alpha/dt = K_0 f(\alpha) \exp(-E_a/RT) \qquad (5)$$

The function $f(\alpha)$ depends on curing reaction mechanisms (see Fig. 2). So, in a single reaction, the function $f(\alpha)$ assumes that the rate of conversion is proportional to the fraction of noncrosslinked material:[20]

$$f(\alpha) = (1 - \alpha)^n, n \geq 1 \qquad (6)$$

where n is the reaction order. A more complex form of the kinetic equation assumes the so-called autocatalytic model, which is given by:[21]

$$f(\alpha) = \alpha^m(1 - \alpha)^n, 0 \leq m \leq 1, n \geq 1 \qquad (7)$$

where m also denotes the reaction order.

In an n-order reaction, the maximum rate of cure occurs at the beginning, when the concentration of reactive groups is maximum, whereas in an autocatalytic reaction, the maximum rate of cure is given for a conversion degree other than zero because the reaction is promoted by the same products of the reaction.[22] As shown in Figure 2(b), the curing reaction of NR is better fitted to an autocatalytic reaction, so to analyze the curing reaction of NR in the presence of
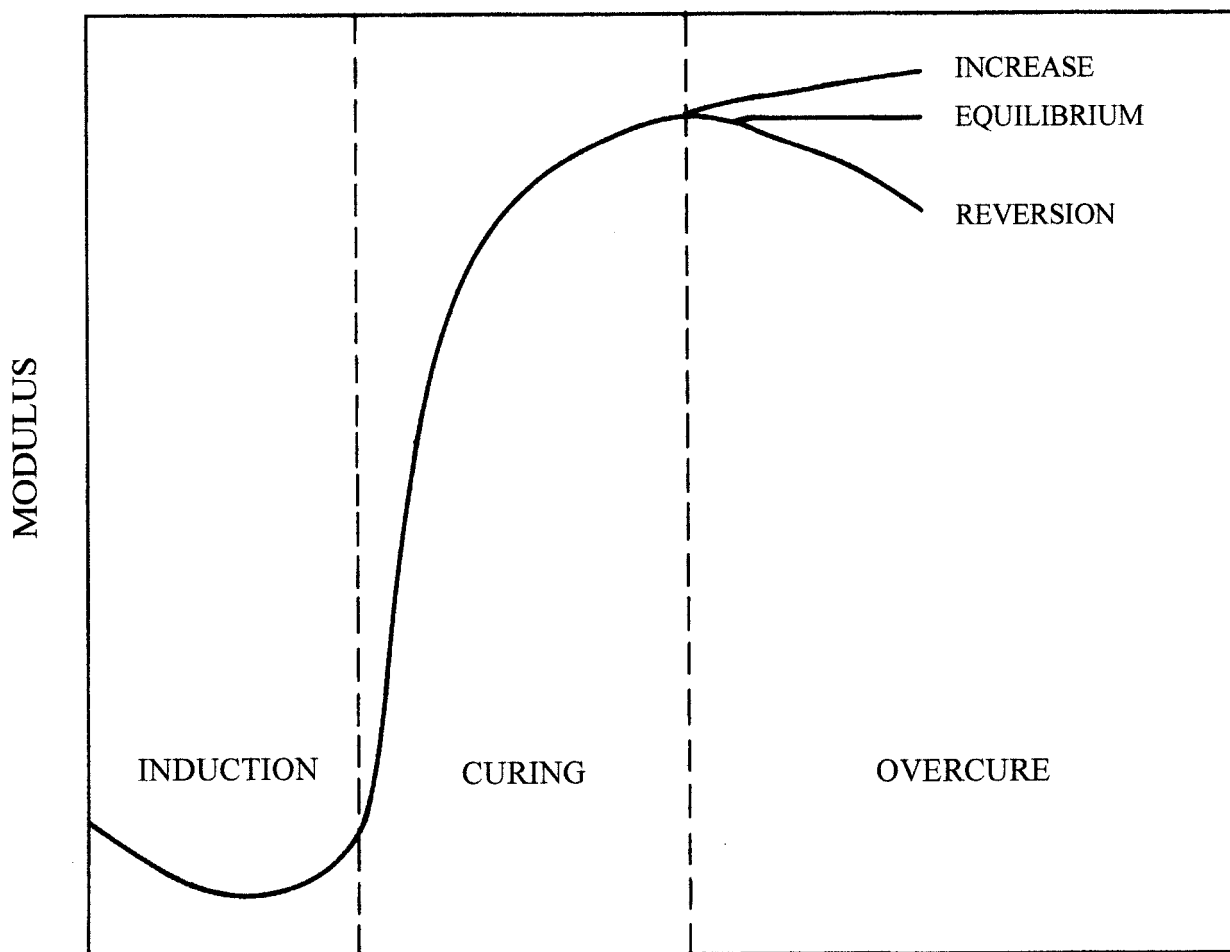
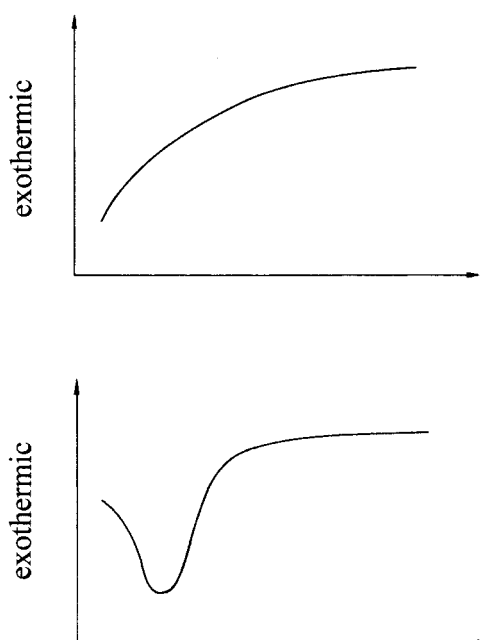**Figure 1** Typical curing curve of a rubber.

Figure 2 Curing curves of (a) n-order and (b) autocatalytic reactions.

nanostructured silicates, the follow expression is proposed:

$$d\alpha/dt = K(T)\alpha^m(1 - \alpha)^n \tag{8}$$

where n and m are the reaction orders. The choice of this specific model was based on the experimental results obtained in the isothermal tests, which confirmed that the reaction rate was equal to zero at both ends of the process ($\alpha = 0$ and $\alpha = 1$) as predicted by eq. (8).

EXPERIMENTAL

Materials and preparation of the compounds

NR was kindly supplied by Malasian Rubber (Berhad, Malaysia) under the trade name CV 60 [Mooney viscosity, ML(1 + 4) 100°C = 60]. Clay with a cation exchange capacity of 70 mmol/100 g was provided by Tolsa S.A. (Madrid, Spain). The interlayer spacing of the unmodified clay was 1.26 nm. To increase the spacing between the layers of the silicate, we modified the clay with octadecylamine following a previously
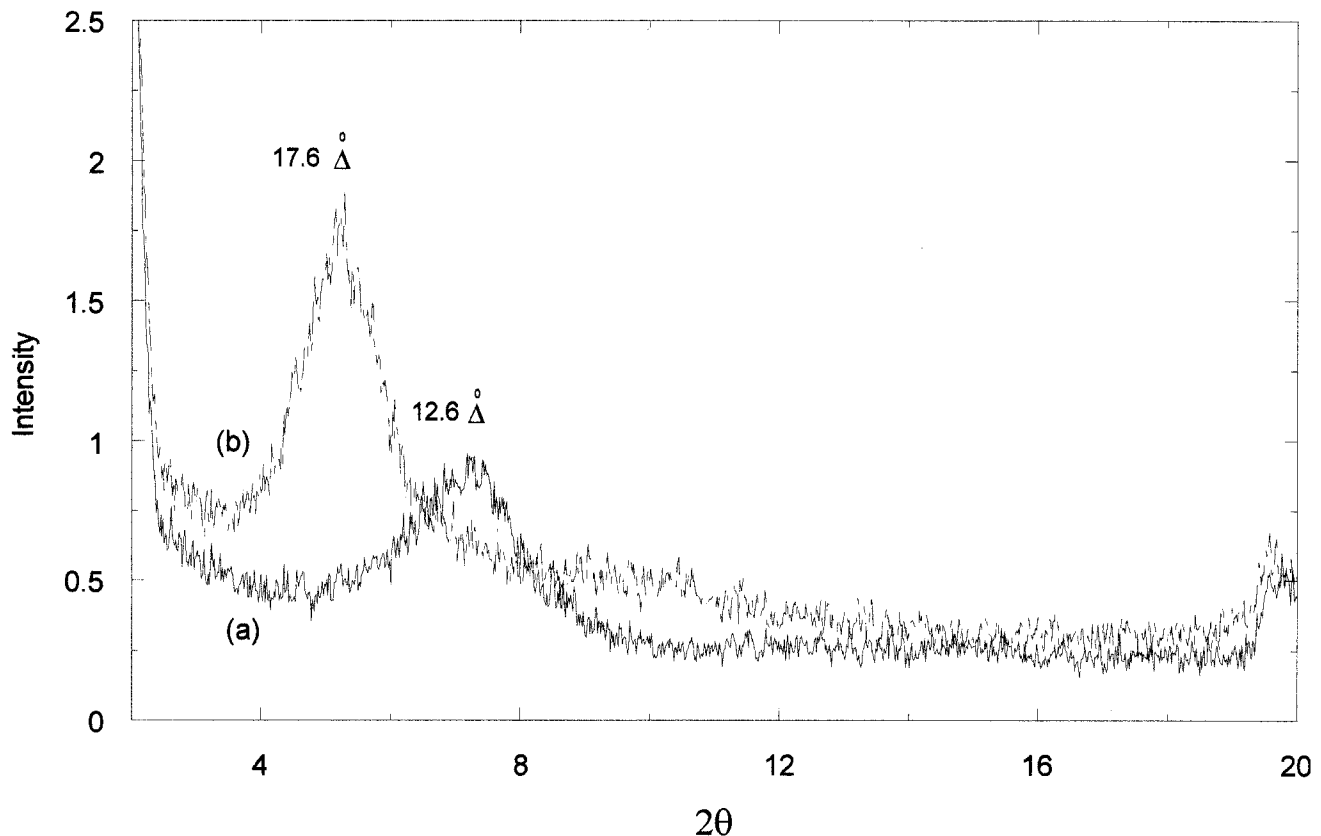
Figure 3 X-ray diffraction patterns of (a) unmodified clay and (b) organoclay.

described procedure.[9] Octadecylamine was supplied by Aldrich (Madrid, Spain). The interlayer distance in the organoclay was 1.76 nm as measured through X-ray diffraction (Fig. 3).

Rubber compounds were prepared in an open two-roll mill at room temperature. The rotors operated at a speed ratio of 1:1.4. All the vulcanization ingredients except the sulfur were added to the elastomer before the incorporation of the clay. Ten parts unmodified clay and organoclay were added to the rubber. We also prepared a blend containing the octadecylamine in the absence of clay to determine the effect of the neat octadecylamine on the cure kinetics of NR. In this case, the amount of neat octadecylamine added to the recipe corresponded with that incorporated in the organoclay. The recipes of the compounds are compiled in Table I.

Testing

Vulcanization characteristics

The curing behavior was determined, at 160, 170, 180, 190, and 200°C with a Monsanto oscillating disc rheometer (MDR 2000) (Alpha Technologies, Swindon, UK). The cure reaction rate constant was calculated from the vulcanization reaction, and then, the vulcanization kinetics were also analyzed.

DSC

DSC measurements were carried out on a Mettler Toledo differential scanning calorimeter (model DSC 822) (Schwerzanbach, Switzerland). The curing reaction was evaluated under isothermal and dynamical conditions. Isothermal curing was performed at five different temperatures, 160, 170, 180, 190, and 200°C, and dynamic testing was evaluated at six heating rates, 2, 5, 10, 15, 25, and 50 C/min. The weight of the samples was in the range 15–20 mg. The normalized heat of vulcanization was determined by integration of the area under the exothermal calorimetric signal.

RESULTS AND DISCUSSION

The curing characteristics, expressed in terms of t_i, optimum cure time (t_{97}), and torque value (ΔS) for the studied materials, are reported in Table II. First, to demonstrate the effect of temperature on the NR vulcanization, we report the cure-meter curves for NR at different temperatures in Figure 4. Rheometric t_i (the time to increase the torque one unit above the minimum torque) is the time available before onset of vulcanization. It was obvious that the t_i decreased with increasing temperature. In addition, the vulcanization rate increased as the temperature increased, which was clearly reflected in a noticeable decrease in

TABLE I
Recipes of the Compounds

Material	NR	NR–octadecylamine	NR–unmodified clay	NR–organoclay
NR CV (60)	100	100	100	100
Oxide Zinc	5	5	5	5
Stearic acid	1	1	1	1
Sulfur	2.5	2.5	2.5	2.5
MBTS	1	1	1	1
PBN	1	1	1	1
Octadecylamine	—	2.88	—	—
Unmodified clay	—	—	10	—
Organoclay	—	—	—	10

MBTS, benzothiazyl disulfide; PBN, phenyl beta naphtyl amine.

t_{97}, as compiled in Table II. An increase of 10°C in the cure temperature involved a decrease of almost two times in the t_{97}. As was expected, the torque value gradually decreased as the cure temperature increased. However, an overcuring reversion reaction was easily observed. Above t_{97}, the rheometer curve tended to descend, which corresponded to a loss of the mechanical characteristics of the material. This was attributed to the breakdown of bonds, in particular, polysulfide bonds. In the same manner and to evalu-

ate the effect of the incorporation of the clay (unmodified and organically modified) on the cure characteristics of NR, we obtained the vulcanization curves of all the studied materials at 160°C; these are represented in Figure 5. From these results, we deduced that the unmodified clay slightly decreased the t_i and t_{97} of the pure NR. However, both times were noticeably reduced when the organoclay was added into the elastomer. Similar behavior was observed at all of the temperatures tested. According to these results, we

TABLE II
Vulcanization Characteristics of the Different Compounds

| Material	T_c (°C)	t_i (min)	t_{97} (min)	ΔS (dNm)	$1/Q$
NR	150	6.00	19.97	4.46	
	160	3.25	9.48	4.30	
	170	1.75	4.88	4.12	
	180	1.00	2.57	3.80	
	190	0.65	1.49	3.64	
	200	0.50	0.99	3.09	
					0.38
NR–unmodified clay	150	4.50	16.68	3.65	
	160	2.35	8.58	3.40	
	170	1.30	4.24	3.18	
	180	0.75	2.10	2.83	
	190	0.55	1.27	2.66	
	200	0.45	0.82	2.41	
					0.28
NR–octadecylamine	150	2.50	6.35	6.03	
	160	1.50	3.64	5.78	
	170	1.00	2.12	5.59	
	180	0.60	1.32	5.36	
	190	0.50	0.90	5.03	
	200	0.35	0.68	4.63	
					0.41
NR–organoclay	150	1.30	4.09	8.98	
	160	0.80	2.34	8.71	
	170	0.65	1.42	8.36	
	180	0.45	0.95	7.65	
	190	0.35	0.78	6.85	
	200	0.20	0.58	6.13	
					0.48

T_c, cure temperature.
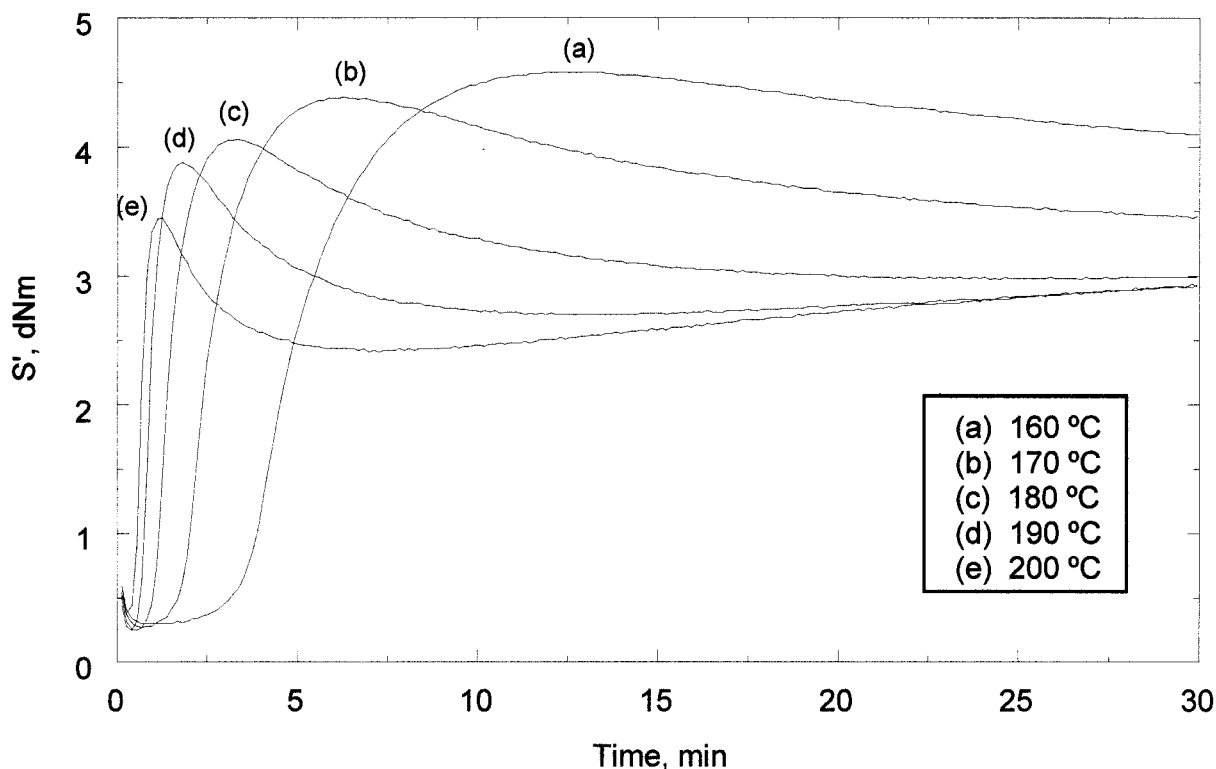
Figure 4 NR rheometer curves at different temperatures.

assumed that the organoclay behaved as a vulcanizing agent for NR, giving rise to a noticeable increase in the elastomer vulcanization rate. This effect was essentially attributed to the amine groups in the nanosilicate structure, which came from the organofilization of the clay, as shown in Figure 5, where the cure curve of NR with octadecylamine in the absence of the clay is represented. It is well known that the amine groups facilitate the curing reaction of styrene-butadiene rubber (SBR) and NR stocks.[23] Moreover, the synergetic combination of a benzothiazyl accelerant with an amine produces a particular accelerating effect on the rubber vulcanization reaction.

Nevertheless, it is worth mentioning that a further prominent effect on NR curing was observed in the presence of the organoclay. In fact, the intercalation of the octadecylamine within the silicate galleries facilitated the vulcanization reaction, which showed a noticeable decrease in the required time for NR vulcanization compared to the blend with only octadecylamine.

However, the torque values (ΔS), measured as the difference between the maximum and minimum torques, were also determined at several temperatures, as compiled in Table II. ΔS decreased in the presence of the unmodified clay, probably due to a poor interaction at the filler–matrix interphase. These results showed that when unmodified clay was added to the rubber, a conventional composite at a mi-

croscale level was formed. However, the organoclay nanocomposite gave rise to a dramatic increase in the torque value in relation to pure NR. Assuming that the torque value obtained from the vulcanization curve was proportional to the final number of crosslinks, we deduced that the organoclay noticeably increased the crosslinking density of NR. These results were attributed to the intercalation of the octadecylamine between the silicate galleries, increasing the interlayer distance, which facilitated the incorporation and confinement of the NR chains into the silicate galleries. Consequently, a better interaction between the filler and rubber was obtained. Interestingly, the pristine octadecylamine gave rise to a slight increase in the torque value compared to the neat NR, this reinforcing effect being more noticeable when the organoclay was added.

This assumption was corroborated by the swelling measurements in toluene. Parks[24] suggested that the value of $1/Q$ gives an idea about the degree of crosslinking, as deduced from the following expression:

$$Q = (\text{Swollen weight} - \text{Dried weight})$$
$$\div \ [(\text{Original weight} \times 100)/\text{Formula weight}] \quad (9)$$

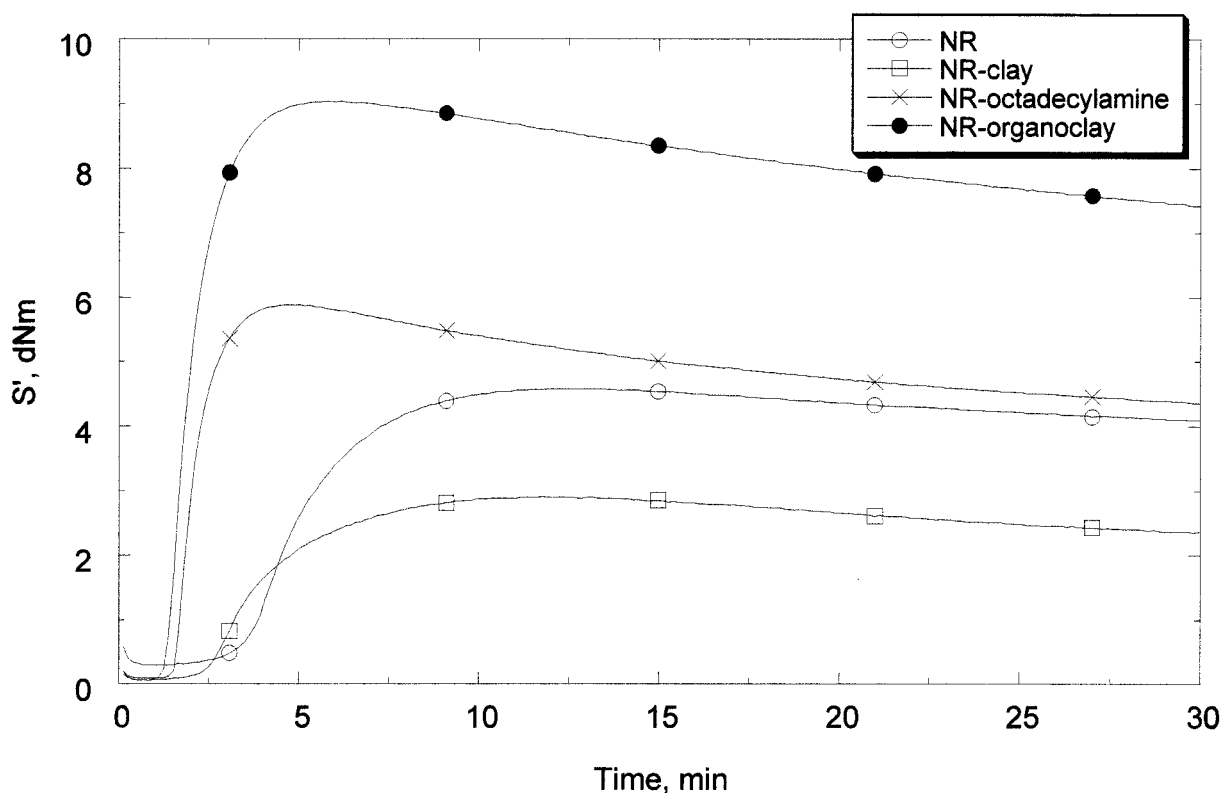where Q is the uptake solvent percentage. The $1/Q$ values for NR and its nanocomposites with unmodi-

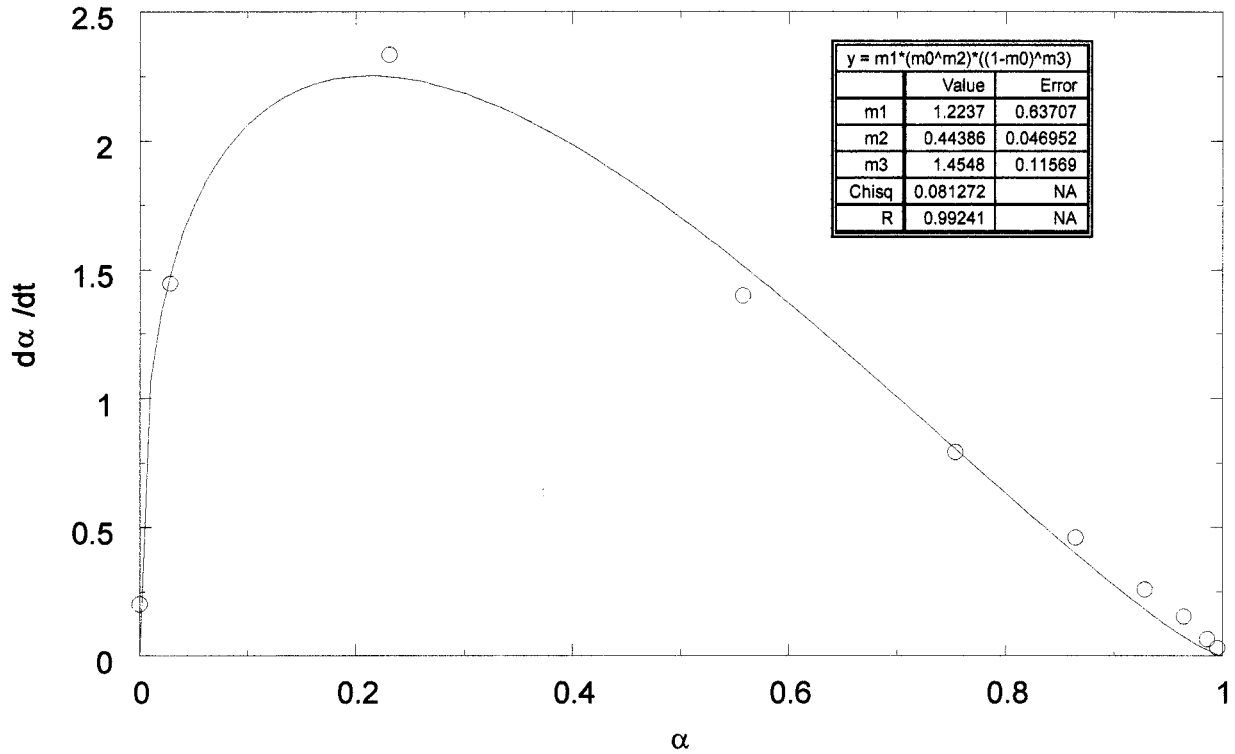**Figure 5** Influence of the clays on the NR rheometer curves at 160°C.

fied clay and organoclay are reported in Table II. The $1/Q$ values slightly decreased in the presence of the unmodified clay. However, a noticeable increase was observed when the clay was organically modified. These results further supported improved interactions between the filler and elastomer because of the confinement of the rubber chains within the silicate galleries. However, a slight increase in the degree of crosslinking was noticed when only the neat octadecylamine was added to the NR.

The kinetic parameters of the curing reaction of NR, NR–octadecylamine, and its NR–clay and NR–organoclay nanocomposites carried out in a Monsanto cure meter were determined from eq. (8). The values of K, n, and m at the different temperatures tested were calculated through linear multiple regression analysis of the experimental data, as is graphically represented in Figure 6. A plot of ln K, versus $1/T$ (Fig. 7) should give a straight line of slope $-E_a/R$, where E_a is the activation energy generated during the vulcanization process and R is the gas universal constant. The complete set of the kinetic parameters, derived from the rheometric curves, are reported in Table III. The values of K were in concordance with the conclusions deduced from the analysis of t_{97}. That is, the cure rate of the NR decreased as the cure temperature increased, and furthermore, the organoclay behaved as an effective vulcanizing agent for NR vulcanization,

showing a noticeable increase in K at all of the temperatures tested. As previously mentioned, this vulcanizing effect was mainly attributed to the amine groups coming from the organofilization of the clay. However, this effect was more noticeable when the octadecylamine was intercalated within the silicate galleries.

However, interestingly, the E_a of the elastomer slightly decreased in the presence of the clay, with this effect being more evident in the organoclay nanocomposite. These results confirmed that the processing conditions of NR improved in the presence of the organoclay because a lower amount of energy was required to transform the plastic unformed material into the elastic finished material. On the basis of these results, we concluded that the octadecylamine modified bentonite behaved as an excellent filler for the NR compounds and improved the cure characteristics of the NR. That is, the organoclay increased the torque value, decreased the cure time, and furthermore, gave rise to a noticeable decrease in the E_a of the vulcanization process. The ability of the model to describe the vulcanization kinetic of the NR and its nanocomposites is shown in Figure 6, where good agreement between the experimental and theoretical curves can be easily observed.

The effect of the unmodified clay and organically modified silicates on the NR vulcanization reaction were also analyzed by DSC, under both dynamic

y = m1*(m0^m2)*((1-m0)^m3)		
	Value	Error
m1	1.2237	0.63707
m2	0.44386	0.046952
m3	1.4548	0.11569
Chisq	0.081272	NA
R	0.99241	NA

Figure 6   Derivative of α as a function of the α of NR–organoclay at 170°C: (○) experimental results and (—) results predicted from eq. (8).

and isothermal conditions. Figure 8 shows the dynamic DSC curves for neat NR, where the heat flow absorbed during the vulcanization process is repre-

sented as a function of temperature at different heating rates. As shown, the curing temperature increased as the heating rate increased. The temper-
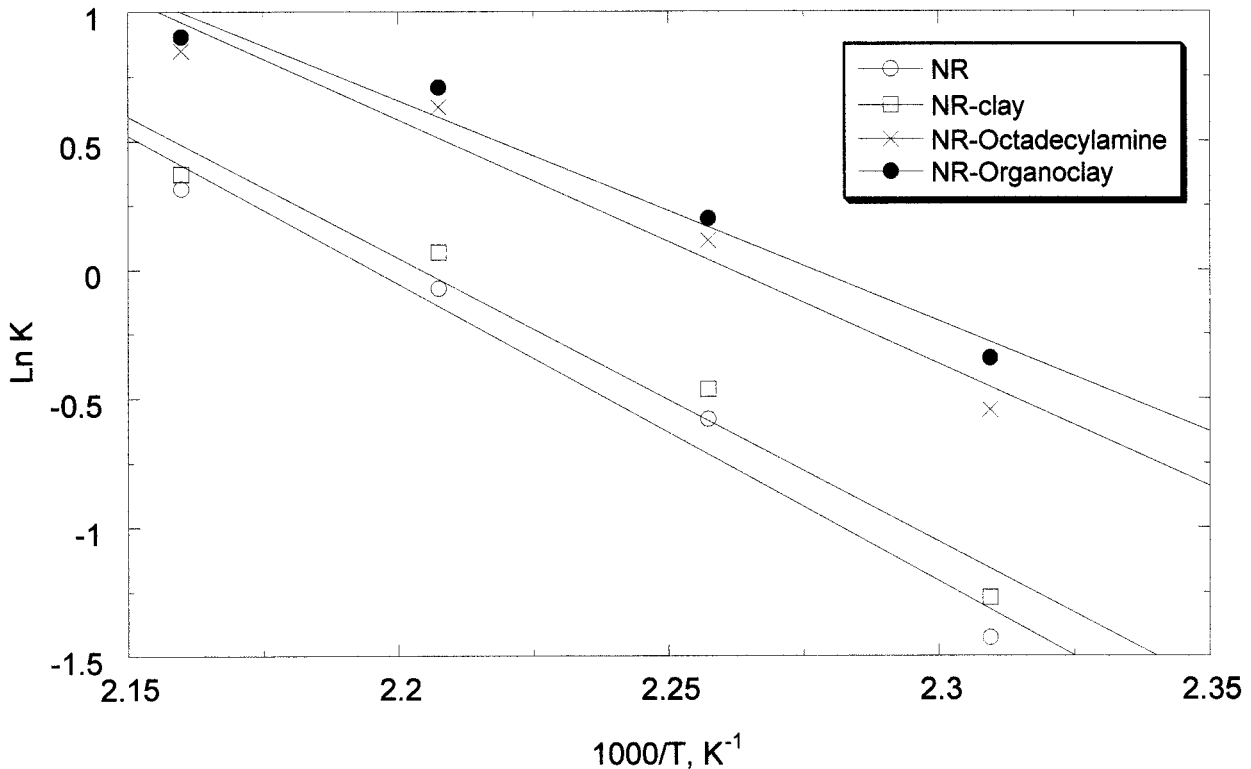
**Figure 7**   Ln K versus $1/T$ and calculation of E_a.

TABLE III
Kinetic Parameters of the Curing Reaction Obtained from Cure Meter Testing

	T_c (°C)	K	n	m	E_a (kJ/mol)
NR	160	0.24	0.68	1.54	
	170	0.56	0.51	1.38	
	180	0.93	0.58	1.49	
	190	1.37	0.52	1.29	
					95.9
NR–unmodified clay	160	0.28	0.53	1.60	
	170	0.63	0.44	1.54	
	180	1.07	0.46	1.52	
	190	1.45	0.55	1.49	
					91.4
NR–octadecylamine	160	0.58	0.58	1.57	
	170	1.12	0.48	1.48	
	180	1.88	0.52	1.46	
	190	2.34	0.53	1.55	
					78.7
NR–organoclay	160	0.71	0.62	1.55	
	170	1.22	0.44	1.45	
	180	2.03	0.51	1.44	
	190	2.47	0.55	1.53	
					71.1

T_c, cure temperature.

atures of the cure peaks (T_p's) for all of the studied materials at different heating rates are reported in Table IV. As shown, the unmodified clay hardly had any effect on T_p. However, the octadecylamine-modified clay gave rise to a dramatic decrease in the T_p values. These results confirmed the vulcanizing ability of the organoclay as previously suggested from the cure-meter studies. Moreover, the results from DSC curves demonstrated that this vulcanizing effect was mainly attributable to the amine
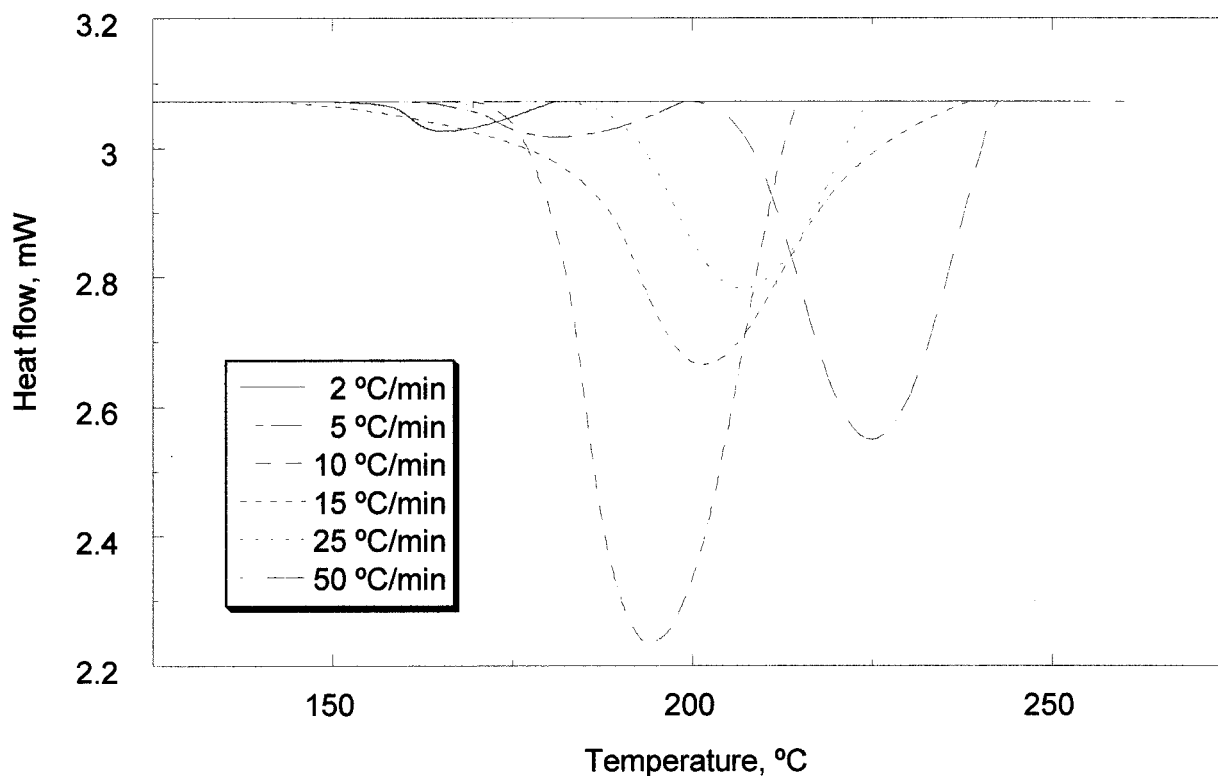
Figure 8 Heat flow versus temperature for NR at different heating rates.

TABLE IV
T_p's and E_a's in the Dynamic DSC Tests

Material	q (°C/min)	T_p (°C)	E_a (kJ/mol) Ozawa	Kissinger
NR	2	166.13		
	5	182.68		
	10	192.12		
	15	201.30		
	25	207.40		
	50	224.11		
			102.9	95.2
NR–unmodified clay	2	163.80		
	5	185.39		
	10	190.60		
	15	200.40		
	25	208.22		
	50	225.72		
			97.5	89.7
NR–octadecylamine	2	139.09		
	5	155.15		
	10	169.46		
	15	178.17		
	25	190.69		
	50	209.51		
			75.5	68.1
NR–organoclay	2	127.51		
	5	143.38		
	10	158.05		
	15	171.20		
	25	180.50		
	50	194.30		
			72.4	65.2

groups present in the nanosilicate structure. However, a further decrease in the temperature curve peak was observed when the octadecylamine was intercalated into the silicate structure.

The E_a of the curing process was easily estimated by means of both the Ozawa and Kissinger equations:

$$E_a = -2.3R \{(d \log q)/[d(1/T_p)]\} \quad (10)$$

$$E_a = -2.3R \{[d \log(q/T_i^2)]/[d(1/T_p)]\} \quad (11)$$

where T_p is the temperature of the exothermic peak and q is the heating rate. Plots of the temperature peak and its derivative versus heating rate (Ozawa and Kissinger equations, respectively) gave rise to straight lines, and from their slopes, the E_a of the process could be calculated (Figs. 9 and 10). The results obtained by both expressions are summarized in Table IV. These results were in concordance with those obtained from cure-meter testing. Hardly any difference existed between the pristine NR and the unmodified clay–NR composite. However, a noticeable decrease in the E_a was observed when the organoclay was added to the NR. These results corroborated the previous conclusions obtained from cure-meter measurements and confirmed that the nanostructured layered clay favored the processing conditions for NR because a lower energetic requirement for vulcanizing was needed.

The kinetics of the vulcanization reaction were also evaluated under isothermal conditions at different temperatures. Figure 11 shows the curing curves of NR as a function of time at different temperatures. As expected, the vulcanization rate increased as the temperature increased. To analyze the effect of the unmodified clay and organoclay on the NR vulcanization under isothermal conditions, the curing degree versus time curves, obtained by integration of the area under the exothermic peaks at 180°C, are graphically represented in Figure 12. As can be deduced, in the presence of the organoclay a noticeable decrease in the crosslinking time was observed, whereas little variation was obtained for the unmodified clay composite. These results supported the existence of a further improvement in the vulcanizing effect of the organoclay on the NR kinetic cure, which accelerated the crosslinking reaction. This behavior was mainly attributed to the amine groups, as deduced from Figure 12, where α of NR in the presence of the octadecylamine and in the absence of clay is represented. Moreover, the ability of the model to represent the curing process was also verified. However, independently of the cure temperature, the vulcanization process was always completed. This assumption was corroborated by a dynamic cure carried out after the isothermal curing of the samples to detect any uncured residual material, as shown in Figure 13. The results showed that in any case, no further residual enthalpy was observed, which confirmed that the vulcanization process was completed during the isothermal vulcanization.

The kinetic parameters of the vulcanization reaction, K, n, and m, were calculated by linear multiple regression analysis of the data of eq. (8), as represented in Figure 14. The kinetic parameters obtained under isothermal conditions are summarized in Table V. On the basis of these results, it was quite reasonable to deduce that the vulcanization rate increased with both the cure temperature and the incorporation of the organoclay. In addition, the vulcanization process of these materials was perfectly described by the proposed model, as shown in Figure 14. The plot of ln K versus temperature gave rise to a straight line whose slope corresponded to the E_a of the vulcanization process (Fig. 15). The obtained results are compiled in Table V, where a considerable decrease of the E_a is again shown for the organoclay nanocomposite in relation to both neat NR and unmodified clay composite.

The kinetic results obtained from DSC agreed well with those obtained from cure-meter testing and supported the strong assumption that the organically modified clay favored the vulcanization process of NR, giving rise to a noticeable decrease of both the t_i and the time for complete vulcanization and a noticeable decrease in the E_a of the process.
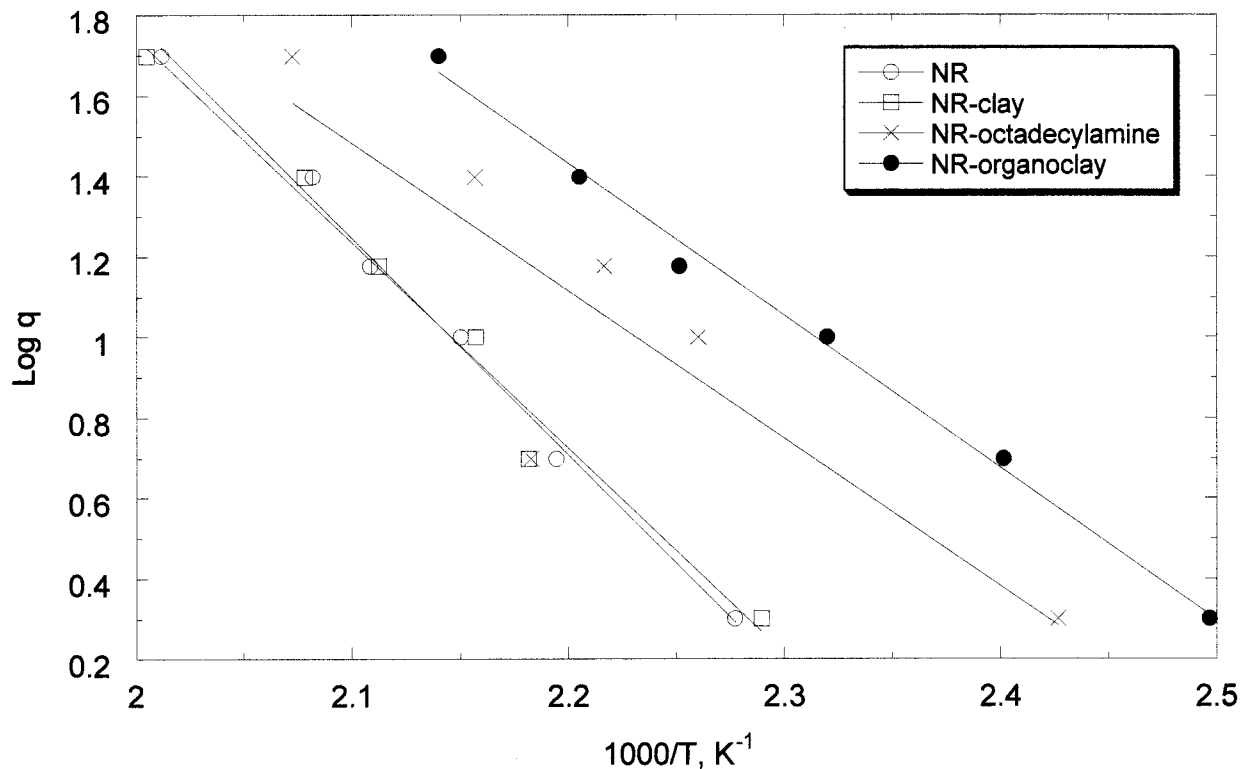
Figure 9 Calculation of E_a from the Ozawa equation.

The ability of the model to represent curing process of neat NR and its NR–clay composites and NR–organoclay nanocomposites is shown in Figures 6, 12, and 14, where a very good agreement between experimental and theoretical curves can be easily observed.
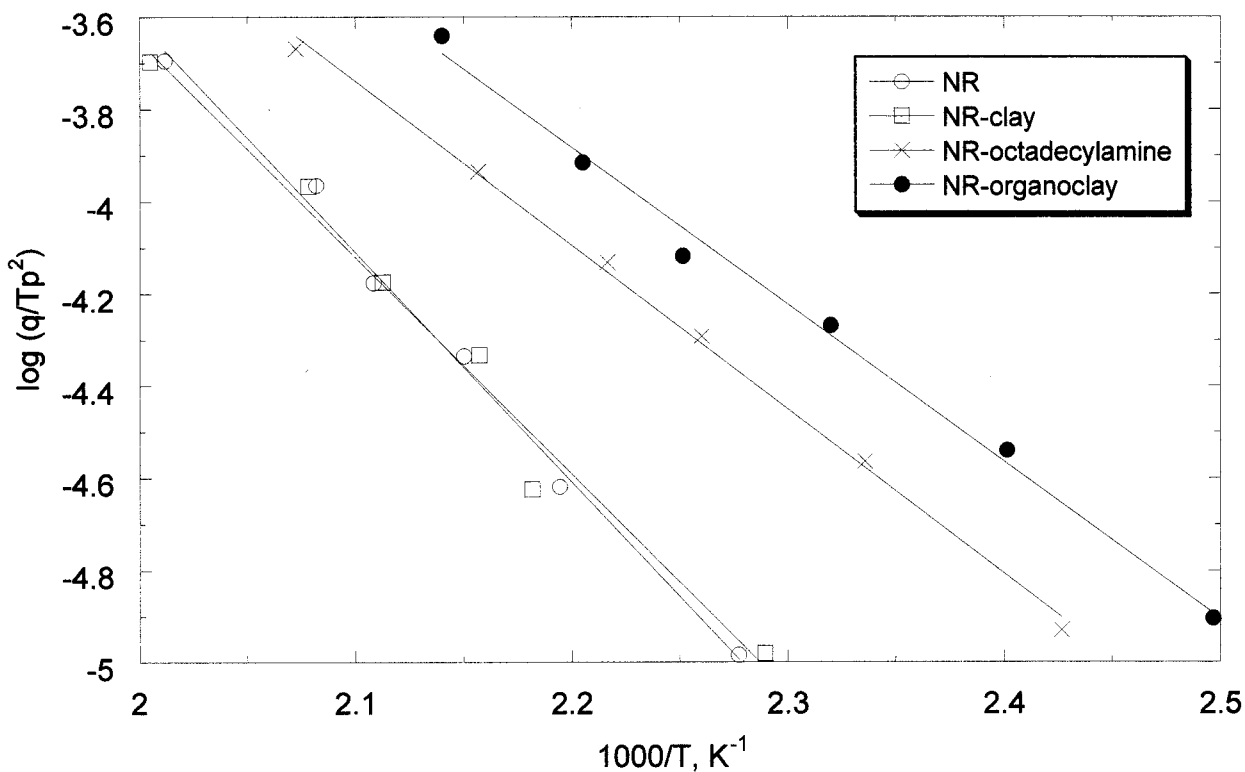

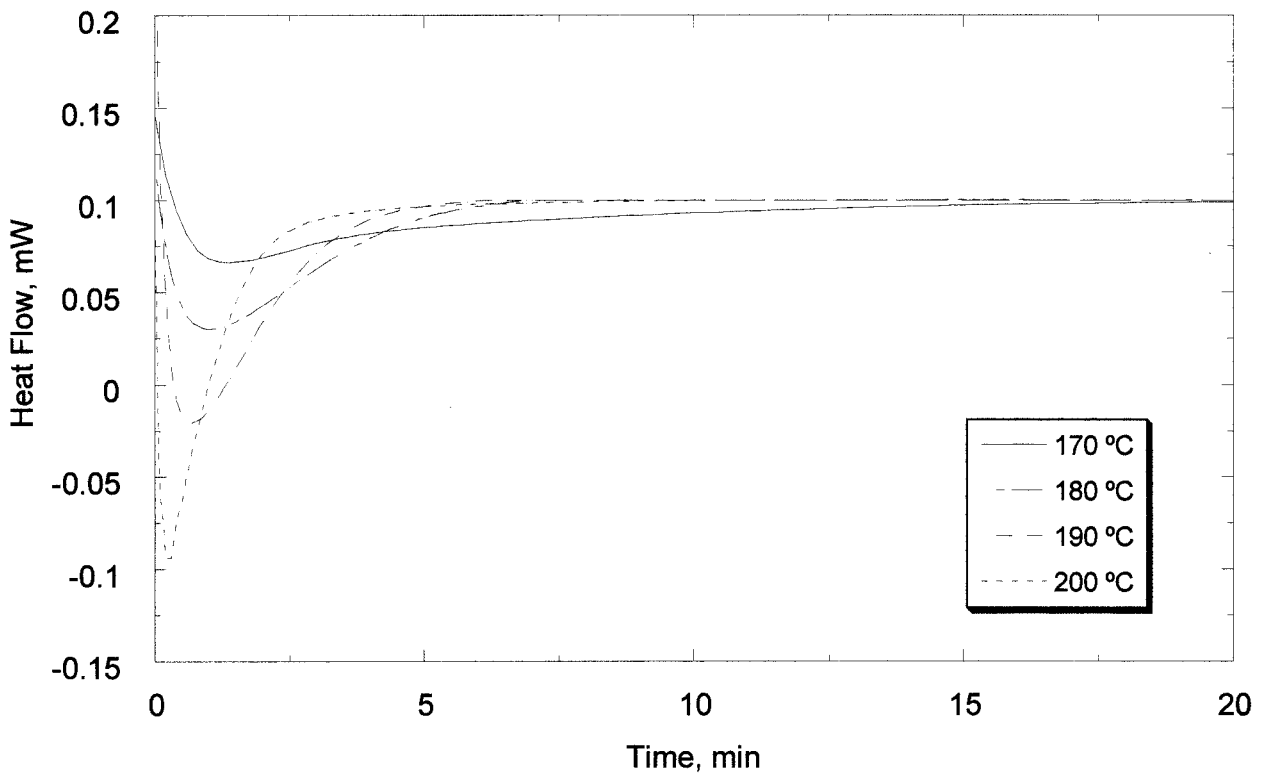**Figure 10** Calculation of E_a from the Kissinger equation.

Figure 11   Heat flow as a function of time for NR at different temperatures.

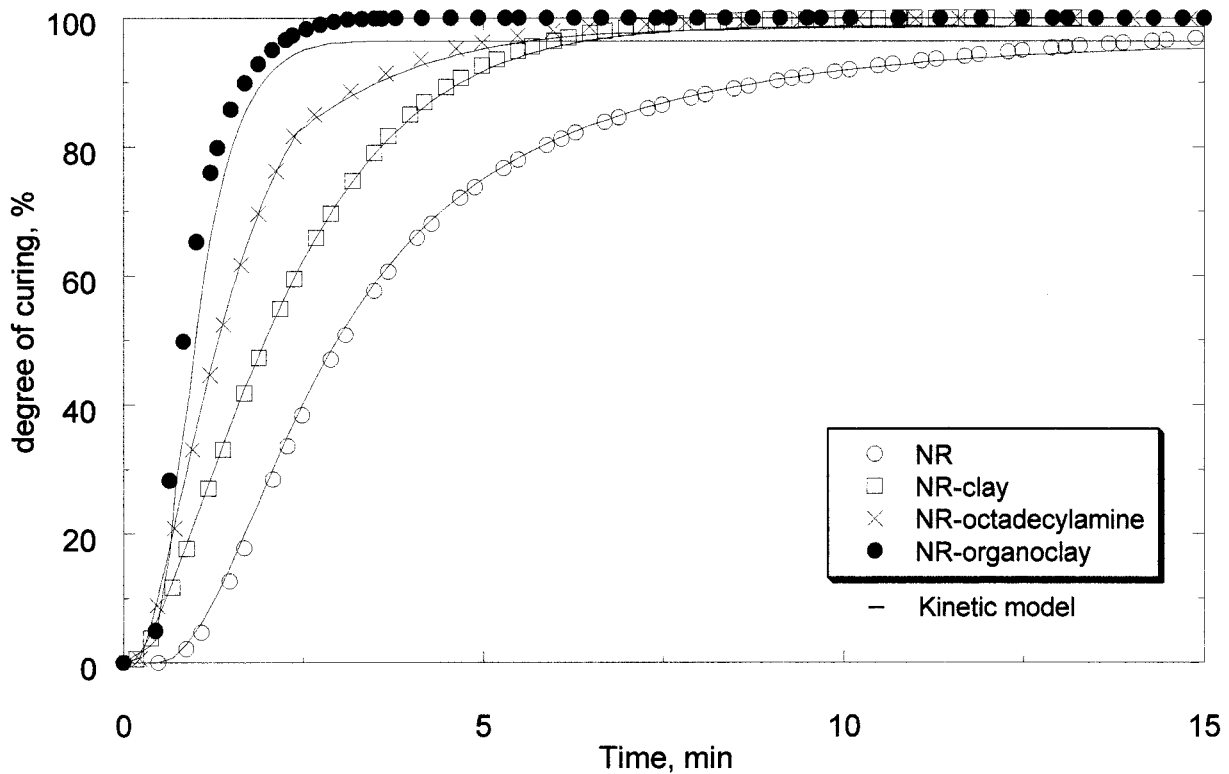**Figure 12**   Influence of the clays on the isothermal curing of NR at 180°C: experimental results and (—) results predicted from eq. (8).
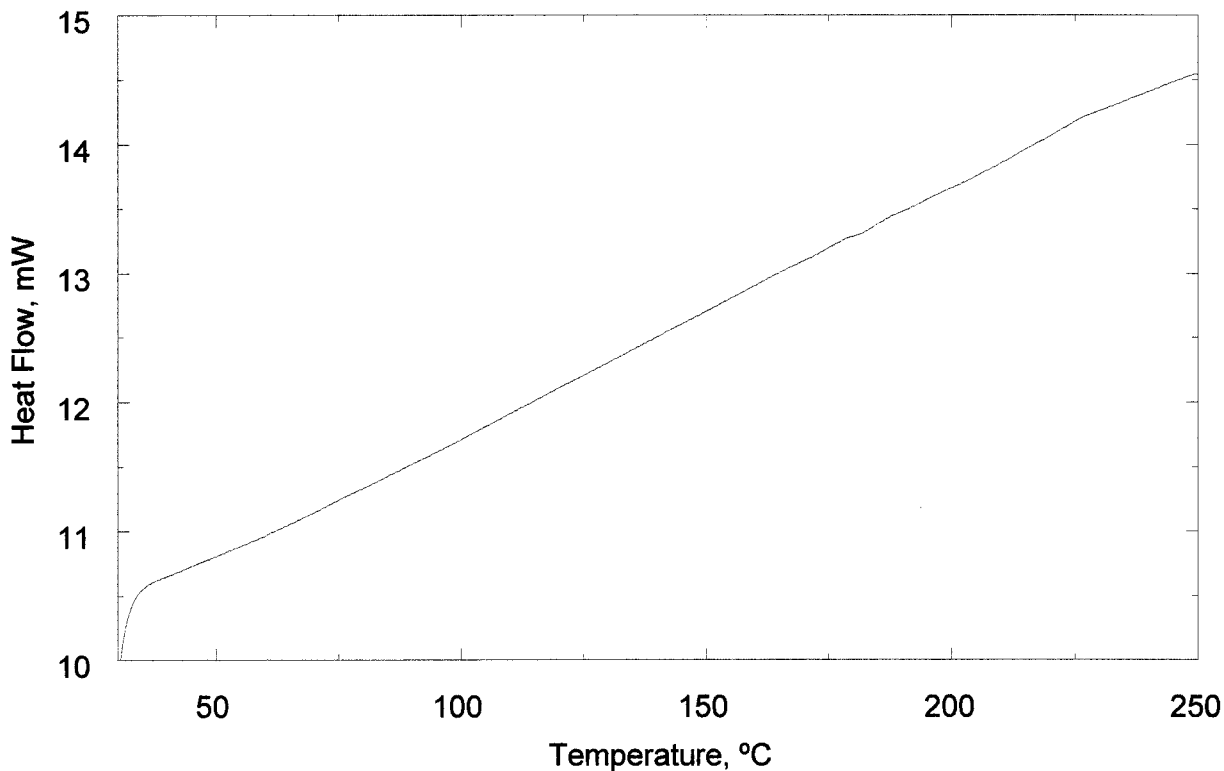
Figure 13 Dynamic curing of the organoclay–NR nanocomposite after isothermal curing.

CONCLUSIONS

The effect of the incorporation of unmodified and organically modified clays on the vulcanization reaction of NR was analyzed by cure-meter tests and thermal analysis. The kinetic studies performed by both techniques demonstrated that the clay hardly
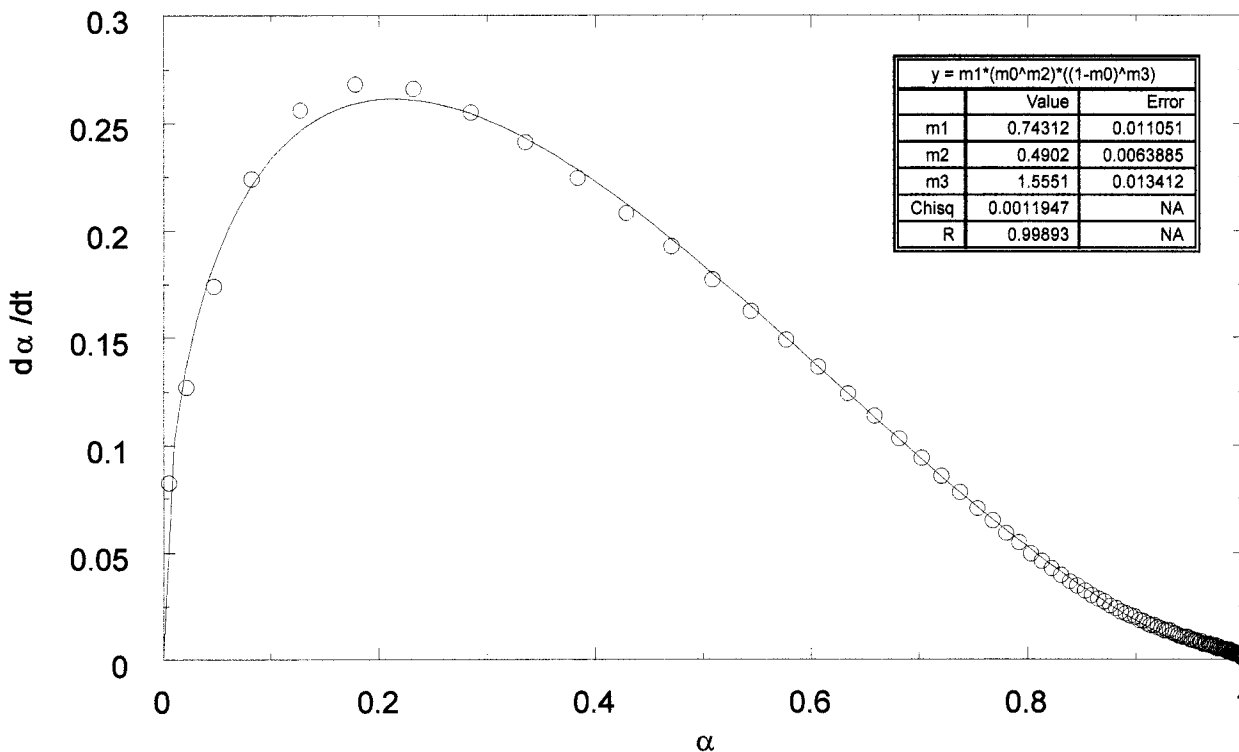

Figure 14 Derivative of α as a function of the α of NR at 180°C: (○) experimental results and (—) results predicted from eq. (8).

TABLE V
Kinetic Parameters of the Curing Reaction
**Obtained from Isothermal DSC**

	T_c (°C)	K	n	m	E_a (kJ/mol)
NR	160	0.21	0.53	1.43	
	170	0.51	0.47	1.48	
	180	0.74	0.49	1.55	
	190	1.17	0.44	1.59	
					92.4
NR–unmodified clay	160	0.23	0.49	1.53	
	170	0.61	0.51	1.56	
	180	0.88	0.53	1.48	
	190	1.23	0.47	1.55	
					90.4
NR–octadecylamine	160	0.52	0.50	1.58	
	170	0.91	0.53	1.56	
	180	1.63	0.56	1.54	
	190	2.08	0.53	1.51	
					79.3
NR–organoclay	160	0.63	0.48	1.60	
	170	1.06	0.51	1.57	
	180	1.88	0.55	1.53	
	190	2.21	0.53	1.49	
					72.5

T_c, cure temperature.

affected the crosslinking reaction of the rubber, but a strong vulcanizing effect was observed when the organically modified clay was added to the NR. This effect was attributed to the amine groups coming from the organofilization of the clay. However, a further increase in the vulcanization rate was obtained when the octadecylamine was intercalated within the nanosilicate structure. Moreover, an increase in the torque value was obtained in the organoclay nanocomposite, which indicated that a higher number of crosslinks were formed. A good theoretical description of the vulcanization behavior of NR compounds was obtained with an autocatalytic model. The proposed model fit the experimental data obtained by both techniques. The E_a of the vulcanization process decreased in the presence of the clay, this effect being particularly relevant when the clay was organically modified. These results indicated that the organoclay improved the processing conditions of the rubber because a lower energetic requirement was necessary for vulcanization.

We concluded that the nanolayered silicate not only exerted a marked reinforcing effect on the NR, as reported elsewhere,[25] but also favored the vulcanization process. In fact, it is well known that the combined effect of a benzothiazyl with an amine produces a vulcanizing effect, accelerating the vulcanization of NR. However, this effect was still more noticeable when the octadecylamine was intercalated between the silicate galleries. This led to a higher interlayer distance, which facilitated the incorporation and confinement of the NR chains within the silicate galleries,
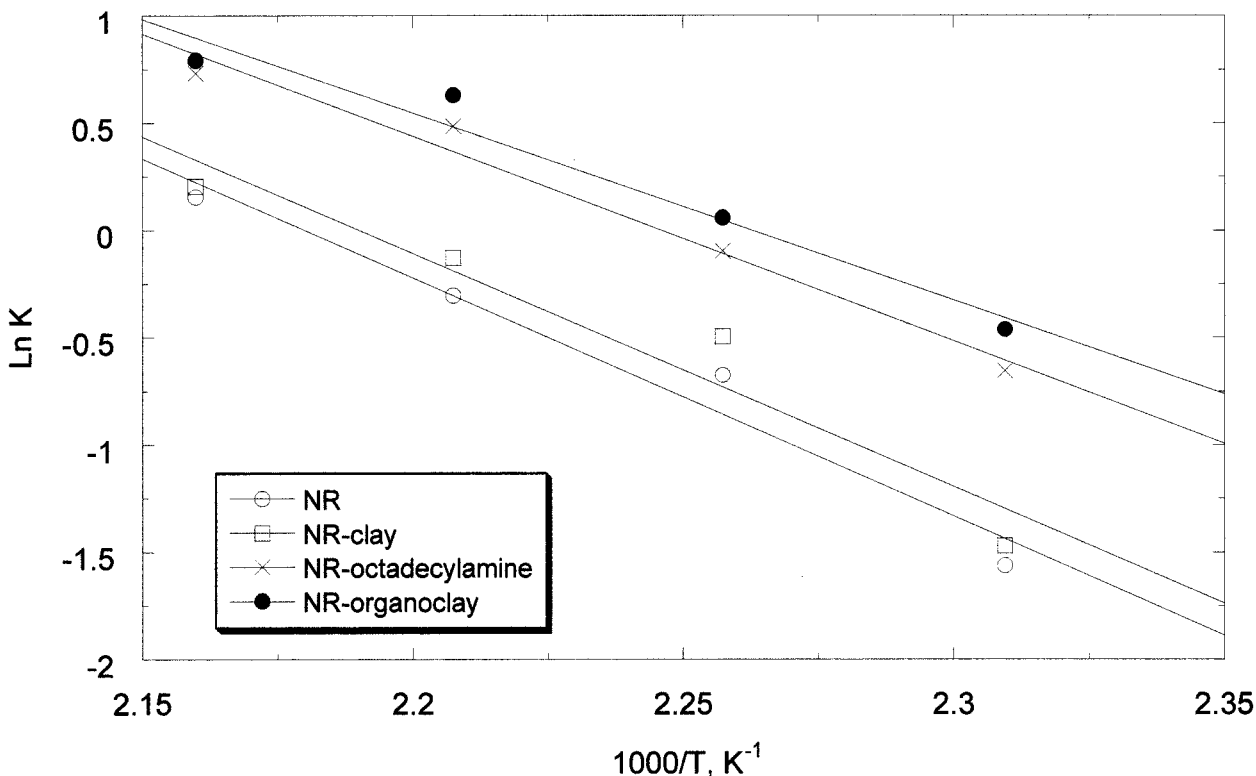
Figure 15 Ln K versus $1/T$ and calculation of E_a.

which implied a further strong interaction between the filler and the rubber.

References

1. Mehrota, V.; Giannelis, E. P. Mater Res Soc Symp Proc 1990, 171, 39.
2. Vaia, R. A.; Janalt, K. D.; Kramer, E. J.; Giannelis, E. P. Macromolecules 1995, 28, 1080.
3. Alexandre, M.; Dubois, P. Mater Sci Eng 2000, 28, 1.
4. Okada, A.; Usuki, A.; Kurauchi, T.; Kamigaito, O. Polym–Clay Hybrids 1995, 73, 117.
5. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. J Mater Res 1993, 8, 1185.
6. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. J Polym Sci Part A: Polym Chem 1993, 31, 1755.
7. Giannelis, E. P. Adv Mater 1996, 8, 29.
8. Yano, K.; Usuki, A.; Okada, A.; Kurauchi, T.; Kamigaito, O. J Polym Sci Part A: Polym Chem 1993, 31, 2493.
9. Kawasumi, M.; Hasegawa, N.; Kato, M.; Usuki, A.; Okada, A. Macromolecules 1997, 30, 6333.
10. Fukushima, Y.; Okada, A.; Kawasumi, M.; Kurauchi, T.; Kamigaito, O. Clay Miner 1998, 23, 27.
11. Reichert, P.; Kressler, J.; Thomann, R.; Mülhaupt, R.; Stöppelmann, G. Acta Polym 1998, 49, 116.
12. Wang, M. S.; Pinnavaia, T. J. Chem Mater 1998, 10, 3769.
13. Zilg, C.; Thomann, R.; Mülhaupt, R.; Finter, J. Macromol Chem Phys 1999, 200, 661.
14. Yangchuan, K.; Chefen, L.; Zongneng, Q. J Appl Polym Sci 1997, 71, 1139.
15. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. J Appl Polym Sci 1993, 49, 1259.
16. Messersmith, P. B.; Giannelis, E. P. J Polym Sci Part A: Polym Chem 1995, 33, 1047.
17. Okada, A.; Usuki, A.; Kurauchi, T.; Kamigaito, O. In Hybrid Organic–Inorganic Composites; Mark, J. E.; Lee, C. Y. C.; Bianconi, P. A., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 1995, 585, 55–65.
18. Ding, R.; Leonov, A. I.; Coran, A. Y. Rubber Chem Technol 1996, 69, 81.
19. Laidler, K. J. In Reaction Kinetics; Pergamon: New York, 1963; Vol. 1.
20. Armand, J. Y.; Vergnaud, J. Thermochim Acta 1997, 121, 381.
21. Piloyan, G. O.; Ryabchikov, I. D.; Novikova, O. S. Nature 1966, 212, 1229.
22. Berglund, L. A.; Kenny, J. M. SAMPE J 1991, 27, 2.
23. Mousa, A.; Karger-Kocsis, J. Macromol Mater Eng 2001, 286, 260.
24. Parks, C. R. Rubber Chem Technol 1982, 55, 1170.
25. Arroyo, M.; López-Manchado, M. A.; Herrero, B. Polymer, 2003, 44, 2247.