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Vulcanization Kinetics of Nitrile Rubber/Layered Clay Nanocomposites

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ABSTRACT: Cure kinetic studies on nitrile rubber(NBR)-layered clay nanocomposites, prepared by a melt mixing process, was investigated using a cure rheometer and differential scanning calorimeter (DSC). The characterization of the structure of the nanocomposites of uncured and cured samples was performed using X-ray diffraction. The results showed that the interlayer spacing of cured nanocomposites was smaller than that of the uncured sample due to partial removal of organoclay from the interlayer spacing. The cure characterization showed a marked decrease in the scorch time of the NBR/organoclay system without affecting the optimum cure time and torque values due to the accelerating and plasticizing effect of organoclay. DSC analysis showed a reduction in cure time and increase in enthalpy of

curing for the compounds added with organoclay. There was a little change in cure behavior of the NBR/unmodified clay system. NBR/clay nanocomposite showed the suitability of autocatalytic model for analyzing the cure parameters of rubber/clay nanocomposites. The activation energy of curing of NBR/O-MMT nanocomposites was lower than that of pristine NBR. The kinetic parameters determined from the model equation showed close fitting with the experimental results, indicating the suitability of autocatalytic model for cure characterization. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1688–1696, 2005

Key words: nitrile rubber; nanocomposite; cure kinetics; clay; autocatalytic model

INTRODUCTION

Polymer–clay nanocomposites have attracted more attention recently due to their outstanding mechanical properties, low gas permeabilities, and excellent fire-retardant properties.^{1–3} Methods for the preparation of nanocomposites include *in situ* polymerization, solution mixing, latex blending, and melt mixing. Melt intercalation is considered a promising method for fabricating polymer–clay nanocomposites due its many advantages including the use of existing processing equipment and its environmentally acceptable nature.⁴ Recently, many review articles on polymer–clay nanocomposites covering various aspects in this field were published.^{5–8} The nanocomposites generally form either intercalated and or exfoliated structure of the dispersed clay in the polymer matrix. To improve the extent of intercalation/exfoliation, the clay is modified by treatment with quaternary ammonium salts containing organic moiety through an ion

exchange reaction. The rubber-layered clay nanocomposites are highly relevant to rubber industries and considered an alternative to the conventionally and highly filled rubber compounds. The nanocomposite derived from acrylonitrile–butadiene rubber (NBR) has widely been studied with respect to cure characteristics, morphological and rheological,⁹ mechanical and dynamic mechanical,¹⁰ and gas barrier properties,^{11,12} fracture behavior,¹³ cure properties,¹⁴ etc. Also, Okada et al.¹⁵ reported that only 10 phr of layered clay was sufficient to achieve similar tensile properties to that of 40 phr carbon-black-filled NBR.

Most of the mechanical properties of rubber compounds are related to the degree of vulcanization and to the type and amount of filler. The vulcanization of the rubber compounds involves multiple and complex reactions, with the compounding ingredients leading to varied physicommechanical properties. So, the study on cure reaction and its kinetics can give insight into the actual mechanism of vulcanization and its effect on mechanical properties.

Several articles on the kinetics of vulcanization of various rubbers are available in the literature.^{16–18} Many of the kinetic studies on rubber vulcanization used a simple *n*th-order kinetic model to describe the cure parameters. However, the studies on the cure kinetics of many thermoset/layered clay nanocom-

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posites reported the use of complex kinetic models due to the presence of multiple steps in thermoset cure reaction.¹⁹ The studies on vulcanization kinetics of rubber nanocomposites using complex models are scanty. The cure kinetics studies on natural rubber–organoclay nanocomposites²⁰ and fluoroelastomer/clay nanocomposites²¹ showed the suitability of the autocatalytic model for analyzing the cure parameters of rubber/clay nanocomposites. Although many works were carried on NBR/layered clay nanocomposites, the cure kinetics of the same system has not been extensively studied so far. In this work, we explored the cure kinetics of NBR/clay nanocomposites using the autocatalytic model. The vulcanization reaction was analyzed from the data obtained from an oscillating die rheometer (ODR) as well as a differential scanning calorimeter (DSC). The influence of clay content on the vulcanization reaction was also evaluated.

EXPERIMENTAL

Materials

An acrylonitrile–butadiene rubber, NBR (Kosyn-KNB 35L, acrylonitrile content: 34%, Mooney Viscosity ML_{1+4} at 100 °C: 41, specific gravity: 0.94) was provided by Korea Kumho Petrochemical, Korea. Montmorillonite (Na-MMT) with a cation-exchange capacity of 119 meq/100 g was provided by Kunimine Industries, Japan. The organomodified MMT (Cloisite 15A) was supplied by Southern Clay Products (Gonzales, TX). Other chemicals, obtained from local manufacturers, were used as such.

Preparation of rubber nanocomposites

Rubber compounds were prepared in an open two-roll mill. The compounding ingredients (zinc oxide, 5 phr; stearic acid, 3 phr; sulfur, 2 phr; and accelerator (NS), 1 phr) were added to the elastomer after the incorporation of the clay and the accelerator was added at the end of mixing. The compounds are denoted NBR-M and NBR-OM for MMT- and OMMT-filled compounds, respectively. The loading of filler is also indicated in the compound notation. The compounds were cured at 160 °C in a heated press (Carver, Wabash, IN) under a pressure of 5 MPa for the optimum cure time, which was determined from a curemeter (ODR-2000, Alpha Technology, Akron, OH), to make a rubber sheet for mechanical testing.

Characterization

X-ray diffraction pattern

To establish the interlayer spacing of Na-MMT, organoclay, and rubber/clay composites, wide-angle X-

ray diffraction data between 2 and 20° of 2θ value at a scanning rate of 2°/min were obtained from the scattering patterns taken with 40 kV, 40 mA $\text{CuK}\alpha$ radiation using an X-ray diffractometer (Rigaku 2500PC, Japan) with a radiation wave length of 1.54 Å at room temperature.

Cure behavior

The vulcanization behavior of the unfilled and clay-filled NBR was determined at four different temperatures viz. 150, 160, 170, and 180 °C using an ODR. Different cure kinetic parameters such as cure rate, degree of crosslinking or conversion, and apparent activation energy were calculated from the torque–time curves.

The DSC measurements were performed with TA instruments (DSC Model No. 2910) under nitrogen atmosphere. The curing reaction was characterized with a sample weight of about 10–15 mg for isothermal and nonisothermal cure behavior. The isothermal curing was carried out at 150, 160, 170, and 180 °C and the nonisothermal method was performed at a heating rate of 10 °C/min. The enthalpy of curing at different conversion times was determined using TA Instruments Universal Analysis software (version V2.3C).

RESULTS AND DISCUSSION

X-ray diffraction pattern

The structure and morphology of NBR/clay nanocomposites have been well discussed in the literature.^{10,12,15} The XRD pattern of the NBR/O-MMT before and after curing shows some unusual peak positions (Fig. 1). In contrast to the observed change in the peak positions reported for many cured rubber/clay nanocomposites,^{22,23} the XRD peak position of our cured samples shows a shift in 2θ values toward higher 2θ with an increase in peak height for all O-MMT loadings. Although the exact reason for decrease in d -spacing after curing could not be identified, it may be due to the increase in mobility of organic moiety of O-MMT and the polymer chains at the molding temperature and pressure. Part of the intercalated components might have been squeezed out from the clay layers due to the plasticizing action of the long-chain organic modifier in the clay before the actual commencement of cure reaction. This might have led to the formation of some clay aggregates, which resulted in increased peak height. However, this phenomenon is only partial without complete deintercalation of O-MMT as evident from the XRD pattern.

Cure behavior

The vulcanization characteristics, expressed in terms of the scorch time, t_{s2} , optimum cure time, t_{90} , and the

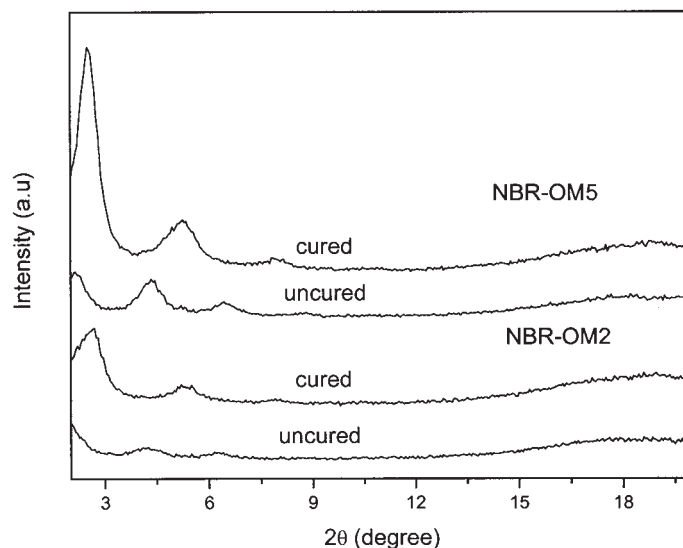


Figure 1 XRD pattern of NBR/O-MMT nanocomposites before and after vulcanization.

difference in minimum and maximum torque value, ΔS , for NBR and NBR/clay systems are reported in Table I. The rheographic profile of NBR and NBR/clay composites with 15 phr clay loading at 160 °C is represented in Figure 2(a). While no appreciable differences in scorch time are observed for pristine clay-filled compounds, the organoclay-filled compounds showed considerable reduction in the scorch time even at a lower loading (2 phr) of organoclay. Similar behavior is also observed for all the organoclay-filled compounds cured at different temperatures. From the above observation, it can be inferred that the clay mineral, as such, has little influence on the cure reaction of the rubber compounds. However, the organoclay behaves like a vulcanizing accelerator for NBR, thus decreasing the scorch time. This effect is essen-

tially attributed to the quaternary ammonium salt present in the nanosilicate structure which comes from the organophilization of the clay. The quaternary ammonium salt involves itself in the cure reaction by forming a complex with zinc salt and sulfur.²⁴ Moreover, the sulfonamide accelerated curing of unsaturated rubber generates cyclic pendent amines, which are involved in the formation of polysulfidic crosslinks.²⁵ The amine group from the organoclay enhanced the cure rate by undergoing complex formation with rubber compounding ingredients, which subsequently forms crosslinks. Another reason for fast curing of NBR in the presence of O-MMT may be due to the facilitation of the cure reaction even in the intercalated silicate galleries. Interestingly, the difference in the minimum and maximum torque, ΔS , for

TABLE I
Cure Characteristics of NBR and NBR/Clay Nanocomposites

Properties	t_c (°C)	NBR	NBR-OM2	NBR-OM5	NBR-OM15	NBR-M15
M_H-M_L	150	25.8			25.6	29.1
	160	26.6	27.7	26.7	26.2	30.2
	170	25.8	—	—	25.6	29.9
	180	25.5	—	—	24.1	29.2
T_{s_2}	150	10.9	—	—	3.0	10.8
	160	6.2	3.8	2.9	2.1	6.0
	170	3.9	—	—	1.6	3.7
	180	2.6	—	—	1.2	2.5
T_{90}	150	31.8	—	—	34.2	30.7
	160	24.8	23.4	25.8	22.9	23.8
	170	11.9	—	—	12.5	14.0
	180	7.0	—	—	6.4	7.3
CRI	150	4.8	—	—	3.2	5.0
	160	5.4	5.4	4.4	5.0	5.6
	170	12.5	—	—	9.1	9.7
	180	23.2	—	—	19.2	20.4

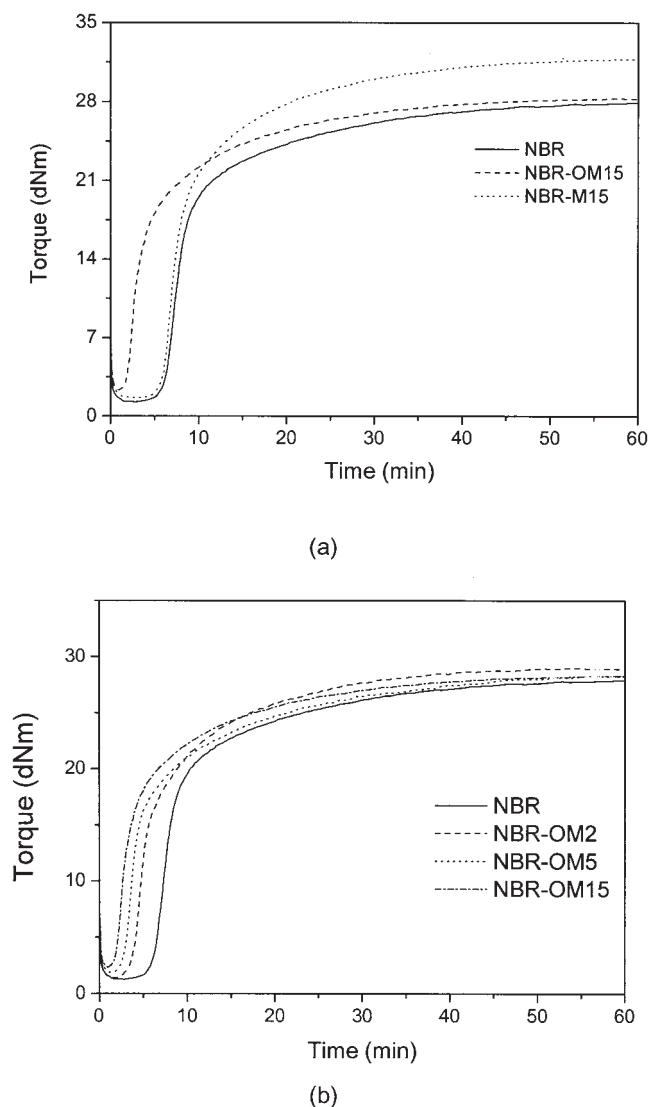


Figure 2 (a) Rheocurves of torque versus time for NBR and its nanocomposites at 160 °C and (b) rheograph showing the effect of O-MMT loadings on torque with time.

this compound is close to or a little less than that of pristine NBR. This may be attributed to the plasticizing effect of long-chain organic moiety in the organoclay.²⁶ On the other hand, NBR/Na-MMT composite shows higher ΔS values due to the presence of filler aggregation, leading to resistance to polymer chain mobility. The effect of loading of organoclay on cure reaction at 160 °C is depicted in Figure 2(b). Increase in clay loading decreases the scorch time without changing the optimum cure time and ΔS considerably. The reduction in scorch time may be due to the availability of a greater amount of quaternary ammonium salt from organoclay for the cure reaction, which is proportional to organoclay loading. It is inferred that the inclusion of organoclay changes the rate of curing by participating in the cure reaction. However, the degree of curing is practically unaffected as seen from similar

values of minimum and maximum torque. The influence of temperature on vulcanization of NBR-OM15 is represented in Figure 3(a). It is obvious that an increase in temperature decreases the t_{s2} and t_{90} while increasing the cure rate due to availability of more thermal energy for the cure reaction. However, when curing at a high temperature, the marching nature of the cure curves becomes flattened, indicating the possibility of thermal degradation of NBR, which will lead to reversion of the compound as seen from the rheograph of NBR-OM15 at 180 °C [Fig. 3(a)]. This fact is reflected in all compounds, irrespective of the nature of the compound, as seen in Table I. The effect of temperature on cure properties is more pronounced in NBR-OM15 compared to other compounds. A plot of conversion against cure time for NBR-OM15 system at various temperatures is shown in Figure 3(b). At a given time, the degree of conversion increases with increasing cure temperature. At lower temperature, the attainment of 100% cure takes a long time with a gradual increase in degree of curing. As the tempera-

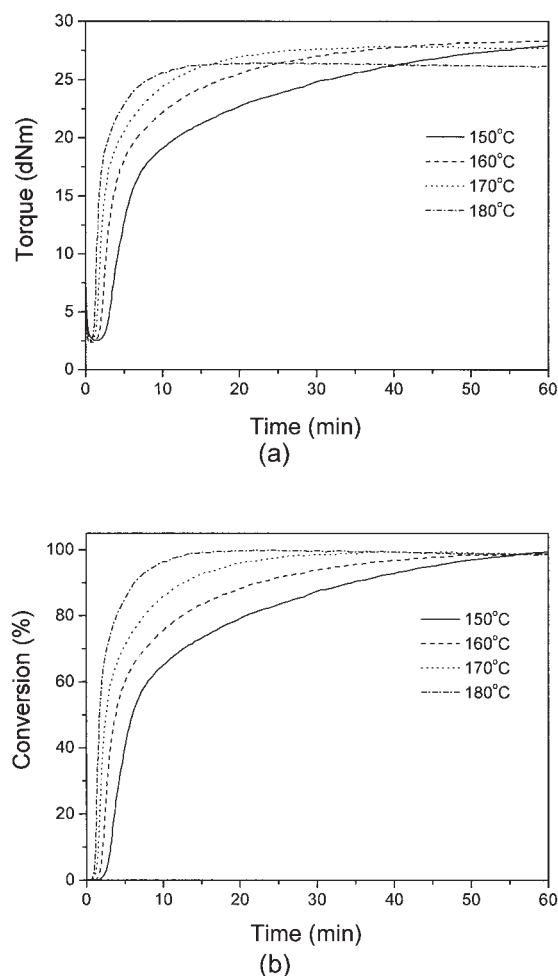


Figure 3 (a) Rheographic profile of NBR-OM15 at four different temperatures; (b) cure conversion versus time of NBR-OM15 at four different temperatures.

ture is increased, the rate of conversion also increased, with a steep rise in the conversion curve. This trend is almost similar to that of all the other compounds. Having similarities between the cure characteristics of compounds in many respects, it will be useful to analyze the kinetic aspect of cure reaction to determine the detailed kinetic parameters, which influence the cure reaction. So the kinetic parameters of the systems were evaluated using a model suitable for kinetic analysis based on the experimental results.

Cure kinetics

The curemeter and the differential scanning calorimetric experiments under isothermal conditions yielded data on torque and heat flow versus time, respectively, which can be used to evaluate kinetic parameters with a series of mathematical expressions. The extent of crosslinking or degree of curing (α) can be calculated from either the torque using cure meter or the heat flow using DSC. The degree of cure at a time, t , is defined as^{27,28}

$$\alpha = \frac{M_t - M_0}{M_h - M_0} \quad (1)$$

and

$$\alpha = \frac{\Delta H_t}{\Delta H_\infty} \quad (2)$$

where, M_0 , M_t , and M_h are the torque values at the time zero, at a given time of curing, and at the end of curing, respectively. ΔH_t and ΔH_∞ are the accumulated heat evolved at time t and the total heat evolved during vulcanization, respectively.

The isothermal vulcanization kinetics of the rubber compounds is usually characterized by two general model equations namely, n th-order and autocatalytic model equations. The n th-order kinetics model, the simplest model to represent the overall curing process, is given by²⁹

$$\frac{d\alpha}{dt} = k(T)(1 - \alpha)^n, \quad (3)$$

where n is the reaction order and k denotes the temperature-dependent rate constant. The n th-order kinetic equation predicts that the maximum reaction rate occurs at the very beginning of the reaction, whereas the autocatalytic equation demonstrates that the maximum reaction rate will be at any point of time other than time $t = 0$. This discrepancy is because the conversion rate is not only related to the amount of unreacted material, but also related to the reaction product. From our experimental results both from

ODR and DSC, it is seen that the maximum rate of conversion occurs at the time greater than zero. So the model for autocatalytic reaction equation, as given below,²⁹ can be used for the cure kinetics characterization of NBR/clay nanocomposites,

$$\frac{d\alpha}{dt} = k(T)\alpha^m(1 - \alpha)^n, \quad (4)$$

where k is the rate constant and m and n are reaction orders that are dependent on temperature. The rate constant, k , obeys an Arrhenius temperature dependency,

$$k = Ae^{-E/RT}, \quad (5)$$

where A is the preexponential factor, E is the activation energy, R is the gas constant, and T is the absolute temperature.

Using eq. (4), three parameters, namely, k , n , and m , can be determined using a nonlinear regression analysis. The values of these parameters for all systems are given in Table II. The suitability of autocatalytic model for cure kinetic analysis was established by fitting the above model parameters with the experimental values, which show a close fitting with each other for the cure rate versus cure conversion curves. Also, the choice of this model is supported by the close correlation between the rate constant (k) values determined from the model equation and the results obtained from optimum cure time (t_{90}). An increase in temperature increases the k values and decreases the t_{90} , showing the inverse relation between k and t_{90} upon increasing temperature. Additionally, this model has been applied successfully to describe the cure kinetics of natural rubber and fluoroelastomer nanocomposites.^{20,21}

Figure 4(a) shows the plot of $d\alpha/dt$ versus time for NBR-OM15 at four different temperatures. The reaction rate is affected by the isothermal curing temperature as well as cure time. At a given temperature, the reaction rate is observed to increase initially with conversion and passes through a maximum and then gradually slows down, finally tending to zero. Additionally, at a given time, higher isothermal curing temperature gains higher cure rate. Moreover, the higher the temperature, the shorter the reaction time. This shows that the reaction rate of the system reaches a maximum at time $t > 0$, which is the characteristic of autocatalytic reaction. So the autocatalytic model is more appropriate to describe the cure behavior of the system. Figure 4b shows the plot of cure rate ($d\alpha/dt$) versus the degree of conversion (α) for NBR and NBR/clay composites loaded with 15 phr of clay. In this plot, a comparison is also made between the experimental curves (points) and the model curves

TABLE II
Vulcanization Kinetics Parameters and Activation Energies of the NBR and Its Nanocomposites
with 15 phr Filler Loading

Sample	$T_c(^{\circ}\text{C})$	K	m	n	ΔH^* (J/g)	E_a (kJ/mol)
NBR	150	1.34 (0.388)	2.82 (0.637)	0.88 (0.708)	4.95	132.04 (124.72)
	160	2.75 (1.131)	3.23 (0.834)	0.99 (1.403)	6.45	
	170	7.63 (1.80)	3.40 (0.933)	1.22 (1.767)	8.87	
	180	15.27 (4.51)	3.51 (0.877)	1.26 (2.447)	10.26	
NBR-M15	150	1.79	2.93	1.05	4.56	118.70 (112.60)
	160	4.80 (0.968)	4.12 (0.932)	1.15 (1.302)	5.54	
	170	13.85 (2.287)	4.50 (0.925)	1.40 (1.782)	8.34	
	180	14.84 (3.844)	3.65 (0.891)	1.26 (2.856)	9.54	
NBR-OM15	150	1.49 (0.427)	3.93 (0.292)	0.78 (0.778)	8.83	73.95 (72.19)
	160	3.38 (0.737)	4.13 (0.373)	0.84 (1.479)	10.40	
	170	4.59 (1.038)	4.51 (0.408)	0.91 (1.826)	12.96	
	180	6.28 (1.727)	3.23 (0.496)	0.78 (2.050)	14.50	

Note. The values within the parentheses were obtained from DSC results.

(solid lines). The model curves show a close fitting with experimental curves with the R^2 (correlation coefficient) value very close to unity ($\cong 0.99$). All compounds show the maximum degree of conversion (α_{\max}) between 0.1 and 0.35. While the NBR shows high value of α_{\max} , the NBR/O-MMT has low α_{\max} , indicating the fast curing nature of the later compound due to the accelerating effect of quaternary ammonium ion present in the O-MMT. These trends are in accordance with the scorch time as well as the rheographic profile of these compounds. A similar trend is also observed for all O-MMT-filled NBR compounds showing the accelerating effect of O-MMT upon increasing its loading (not shown). Figure 4(c) represents the influence of temperatures on the cure parameters of NBR-OM15. The cure rate versus conversion curves at four different temperatures indicates an increase in cure rate upon rising temperature. This trend is analogous to all other compounds, indicating the effect of temperature in increasing the cure rate. Here again, the autocatalytic models curves fit quite well with the experimental results at all conversions. The slow conversion at low temperature may be attributed to the effect of higher viscosity of compounds, which hindered the formation of crosslinks between adjacent polymer chains.

To understand further the kinetics of vulcanization of NBR in the presence of layered clay, an Arrhenius plot of $\ln k$ versus $1/T$ is drawn to determine the activation energy of vulcanization (E_a). A typical plot is shown in Figure 5 for pristine and clay-filled NBR cured at four different temperatures. The activation energies for these systems obtained from the slope of the straight line is given in Table II. It is seen from the Arrhenius plot that the slope of NBR and NBR-M15 showed a similar trend, whereas NBR-OM15 showed a moderate slope, having crossover points with the NBR at lower temperature. This suggests that the organoclay-containing compounds need a lower amount

of energy for curing, as depicted in the form of activation energy. An increase in temperature does not change the rate constant considerably, indicating that curing of this compound can be done at a relatively lower temperature compared to either NBR or NBR-M15 compounds. The E_a decreased upon the addition of clay. The reduction in E_a is appreciable in the case of O-MMT-filled NBR. This observation is consistent with the discussion mentioned above that the cure rate of clay filled systems was higher than that of pure NBR. The large decrease in E_a of the NBR-OM15 system may be attributed to the cure accelerating effect of quaternary ammonium salt used for clay modification.

Cure characterization by DSC

DSC is one of the most useful techniques applicable to the assessment of enthalpy changes that accompany various material transformations. DSC measurement can identify and characterize polymerization, crosslinking, crystallization, and melting of crystallites in terms of heat evolved or absorbed and the associated transition temperatures. Furthermore, these thermal data enable one to deduce the reaction rate constant, kinetic reaction order, activation energy, etc. We used DSC for the analysis of vulcanization reaction of NBR/layered clay nanocomposites. A typical isothermal DSC scan for NBR and its nanocomposites at 170 $^{\circ}\text{C}$ is represented in Figure 6(a). The exothermic peak position and the area under curves can be used to predict the speed and amount of crosslinking. As indicated in Figure 6a, the NBR-OM15 system exhibits faster curing and higher crosslinking compared to pristine NBR and NBR-M15. This result almost matches the rheometer data. Also, the DSC study on the effect temperature on the cure reaction of systems shows a similar trend to that of rheometer results. A representative trace of isothermal DSC of NBR-OM15 at four different temperatures is depicted in Figure

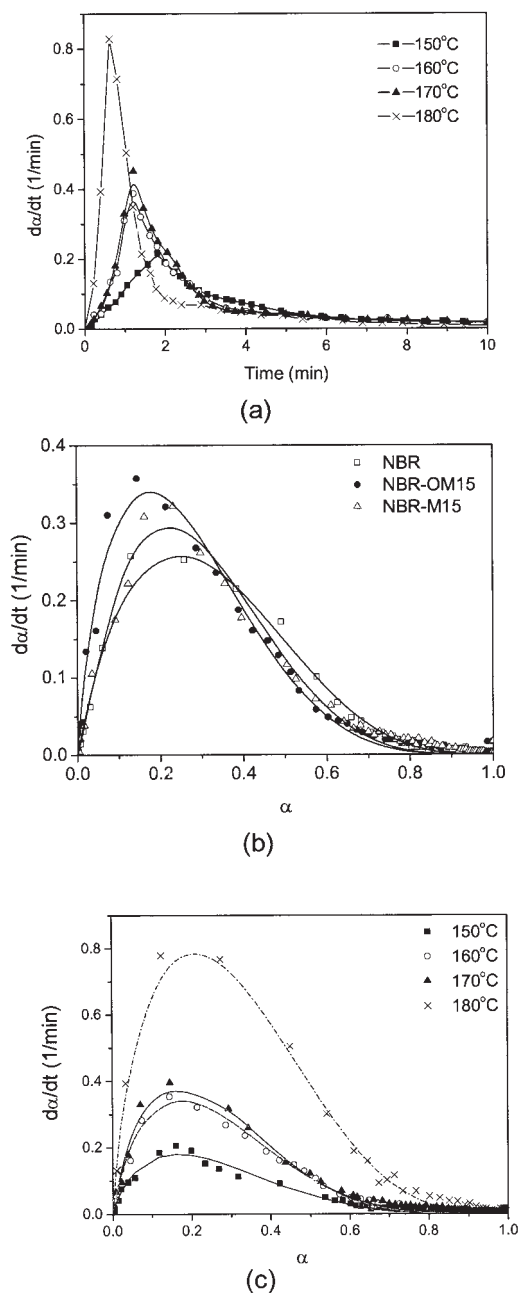


Figure 4 (a) Vulcanization rate versus cure time curves for NBR and its nanocomposites. (b) Vulcanization rate versus degree of conversion for NBR and its nanocomposites. (c) Trend of rate of conversion obtained for NBR-OM15 in isothermal curing at four different temperatures.

6(b). As expected, the curing rate is increased with increase in temperature by shifting the exotherm peak position toward the lower end of the time scale. The same trend is followed by the other systems too. However, the NBR-OM15 system demonstrates a pronounced effect in reducing the cure time compared to pristine and Na-MMT-filled systems. The enthalpy of curing, ΔH (total heat evolved during curing), and the fraction of heat liberated at a time, H_t , were measured

to study the kinetics of vulcanization reaction. Table II shows the ΔH for all the systems studied for kinetic analysis at different temperatures. The degree of conversion (α , using eq. (2)) and rate of curing ($d\alpha/dt$) were calculated and the kinetic parameters such as k , m , and n (in eq. (4)) were evaluated using nonlinear regression analysis and the values are listed in Table II. Similar to curemeter data, DSC kinetic analysis also shows direct proportionality between the k values and the temperatures. The difference in k values between the curemeter and DSC analysis may be due to the different nature of the experimental background. Figure 7 depicts the plot of cure rate ($d\alpha/dt$) versus α for NBR-OM15 at four different temperatures. The rate of cure during or the curing process is accelerated by increasing the temperature. As a result, for the same amount of O-MMT in the nanocomposite, the higher temperature, the higher the rate of cure at a given cure conversion due to the availability of additional thermal energy. Figure 7 also compares the curves obtained from the model equation with the experimental curves. A good agreement is observed between the model and the experimental curves, indicating the suitability of the autocatalytic model for the study of cure kinetics of this system. The activation energy of the cure reaction was determined from the slope of the straight line obtained by plotting $\ln k$ versus $1/T$ (Fig. 8). The comparison of activation energies of gum- and clay-filled NBR calculated from the curemeter with that of DSC measurements (Table II) shows almost identical values and similar trend. A considerable decrease in the E_a for NBR-OM15 is again observed relative to pristine NBR.

The cure kinetic analysis of gum and clay filled NBR nanocomposite using the autocatalytic model using eq. (4) shows good agreement with the experimental

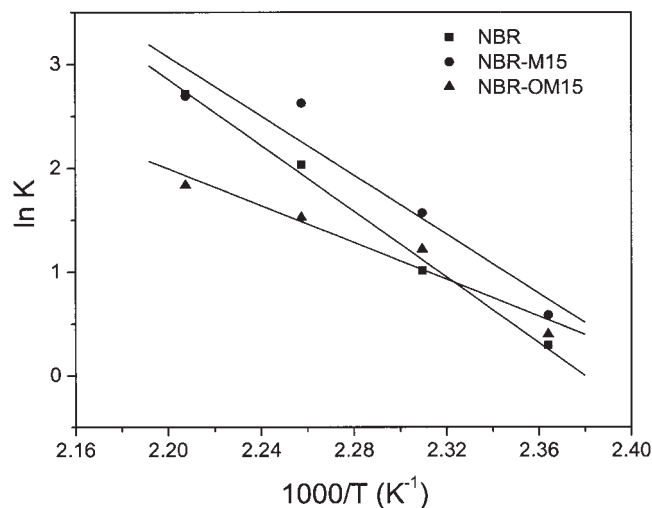
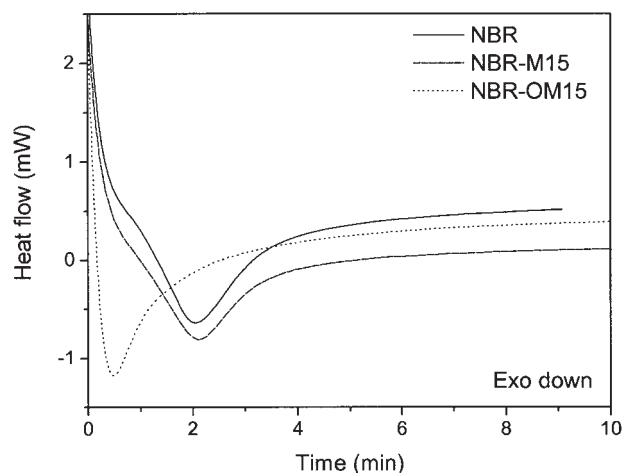
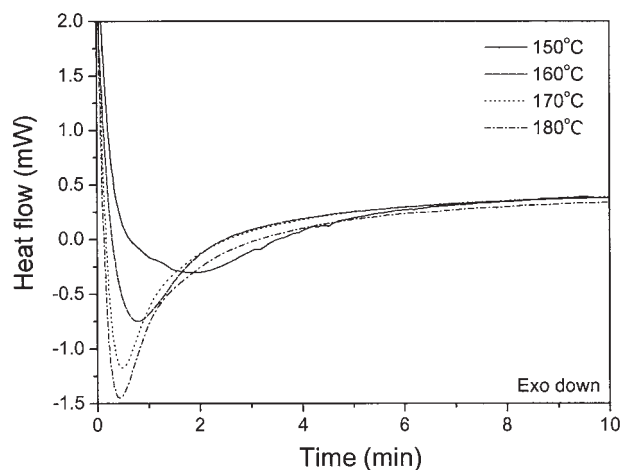


Figure 5 Arrhenius plot of $\ln k$ versus $1/T$ for NBR and its nanocomposites.



(a)



(b)

Figure 6 (a) DSC thermograms under isothermal conditions for NBR and its nanocomposites. (b) DSC traces at isothermal temperatures of 150, 160, 170, and 180 °C for NBR-OM15.

results. The parameters of the model equation well described the vulcanization reaction of NBR compounds.

The influence of modified and unmodified MMT on the vulcanization of NBR was also studied under nonisothermal condition. Figure 9 represents typical DSC exothermic curves for nonisothermal crosslinking reaction of pristine and clay-filled NBR at a heating rate of 10 °C/min. The onset of curing (T_0) and the exothermic peak temperature of curing (T_p) of the NBR/O-MMT nanocomposite were shifted to lower temperatures from 169.1 and 183.0 °C for pure NBR to 146.6 and 164.5 °C, respectively. This indicates that the curing reaction of O-MMT-filled NBR is faster than that of either pure NBR or NBR-M15. As the heating rate is increased, the peak position was shifted toward

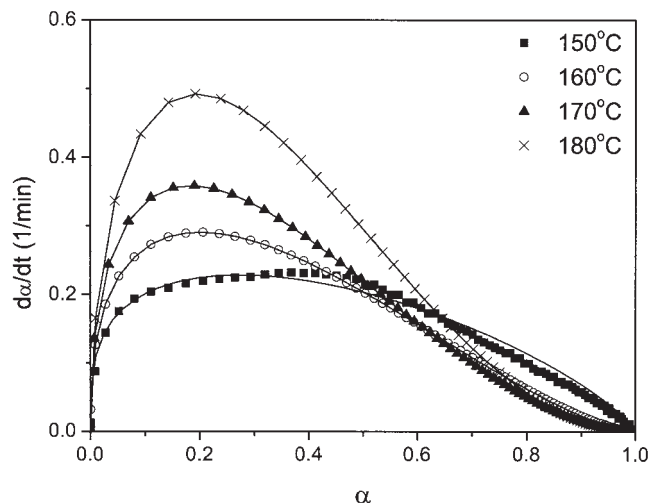


Figure 7 Vulcanization rate versus degree of conversion obtained from DSC results for NBR and its nanocomposites.

higher temperatures (not shown). The temperature of maximum cure reaction (T_{max}) for the organoclay-filled system is shifted toward a lower temperature, indicating the initiation of cure reaction at the early stage due to the accelerating effect of organoclay (Fig. 9). However, the unmodified clay-added system shows no effect on the cure reaction. The above results were in accordance with the ODR.

CONCLUSIONS

The nitrile rubber/layered clay nanocomposites were prepared by a melt mixing process and characterized by XRD for interlayer spacing and clay structure. The cure behavior of the nanocomposites was also investigated using both ODR and DSC. NBR/O-MMT

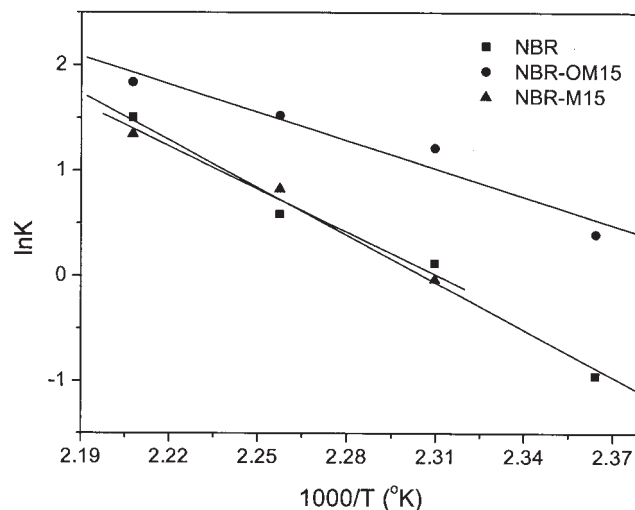


Figure 8 Arrhenius plot of $\ln k$ versus $1/T$ obtained from DSC data for NBR and its nanocomposites.

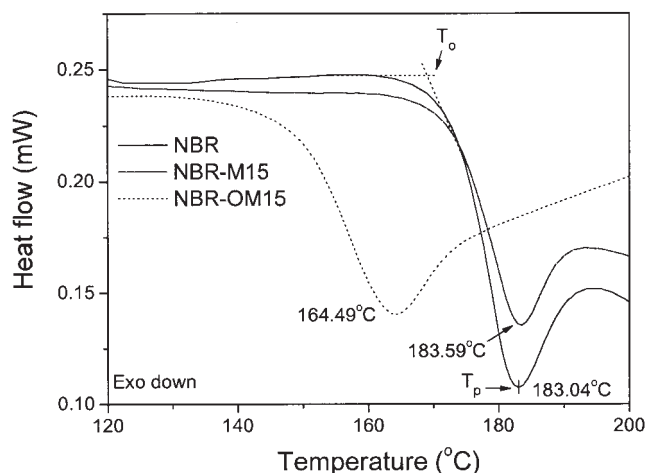


Figure 9 Heat flow versus temperature curves for NBR and its nanocomposites at a heating rate of 10 °C/min.

nanocomposites reduced the scorch time due to cure acceleration by organic modifier present in the O-MMT. However no appreciable change in the optimum cure time and minimum and maximum torque was observed due to the plasticizing effect of O-MMT. The experimental results showed good agreement with the model parameters determined from autocatalytic model equations and the suitability of this model in characterizing the cure kinetics. The activation energy of NBR/O-MMT system was lower than that of pristine NBR and NBR/Na-MMT systems, indicating ease of cure processing of nanocomposites.

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