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# Influence of clay on the vulcanization kinetics of fluoroelastomer nanocomposites

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**Abstract**

The vulcanization kinetics of gum and montmorillonite (Na-MMT) clay filled fluoroelatomer (FKM) nanocomposite was studied using both oscillating disc rheometer and differential scanning calorimetry under isothermal and dynamic conditions. The X-ray diffraction pattern of clay filled FKM showed a shift in *d*-spacing toward higher values indicating the formation of intercalated silicate layer. The cure characterization showed higher rate and state of vulcanization of modified clay filled compound than that of gum and unmodified clay filled FKM indicating the accelerating effect of quaternary ammonium salt modified clay. Although the unmodified clay slowed down the cure reaction, there was marked increase in cure rate at higher level of curative. Higher loading of clay decreased the cure rate with lowering of maximum torque values. The presence of organoclay increased the torque value through the formation of confined elastomer network within the silicate galleries. The experimental data obtained provided the evidence that the curing behavior illustrated autocatalytic characteristics. The kinetic parameters determined from the model equation had good agreement with the experimental results. The calculated activation energy of the gum and clay filled systems indicated the ease of cure process with respect to the type of clay. The cure kinetics measured by different methods was well correlated with each other.

*Keywords:* Fluoroelastomer; Nanocomposite; Cure kinetics

## 1. Introduction

Fluoroelastomers are widely used in many industrial applications due to their excellent heat, oil and solvent resistance properties. These elastomers are mostly compounded with inorganic fillers such as carbon black, silica, clay, etc. to improve many useful properties [1]. In order to get maximum reinforcement, the loading of filler should be appreciably high. This, in fact, will create many problems in processing and curing. Recently, the concept of nanocomposite gives a way to alleviate the problem of higher loading of particulate fillers in the elastomeric matrix. Nanocomposites give manifold increase in useful properties by dispersing small amount of nano scale filler such as layered silicate clay in the polymer matrix. However, to achieve good dispersion, the layers of the silicate should undergo intercalation and or exfoliation (delamination) in the polymer matrix [2]. The chemistry of cation exchange reaction with suitable intercalants is used to modify the clay interlayer thickness to facilitate the intercalation to higher level. Among many clay materials, montmorillonite (MMT) is probably the most widely used [3]. The crystal structure MMT consists of two-dimensional layers obtained by combining two tetrahedral silica layers with Mg or Al to form an octahedral metal oxide structure. Each layer is separated from the next by an interlayer or a gallery containing cations ($Na^+$, $K^+$, $Ca^{2+}$, etc) which balance the excess negative charge created by a natural substitution of some atoms forming the crystal [4]. A primary particle is composed of many silicate layers. The interlayer cations are usually exchanged by alkylammonium, phosphonium, or sulfonium cations to make the silicate layer more compatible with a typical organic matrix [5]. This results in dramatic improvement in thermal and mechanical properties such as modulus, impact strength, heat distortion temperature, etc. even at small fraction of clay [6–9]. It has been shown by Okada et al. [10] that only 10 phr of clay was sufficient to achieve the similar tensile properties to that of 40 phr carbon black filled NBR.

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Although many methods are available for the preparation of polymer–clay nanocomposite, the melt compounding technique (melt intercalation or melt exfoliation) is dominant due to added advantage of utilization of existing compounding lines of high out-put [11]. Most of the works on nanocomposites employed the modified clays to reinforce thermoplastic matrix such as polyamide, PA [12], polypropylene, PP [13], polystyrene, PS [7], unsaturated polyester [14], etc. In addition, there are few studies available on rubber–clay nanocomposite [15]. The important rubber–clay nanocomposites studied so far include the matrix of variety of rubbers such as natural rubber, NR, [16, 17], styrene–butadiene rubber, SBR [18], butadiene rubber, BR [19]), acrylonitrile–butadiene rubber, NBR [20,21], ethylene propylene diene rubber, EPDM [22], silicone rubber [23], etc. There are essentially, until now, no reports on the rubber–clay nanocomposite based on high performance rubber like fluoroelastomer. The development of this type of nanocomposite will give a way for newer application where stringent operating conditions are imposed in industrial and aerospace parts.

It is also observed that the mechanical properties of any rubber are depended on the state of cure. The energy consumed during processing and vulcanization of rubber is linked to the cost of the final product. The vulcanization of rubber compound may involve multiple and complex reaction with the compounding ingredients leading to varied physico-mechanical properties. So, it is essential for any rubber industry to evaluate the cure, thermal and rheological properties of the rubber compound for process optimization and cost reduction.

Several articles on the kinetics of vulcanization of various rubbers are available in the literature. Also, the cure reaction of many thermoset-nanocomposites based on layered clay has been investigated by many workers [24]. However, the studies on vulcanization kinetics of rubber nanocomposites are scanty. Recently, López-manchado et al. reported the cure kinetics of NR-organoclay nanocomposite [25]. In this context, it will be appropriate to study the cure kinetics of rubber/clay nanocomposites to evaluate the kinetic parameters.

The present investigation was aimed at developing a fluoroelastomer–clay nanocomposite using unmodified and organo-modified MMTs. The FKM/clay nanocomposite was prepared by melt mixing process and characterized by X-ray diffraction and transmission electron microscopy. A study on the effect of clay and curative level on the cure kinetics of the nanocomposite was also carried out. The vulcanization reaction was analyzed and correlated by both torque rheometer and differential scanning calorimetry (DSC).

## 2. Theoretical consideration of vulcanization reaction

In a typical vulcanization reaction of a rubber compound, there are several steps of chemical reaction occurring between the compounding ingredients and polymer. In the first step, called induction step, most of the curative or accelerator undergo chemical reaction. The second step (curing step) involves the formation of crosslinks between the polymer chains. The final step involves essentially the formation of additional crosslinking leading to over curing [26]. These reaction steps can be quantitatively measured in order to determine the kinetics of cure reaction. Among many methods of determining the extent of vulcanization reaction, the torque rheometer (cure meter) and DSC are most popular due to their simple operation and reliable results. While the torque rheometer measures the change in the stiffness of a rubber compound, the DSC measures change in heat flow upon crosslinking. Based on the above observation, the extent of crosslinking or degree of curing ($\alpha$) can be calculated from either heat flow using DSC or from change in torque using cure meter. The kinetics of the cure reaction after the induction step can be related to time and temperature through a mathematical equation. The basic rate equation governing the kinetic parameters may be given as [26]

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \tag{1}$$

where $d\alpha/dt$ is the vulcanization rate, $t$, the time, $K$, the specific rate constant at temperature $T$ and the $f(\alpha)$ is the function corresponding to the phenomenological kinetic model. The $\alpha$ is defined in the following ways depending on the method of determination under isothermal condition.

For cure meter study [27,28]

$$\alpha = \frac{M_t - M_0}{M_h - M_0} \tag{2a}$$

and for DSC study

$$\alpha = \frac{\Delta H_t}{\Delta H_\infty} \tag{2b}$$

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 crosslinking, $\Delta H_t$ is the accumulated heat evolved at the time $t$ and $\Delta H_\infty$ is the total heat evolved during vulcanization.

The function $K(T)$ in Eq. (1) is related to the activation energy by the Arrhenius equation

$$K(T) = K_0\, e^{-E_a/RT} \tag{3}$$

where $K_0$ is a pre-exponential factor, $E_a$, the activation energy and $R$ is the universal gas constant. Combining Eqs. (1) and (3), the following relationship can be obtained

$$\frac{d\alpha}{dt} = K_0\, e^{-E_a/RT} f(\alpha) \tag{4}$$

In curing reaction the function $f(\alpha)$ may get different forms depending upon the reaction mechanism. For the $n$th order kinetics of chemical reaction, $f(a)$ is given by Borchardt and

Table 1
Formulation of FKM compounds for cure characterization

| Materials (in phr) | FD1 | FM5D1 | FM10D1 | FM20D1 | FM10D1.5 | FM10D2.0 | FOM5D1 |
|---|---|---|---|---|---|---|---|
| VITON A500 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Na-MMT[a] | – | 5.26 (5) | 11.1 (10) | 25 (20) | 11.1 (10) | 11.1 (10) | – |
| O-MMT[b] | – | – | – | – | – | – | 5.26 (5) |
| $Ca(OH)_2$ | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
| MgO | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| DIAK#1[c] | 1 | 1 | 1 | 1 | 1.5 | 2.0 | 1 |

The values within the parenthesis indicate the weight percent.

[a] Sodium −montmorillonite.

[b] Organic modified MMT.

[c] Hexamethylene diamine carbamate (vulcanizing agent).

Daniel [29] as follows

$$f(\alpha) = (1 - \alpha)^n \tag{5}$$

where $n$ is the order of reaction. However, when a chemical reaction follows multi-step reaction, more complex reaction model is used to describe the kinetics. A model for autocatalytic reaction is given as Ŝesták–Berggren equation [30].

$$f(\alpha) = \alpha^m (1 - \alpha)^n \tag{6}$$

The choice of model depends on the type of chemical reaction. In the $n$th order reaction, all the reacting species are converted at the beginning of the reaction and the reaction rate will be maximum at the initial stage. However, in the autocatalytic reaction, the maximum rate of conversion will be other than zero due the involvement of product of reaction in the ongoing reaction. The results of our isothermal DSC experiments showed that the rate of conversion was almost equal to zero at both the beginning and end of the conversion. So, the following kinetic model can be obtained by the substitution of $f(\alpha)$ in Eq. (1) [25].

$$\frac{d\alpha}{dt} = K(T)\alpha^m (1 - \alpha)^n \tag{7}$$

For non-isothermal reaction using DSC measurements, the change of degree of conversion with temperature is given by

$$\frac{d\alpha}{dt} = \frac{1}{\beta}\frac{d\alpha}{dT} = \frac{k_0}{\beta} e^{-E_a/RT_{max}} \alpha^m (1 - \alpha)^n \tag{8}$$

where $\beta = dT/dt$ (heating rate), $T_{max}$ is the temperature at the maximum rate of conversion while $d(d\alpha/dt)/dt = 0$. The activation energy ($E_a$) of vulcanization reaction can be calculated using Kissinger [31] and Ozawa [32] methods through the following equations, respectively.

$$E_a = -R\frac{d\,\ln(\beta/T_{max}^2)}{d(1/T_{max})} \tag{9a}$$

$$E_a = -R\frac{d\,\ln\beta}{d(1/T_{max})} \tag{9b}$$

Therefore, a plot of $\ln(\beta/T_{max}^2)$ versus $1/T_{max}$ (Kissinger plot) or $\ln\beta$ versus $1/T_{max}$ (Ozawa plot) gives the activation energy without a specific assumption on the conversion-dependent function. This enables a single value of $E_a$ to be determined by model free way.

## 3. Experimental

### 3.1. Materials

Fluoroelastomer [FKM, VITON A-500, specific gravity: 1.82, Mooney Viscosity (ML 1 + 10 at 121 °C:50)] and DIAK 1 (hexamethylenediamine carbamate) were supplied by DuPont Dow elastomers, Wilmington, USA. Montmorillonite (Na-MMT) with a cation-exchange capacity (CEC) of 119 mequiv./100 g was provided by Kunimine Industries Co Ltd, Japan. The organo-modified MMT (Cloisite® 15A) was supplied by Southern Clay Products, Inc. Texas, USA. Other chemicals, obtained from local manufacturers, were used as such.

### 3.2. Preparation of rubber nanocomposites

Rubber compounds were prepared in an open two-roll mill. The vulcanization ingredients were added to the elastomer after the incorporation of the clay and DIAK#1 was added at the end of the mixing. The formulations of the compounds are described in Table 1. The vulcanization time was determined from the oscillating disc rheometer (ODR, Alpha Technologies, and USA).

### 3.3. Characterization

#### 3.3.1. X-ray diffraction pattern

To establish the inter-layered spacing of Na-MMT, organoclay and their composites, Wide angle X-ray Diffraction (WAXD) data between 2 to 10° of $2\theta$ value were obtained from the scattering patterns taken with 40 kV, 40 mA Cu Kα radiation using a X-ray diffractometer (Rigaku 2500PC, Japan) with the radiation wave length of 1.54 Å at room temperature.

#### 3.3.2. Transmission electron microscopy (TEM)

TEM images were taken from cryogenically microtomed ultra thin sections using a ZEISS EFTEM (model: EM912 OMEGA H-800) operating at 120 kV.

### 3.3.3. Cure behavior

The vulcanization behavior of the unfilled and clay filled FKM was determined at four different temperatures viz. 150,170,180 and 200 °C using ODR. Different kinetic parameters such as cure rate, degree of crosslinking or conversion, apparent activation energy ($E_a$), etc. were calculated from the torque–time curves. The cure rate index (CRI) of the compounds cured with the same level of curative was calculated according to equation as given below [33].

$$\mathrm{CRI} = \frac{100}{t_{90} - t_{s2}} \tag{11}$$

where, $t_{90}$ is the optimum cure time and $t_{s2}$, the scorch time.

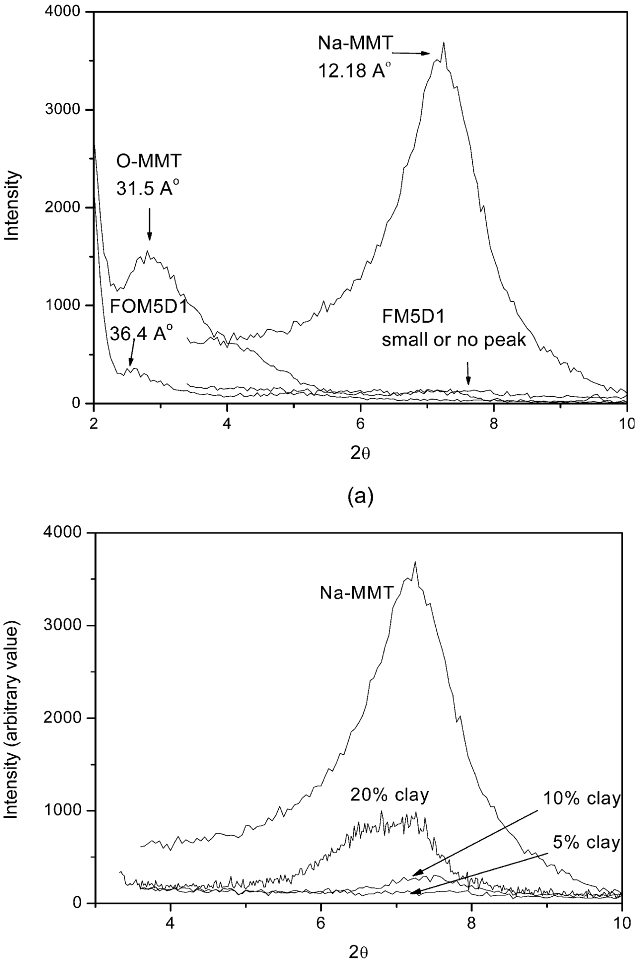
The DSC measurements were performed with TA instruments (DSC model 2910) under nitrogen atmosphere. The curing reaction was characterized both under isothermal and dynamic methods with a sample weight of about 10–15 mg. The isothermal curing was carried out at 150, 170 and 200 °C and the dynamic testing was performed at four heating rates viz. 5, 10, 15 and 20 °C/min. The determination of enthalpy at different conversion time was done using TA instruments Universal Analysis software (version V2.3C).

Swelling of cured rubber compounds was carried out in methyl ethyl ketone (MEK), a solvent for FKM. Samples were weighed ($w_1$) before immersion into MEK at 30 °C. After 72 h, when equilibrium swelling is reached, the swollen samples were removed, wiped dry and weighed ($w_2$). The degree of swelling was calculated using the following equation [34].

$$\%\ \text{swelling} = \frac{w_2 - w_1}{w_1} \times 100 \tag{12}$$

## 4. Results and discussion

### 4.1. XRD characteristics



(a)

(b)

Fig. 1. X-ray diffraction pattern of (a) Na-MMT, O-MMT, FKM/Na-MMT and FKM/O-MMT nanocomposites and (b) FKM/Na-MMT with different proportions of Na-MMT.

The development of nanocomposite from high-temperature elastomer and layered clay may pave a way for enhanced durability of automotive rubber components, which are subjected to rigorous operating conditions. As a first step to develop a nanocomposite, the clay should be dispersed thoroughly in the polymer matrix. In order to characterize the dispersion of clay layers, XRD technique is most widely used. Fig. 1a shows the X-ray diffraction patterns of Na-MMT, O-MMT and FKM/clay nanocomposites having 5% of Na-MMT and O-MMT. Na-MMT showed a characteristic diffraction peak corresponding to the (001) plane at 12.18 Å. On the other hand, O-MMT showed two peaks at 31.5 Å due to organic modification and a low intensity small peak at 12.18 Å corresponding to residual unmodified Na-MMT. The increase in interlayer distance in the O-MMT demonstrates the advantage of the modification of clay for increased intercalation. The organic part of the organoclay enables conversion of the hydrophilic interior clay surface to hydrophobic and increases the layer distance as well. Under this condition, the polymer chain is capable of diffusing easily into the clay galleries to increase the layer distance further. FKM/Na-MMT nanocomposite showed no peak or a peak with very low intensity with respect to crystalline structure of Na-MMT. However, upon increasing the clay content, the peak became noticeable and there was a predominant peak at 20% clay loading indicating the formation of clay aggregates at higher proportions (Fig. 1b). On the other hand, FKM/O-MMT nanocomposites showed a very small peak with a shift in the 001 plane $d$-spacing of modified clay from 31.5 to 36.4 Å. The reduction in the peak height of organo clay may be due to partial exfoliation of clay layers leading to the formation of intercalated/exfoliated FKM/O-MMT nanocomposite. In

Table 2
Vulcanization characteristics of gum and clay filled FKM

| Properties | $t_c$ (°C) | FD1 | FM5D1 | FM10D1 | FM10D1.5 | FM10D2.0 | FOM5D1 |
|---|---|---|---|---|---|---|---|
| $M_L$ | 150 | 9.67 | 8.93 | – | – | – | 13.18 |
| | 170 | 5.94 | 6.47 | 8.20 | 6.58 | 6.48 | 8.33 |
| | 180 | 11.62 | 6.54 | – | – | – | 12.50 |
| | 200 | 7.27 | 5.77 | – | – | – | 10.86 |
| $M_H$ | 150 | 34.06 | 28.23 | – | – | – | 37.99 |
| | 170 | 35.90 | 28.09 | 17.43 | 37.21 | 58.71 | 40.75 |
| | 180 | 36.32 | 28.01 | – | – | – | 37.25 |
| | 200 | 30.91 | 25.08 | – | – | – | 34.56 |
| $M_H - M_L(\Delta S)$ | 150 | 24.39 | 19.3 | – | – | – | 24.81 |
| | 170 | 29.96 | 21.62 | 9.22 | 30.63 | 52.23 | 32.42 |
| | 180 | 24.7 | 21.47 | – | – | – | 28.92 |
| | 200 | 23.64 | 19.31 | – | – | – | 23.7 |
| $t_{s2}$ | 150 | 2.93 | 4.69 | – | – | – | 2.03 |
| | 170 | 1.67 | 3.13 | 7.42 | 2.91 | 1.38 | 1.13 |
| | 180 | 1.16 | 2.46 | – | – | – | 1.02 |
| | 200 | 1.05 | 1.85 | – | – | – | 0.87 |
| $t_{90}$ | 150 | 15.83 | 22.71 | – | – | – | 11.42 |
| | 170 | 7.00 | 16.7 | 31.45 | 12.77 | 8.17 | 5.50 |
| | 180 | 4.15 | 9.56 | – | – | – | 4.42 |
| | 200 | 3.17 | 4.9 | – | – | – | 2.52 |
| CRI | 150 | 7.75 | 5.55 | – | – | – | 10.65 |
| | 170 | 18.76 | 7.37 | 4.16 | 10.14 | 14.73 | 22.88 |
| | 180 | 33.44 | 14.08 | – | – | – | 29.41 |
| | 200 | 47.17 | 32.79 | – | – | – | 60.61 |
| Swelling[a] (%) | | 171 | 227 | 254 | 187 | 127 | 151 |

$T_c$—cure temperature; $t_{90}$—optimum cure time; $t_{s2}$—scorch time. $M_L$—minimum torque; $M_H$—maximum torque.

[a] Samples were cured at 170 °C for swelling study.

order to support results obtained from X-ray diffraction pattern of the FKM/ Na-MMT nanocomposites, the representative TEM micrograph of FKM/Na-MMT nanocomposite containing 5% clay shown in Fig. 2. The TEM micrograph showed the presence of intercalated/exfoliated state of Na-MMT with stacks of platelets having only few layers dispersed in the FKM matrix. A detailed study on the extent of intercalation/exfoliation, effect of clay content on physico-mechanical and viscoelastic properties are under investigation.

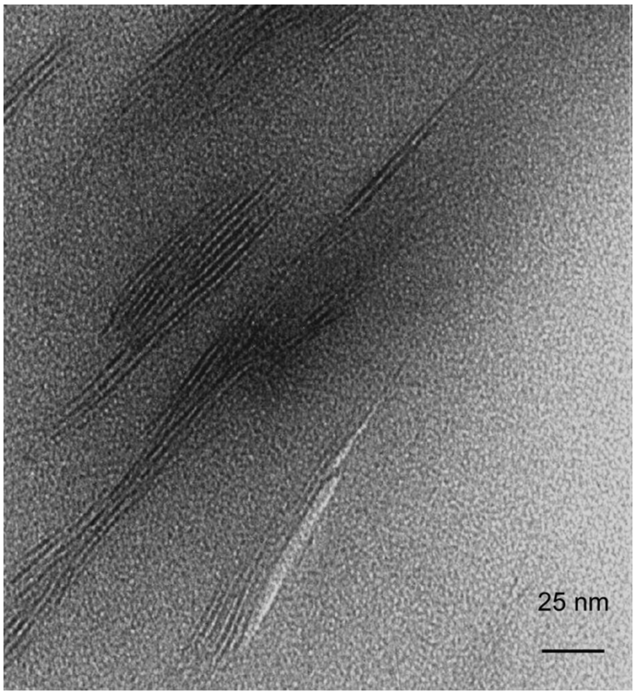


Fig. 2. TEM micrograph of FKM/Na-MMT nanocomposite containing 5% Na-MMT.

### 4.2. Vulcanization characteristics

The vulcanization characteristics of FKM and FKM–clay nanocomposites with different loading of clay and curative are listed in Table 2. The effect of 5% Na-MMT and O-MMT on the rheographic profile obtained at 170 °C is shown in Fig. 3a. The presence of organoclay in FKM compound increased both minimum and maximum torque noticeably while decreasing the scorch time and the optimum cure. The difference of minimum and maximum torque, $\Delta S$, for this compound was higher than that of unfilled FKM. This may be attributed to the influence of organic moiety (quaternary ammonium compound) of the modified clay on vulcanization reaction [35]. This would

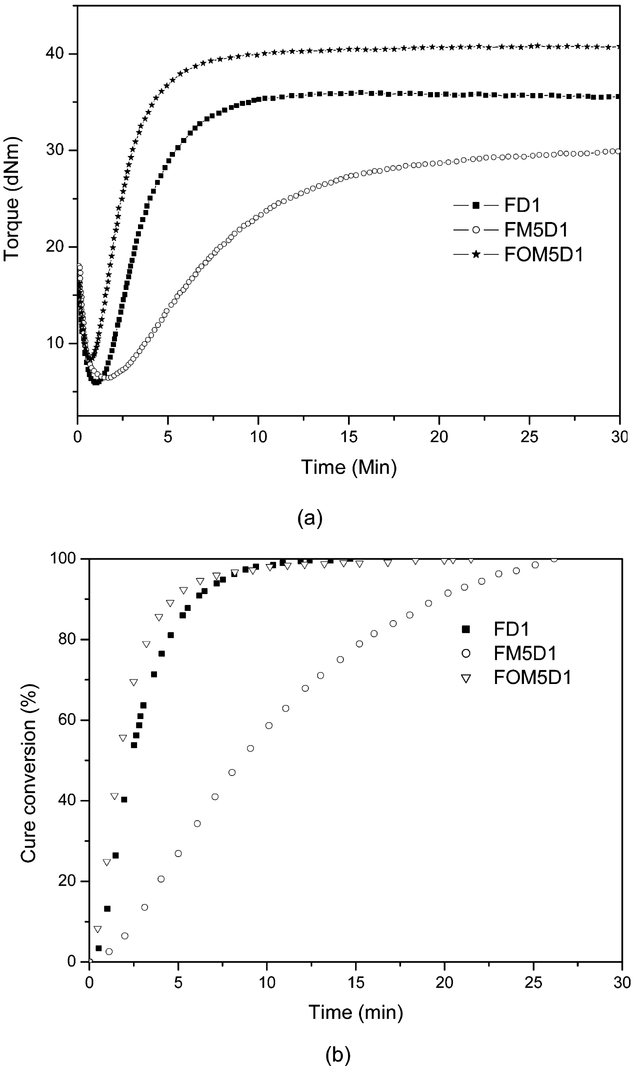


Fig. 3. (a) ODR rheograph of gum and Na-MMT, O-MMT filled FKM; (b) influence of clay on cure conversion of FKM.

give rise to the increased crosslink density of FKM in presence of organoclay. Another reason for fast curing of FKM in presence of O-MMT might be due to the facilitation of cure reaction by intercalated silicate galleries as evidenced from the XRD pattern (Fig. 1a). However, the cure characteristics of Na-MMT containing compound showed the reverse trend with increasing values of scorch and optimum cure time and decreasing $M_H$ and $\Delta S$. Also, the CRI was considerably lower for this compound. The slower curing reaction of unmodified clay–rubber nanocomposite might probably due to cure retardation effect of Na-MMT by absorbing part of curative. The absorbed curative might be utilized to carryout in situ modification of clay. This would reduce the amount of curative available for the cure reaction. The above facts were verified by the swelling measurements. FKM/Na-MMT composite showed more swelling compared to either gum FKM or organoclay filled FKM indicating lower amount of crosslinks. The influence of clay type on the degree of curing of FKM is represented in Fig. 3b. The unmodified clay added FKM showed attainment of cured state after long time with a gradual increase in the degree of curing. However there was not much difference between gum and organoclay added FKM. So it was inferred that the addition of unmodified clay delayed the cure reaction with lower level of curing as evidenced from the torque values.

In order to study the effect of clay loading and the level of curative on cure characteristics of FKM, experiments were carried out with higher loading of unmodified clay and

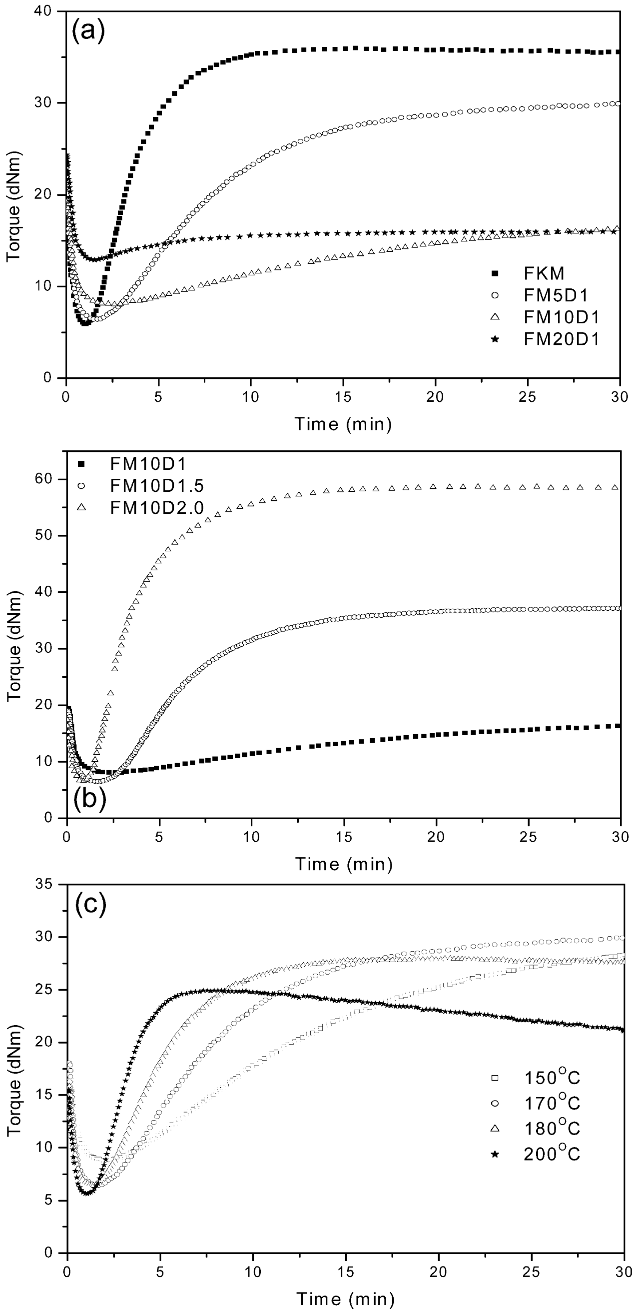


Fig. 4. Rheograph of FKM formulations (a) FKM containing different level of Na-MMT at 170 °C, (b) effet of curative level on Na-MMT filled FKM at 170 °C, and (c) influence of temperature on cure curve of Na-MMT filled FKM.

different level of DIAK#1. It is seen from Table 2 that increase of clay loading at the same level of curative reduced the cure rate with increase in $t_{s1}$ and $t_{90}$ values. Upon addition of 20% clay (not shown in Table), there was very little rise in torque (Fig. 4a) with almost uncured state of the resulting compound. The slower curing reaction of rubber at higher proportion of unmodified clay might lead the formation of clay aggregates. The XRD pattern confirmed the formation of clay aggregation by showing the characteristic peak of Na-MMT (Fig. 1b). It was therefore emphasized that the amount of unmodified clay and the curative level have some influence on the vulcanization of the FKM.

Fig. 4b shows the effect of curative level on cure characteristic of 10% Na-MMT filled compound. Upon increasing the amount of curative, there was a considerable rise in $M_H$ values from 17.43 dNm for 1 phr to 58.71 dNm for 2.0 phr of DIAK#1. Similar increase in $\Delta S$ and CRI were also observed for the compound with higher level of curative. The swelling studies also showed similar results by reducing the swelling index to about half of the values for 2 phr level. Therefore, it was inferred that, the higher cure rate and cure state could be achieved by just including little excess of curative which would improve the cure properties of the nanocomposite at the lower loading of clay. Similar to the effect of curative, the temperature also had influence on vulcanization properties. To study the effect of temperature on vulcanization, the curing was carried out at three additional temperatures (150, 180 and 200 °C) and the results are depicted in Fig. 4c. It was obvious that increase of temperature decreased the $t_{s2}$ while increasing the cure rate with noticeable reduction in the optimum cure time irrespective of the nature of the compound as seen from Table 2. The influence of temperature was more pronounced in the compound containing the modified clay compared to the either pure FKM and the compound containing the unmodified clay. Similarly, the $\Delta S$ was also decreased with increase of temperature. Upon over curing after crossing the optimum cure, the compounds showed some amount of reversion at higher temperature due to breakdown of polymer chain through dehydrofluorination of FKM around 200 °C [36]. It should be mentioned here that, none of the compound was added with any antidegradant to prevent degradation of FKM. Interestingly the amount of reduction in torque during reversion was lower for the clay filled compound compared to gum FKM indicating some thermal resistant characteristics of clay filled FKM.

### *4.3. Kinetic parameter of vulcanization*

The kinetic parameters of vulcanization, such as order of reaction $(n, m)$ and temperature dependant specific rate constant, $K(T)$ and the pre-exponential factor of unfilled and filled FKM, carried out by cure-meter, were determined from the kinetic model expression of Eq. (7). The values of $K$, $n$ and $m$ were calculated at four different temperatures using non-linear regression analysis using ORIGIN 6.0 computer software and are listed in Table 3. It was observed from the kinetic analysis that the order of reaction did not follow the $n$th order kinetics and the sum of the values of $n$ and $m$, related to reaction order, changed with different curing conditions such as temperature, type and amount of filler and the curative level. The conversion rate curve obtained from model parameters and the experimental values were closely fitted for almost all the systems throughout the entire degree of conversion. As a supportive evidence of choice of right model of reaction kinetics, the rate constant ($K$) determined from the model equation was in accordance with the results obtained from optimum cure time ($t_{90}$). Increase of temperature, increased the $K$ values and decreased the $t_{90}$. This effect was more pronounced in the organoclay added compound indicating the cure accelerating affect of organoclay.

A plot of rate of conversion ($d\alpha/dt$) versus the degree of conversion ($\alpha$) of FKM/Na-MMT clay composite at four different temperatures obtained from the rheograph curves is represented in Fig. 5. It was seen that the shape of the conversion curve was depended on temperature. As the temperature was increased, the peak height of the conversion rate curve was also increased with a shift in peak position toward higher $\alpha$ values. The maximum conversion was achieved below $\alpha = 0.4$ at all the measured temperatures. The best fit of experimental and the model values were obtained at higher temperature. The above observation indicated the dependence of cure reaction on temperature. At lower temperature, the change in conversion was more gradual irrespective of the compound. This might be attributed to the effect of higher viscosity at lower temperature which prevented the formation of crosslink between the adjacent polymer chains.

Table 3
Kinetic parameters and activation energies of the vulcanization of gum and clay filled FKM obtained from ODR data using kinetic model Eq. (7)

| Sample | $t_c$ (°C) | $K$ | $n$ | $m$ | ln $K_0$ | $E_a$ (kJ/mol) |
|---|---|---|---|---|---|---|
| FD1 | 150 | 0.43 | 0.55 | 1.57 | 10.95 | 56.83 |
| | 170 | 1.27 | 0.82 | 1.45 | | |
| | 180 | 2.11 | 0.98 | 1.29 | | |
| | 200 | 2.25 | 0.77 | 1.28 | | |
| FM5D1 | 150 | 0.15 | 0.40 | 0.87 | 14.25 | 72.18 |
| | 170 | 0.13 | 0.35 | 0.84 | | |
| | 180 | 0.67 | 0.66 | 1.32 | | |
| | 200 | 1.05 | 0.58 | 0.93 | | |
| FOM5D1 | 150 | 0.81 | 0.68 | 1.68 | 7.02 | 39.18 |
| | 170 | 1.71 | 0.87 | 1.46 | | |
| | 180 | 2.14 | 0.92 | 1.81 | | |
| | 200 | 2.72 | 0.83 | 1.08 | | |
| FM10D1 | 170 | 0.09 | 0.23 | 0.63 | – | – |
| FM10D1.5 | 170 | 0.65 | 0.69 | 1.51 | – | – |
| FM10D2 | 170 | 1.82 | 0.91 | 1.94 | – | – |

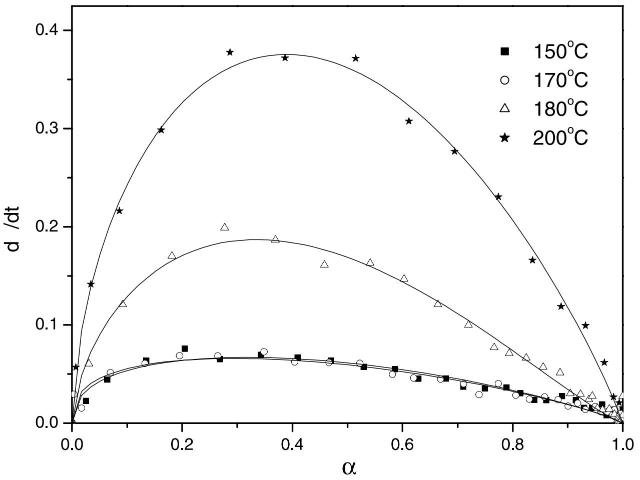


Fig. 5. Vulcanization rate, d$\alpha$/d$t$, versus $\alpha$ curves for different curing temperatures. Solid line represents the theoretical curve obtained from Eq. (7).

The activation energy, $E_a$, related to the ease of crosslinking process, was calculated from the slope of the Arrhenius plot of ln $K$ versus 1/$T$ (Fig. 6) and the values are given in Table 3. The organoclay reduced the $E_a$ value from 56.83 to about 39.18 kJ/mol compared to gum FKM through accelerating effect of quaternary ammonium salt used in clay modification [35]. This effect was observed in cure behavior by increasing the torque value and reducing the cure time indicating advantage of organoclay for making FKM/clay nanocomposite. However, inclusion of unmodified clay into compounding formulation increased the $E_a$ due to absorption of part of curative which was not available for cure reaction and thereby reducing the curing process. With the above results, it was obvious to study the effect of proportion of curative in the rubber formulation and the use of autocatalytic model. Fig. 7 shows the comparison of experimental values with the model data for the system added with different level of curative. Similar to the effect of temperature, the sample with a lower level of curative,

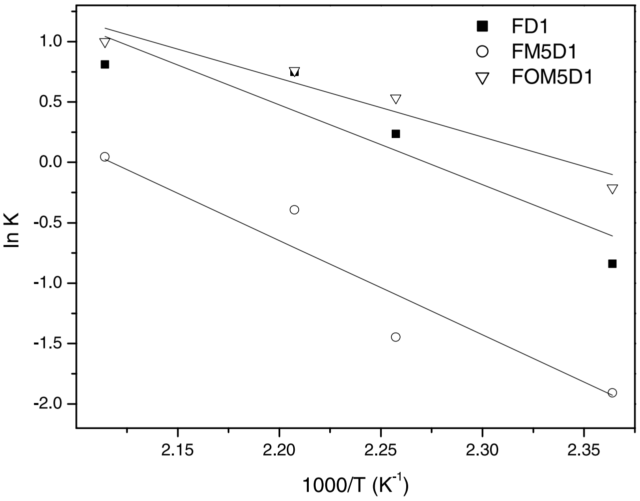


Fig. 6. Arrhenius plot of rate constant versus 1/$T$.

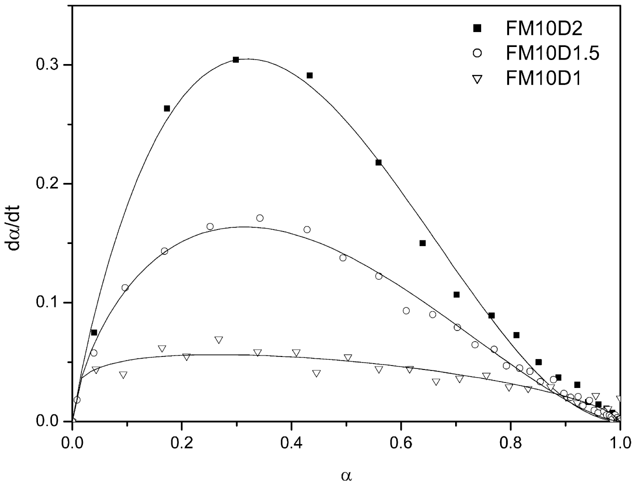
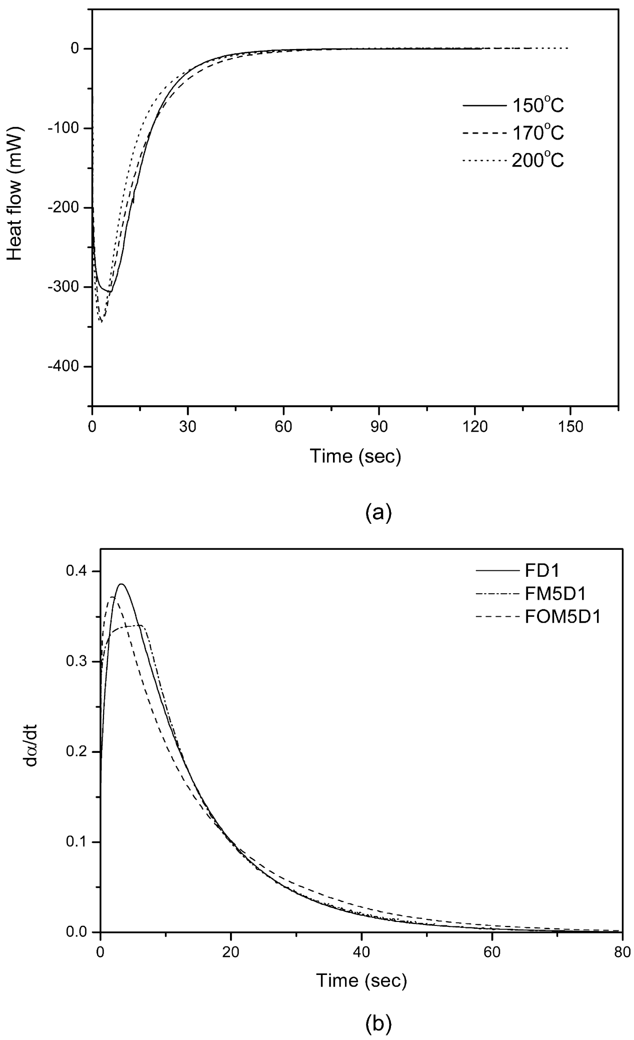


Fig. 7. Vulcanization rate, d$\alpha$/d$t$, versus $\alpha$ curves for compounds filled with different proportion of DIAK#1. Solid line indicates the theoretical curve obtained from Eq. (7).



(a)

(b)

Fig. 8. (a) Isothermal DSC curves of gum FKM at different temperatures and (b) vulcanization rate versus time for gum and clay filled FKM determined from DSC data.

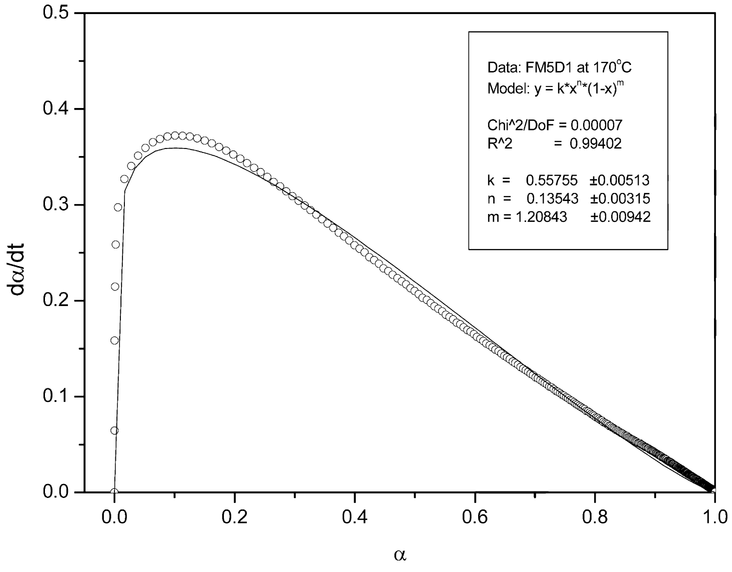


Fig. 9. Vulcanization rate, $d\alpha/dt$, versus $\alpha$ curves for FM5D1 at 170 °C curing temperatures. Solid line represents the theoretical curve obtained from Eq. (7).

showed shallow curve with very small increase in degree of conversion. Upon increasing the curative content, there was a sharp increase in degree of conversion. There was a maximum conversion before $\alpha = 0.4$. A good agreement between experimental and the model values was observed in all the cases, however there was little deviation at lower proportion of curatives which was in accordance with the effect of temperature.

### 4.4. DSC studies on cure kinetics

DSC is one of the powerful techniques to study the cure reaction kinetics of many rubber compounds so as to elucidate some of the important parameters such as rate and state of cure. The method assumes that the amount of heat flow is proportional to the rate of conversion. The curing reaction of the FKM compound with and without clay was analyzed by DSC, under isothermal and dynamic conditions. A representative trace of isothermal DSC of unmodified clay filled FKM at three different temperatures is depicted in Fig. 8a. As expected, the curing rate was increased with increase in temperature by shifting the exotherm peak position towards the lower time. The same trend was followed for others systems also. However, the influence of organically modified clay on the cure reaction of FKM was more pronounced compared to either pure FKM or the unmodified clay filled FKM. The results were similar to cure-meter studies. The amount of heat released during the cure reaction was determined by integrating the area under exothermic curve of heat flow versus time plot. It was assumed that the total heat evolved is due to the crosslinking reaction only. The total heat liberated during entire curing process ($\Delta H$) and the fraction of heat liberated at a time, ($H_t$), were measured in order to study the kinetics of vulcanization reaction. The degree of conversion ($\alpha$) was calculated using Eq. (2b) and the kinetic parameters such as $K$, $n$ and $m$ were evaluated using Eq. (7) with the help of non-linear regression analysis and are tabulated in Table 4. Fig. 8b shows the plot of cure rate ($d\alpha/dt$) versus time of gum and clay filled FKM compounds at 170 °C. The reaction rate was seen to increase rapidly and passed through a maximum and then gradually slowed down toward zero. Comparison of reaction rate at any given time of the filled and unfilled FKM showed different values of maximum rate. The presence of organoclay influenced the cure rate by shifting the maximum rate toward the lower time, whereas the unmodified clay gave the opposite effect, which was in accordance with the result obtained from the rheometer. The kinetic parameters determined from the model equation was compared with the experimental results and a representative plot of $d\alpha/dt$ versus $\alpha$ for the compound containing unmodified clay at 170 °C is depicted in Fig. 9. A good agreement was observed between the model and the experimental curves indicating the suitability of the model for the study of cure kinetics of this system. The comparison of activation energies of gum and clay filled FKM calculated from DSC measurements (Table 4) with that of

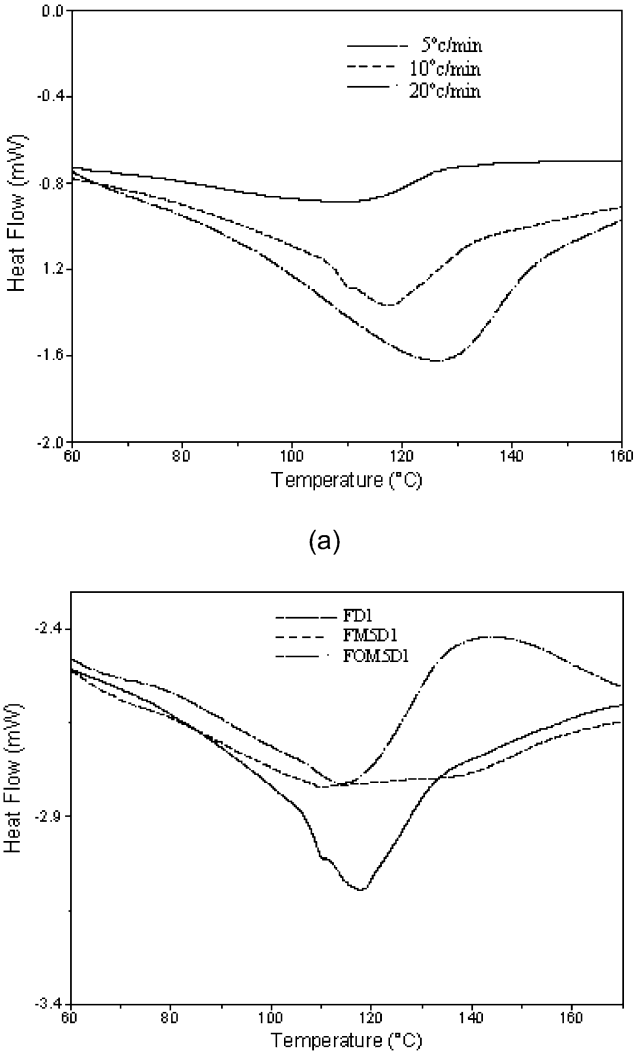
Table 4
Kinetic parameters and activation energies of the vulcanization of gum and clay filled FKM obtained from DSC data using kinetic model Eq. (7)

| Sample | $t_c$ (°C) | $K$ | $n$ | $m$ | ln $K_0$ | $E_a$ (kJ/mol) |
|---|---|---|---|---|---|---|
| FD1 | 150 | 0.33 | 0.35 | 1.23 | 9.82 | 52.36 |
| | 170 | 0.95 | 0.82 | 1.17 | | |
| | 200 | 1.65 | 0.77 | 1.13 | | |
| FM5D1 | 150 | 0.13 | 0.22 | 1.12 | 14.21 | 70.83 |
| | 170 | 0.56 | 0.14 | 1.21 | | |
| | 200 | 1.15 | 0.28 | 1.06 | | |
| FOM5D1 | 150 | 0.69 | 0.68 | 1.19 | 6.32 | 37.95 |
| | 170 | 1.13 | 0.87 | 1.15 | | |
| | 200 | 2.16 | 0.83 | 1.06 | | |

cure meter (Table 3) showed almost identical values and similar trend. Considerable decrease of the $E_a$ for organoclay filled FKM nanocomposite was again observed relative to gum FKM.

The cure kinetic analysis of gum and clay filled FKM nanocomposite using autocatalytic model using Ŝesták–Berggren equation showed good agreement with the experimental results as seen from Figs. 5, 7 and 9. It was observed that the parameters of model equation well described the studied vulcanization process.

The influence of modified and unmodified MMT on the vulcanization of FKM was also studied by non-isothermal condition. Fig. 10a represents a typical DSC curves of FKM/Na-MMT nanocomposite at three different heating rates showing a broad exothermic peak between 80 and 160 °C with a maximum in the range of 100 and 130 °C depending on the heating rate. As the heating rate was increased, the peak position was shifted towards higher temperature. The temperature of maximum of the cure reaction ($T_{max}$) for all the systems at different heating rates is reported in Table 5. It was seen that, the $T_{max}$ of organoclay filled system was shifted towards lower temperature indicating the beginning of cure reaction at the early stage due to accelerating effect of organoclay (Fig. 10b). However, the curing reaction of the unmodified clay added system showed the opposite effect. Moreover, the difference in $T_{max}$ was higher for the former system compared to latter one. The above results were in accordance with the ODR observation.



(a)

(b)

Fig. 10. (a) Typical DSC curves recorded for FD1 at different heating rates and (b) heat flow versus temperature for gum and clay filled FKM at a heating rate of 10 °C/min.

The activation energy of the cure reaction can also be determined from the non-isothermal cure reaction without the use of any specific model. The Ozawa and Kissinger equations [Eqs. (9a) and (9b), respectively] can be used for this purpose. The plots of $1/T_{max}$ versus ln $\beta$ (Ozawa) and $1/T_{max}$ versus $\ln(\beta/T_{max}^2)$ (Kissinger) are given in Fig. 11a and b, respectively. The calculated $E_a$ from the slope of these plots are included in Table 5. The $E_a$ values are almost similar to those calculated from the autocatalytic model. The Kissinger equation resulted in lower $E_a$ values compared to Ozawa equation. The calculated $E_a$ values, using kinetic model, were in between these equation values. Again, the FKM/O-MMT nanocomposite proved to be good system by keeping the $E_a$ at the lower values compared to gum or unmodified clay filled FKM.

## 5. Conclusions

The FKM/clay nanocomposite was prepared by melt mixing process and characterized for dispersion using XRD and TEM. The vulcanization characterization was also carried out using both cure-meter and DSC. The inclusion of clay altered the cure reaction by changing the rate and state of cure. While the organo-modified clay enhanced the curing through accelerating effect of quaternary ammonium

Table 5
Activation energies of curing of gum and clay filled FKM obtained from DSC under non-isothermal condition

| Sample | Heating rate ($\beta$) | $T_{max}$ | $\Delta H$ | $E_a$ (kJ/mol) | |
|---|---|---|---|---|---|
| | | | | Ozawa | Kissinger |
| FD1 | 5 | 100.4 | 8.25 | 61.61 | 55.17 |
| | 10 | 115.5 | 11.87 | | |
| | 15 | 120.3 | 13.07 | | |
| | 20 | 129.2 | 14.40 | | |
| FM5D1 | 5 | 108.2 | 5.11 | 72.76 | 66.23 |
| | 10 | 117.7 | 10.99 | | |
| | 15 | 126.8 | 11.47 | | |
| | 20 | 132.2 | 12.17 | | |
| FOM5D1 | 5 | 92.1 | 9.11 | 48.23 | 41.79 |
| | 10 | 111.3 | 12.10 | | |
| | 15 | 119.7 | 14.72 | | |
| | 20 | 127.0 | 17.09 | | |

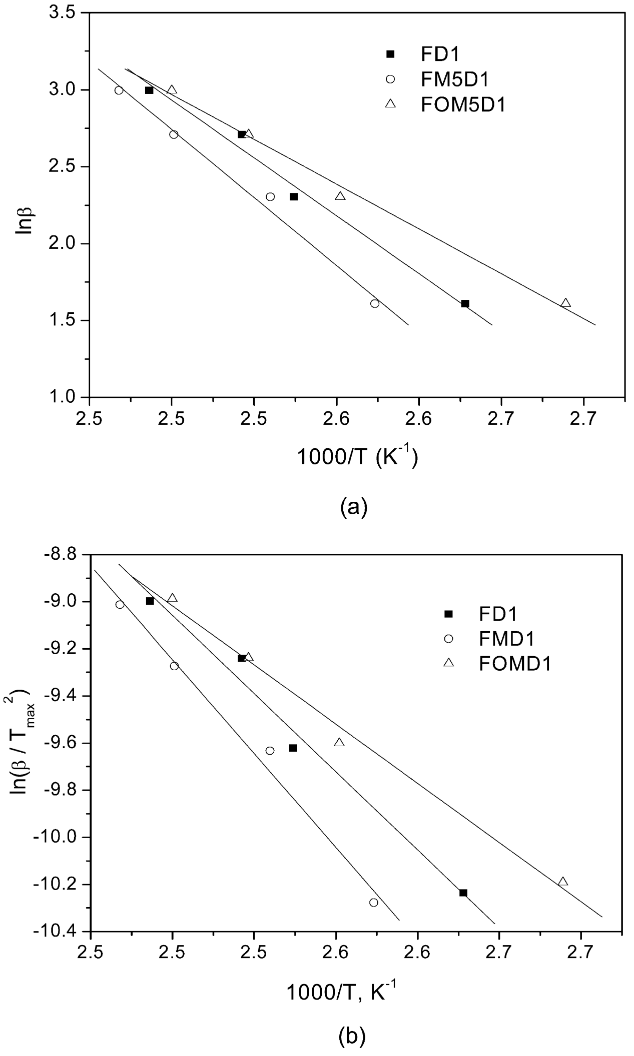


Fig. 11. Calculation of $E_a$ from non-isothermal DSC data using (a) Ozawa equation and (b) Kissinger equation.

salt used in the clay modification, the unmodified clay showed cure retardation due to absorption of curative by clay for in situ clay modification. The increase of unmodified clay loading further reduced the cure rate augmenting the above fact. However, at higher proportion of curative, there was a marked increase in cure rate indicating availability of curative of cure reaction. The kinetic analysis showed the suitability of autocatalytic model for cure characterization. The determined kinetic parameters were in good agreement with the experimental values. The calculated activation energy from the curemeter data and the DSC data were almost in a close range proving the validity of the kinetic model. The result indicated that the organoclay was efficient in reducing the energy requirement for the cure process. As a whole, the present study revealed that the nature of clay is one of the important factors which is influential on the vulcanization process.

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## References

[1] Améduri B, Boutevin B, Kostov G. Prog Polym Sci 2001;26:105.
[2] Alexandre M, Dubois P. Mater Sci Engng Rep 2000;28:1–63.
[3] IMA 2002 Conference Proceedings on 'Industrial Minerals: A World of Possibilities—From quarry to high-tech', Brussels; 6 June 2002.
[4] Whittingham MS, Jacobson AE. Intercalation chemistry. New York: Academic; 1982.
[5] Vaia RA, Teukolsky RK, Giannelis EP. Chem Mater 1994;6:1017.
[6] Kawasumi M, Hasegawa N, Kato M, Usuki A, Okada A. Macromolecules 1997;30:6333.
[7] Giannelis EP. Adv Mater 1996;8:29.
[8] Zilg C, Reichert P, Dietsche F, Engelhardt T, Mülhaupt R. Kunststoffe 1998;88:1812.
[9] Pinnavaia TJ, Beall GW, editors. Polymer-layered silicate nanocomposites. New York: Wiley; 2001.
[10] Okada A, Usuki A, Kurauchi T, Kamigaito O. In: Mark JE, Lee CYC, Bianconi PA, editors. Hybrid organic–inorganic composites. ACS Symposium Series; 1995.
[11] Vargheese S, Korger-Kocsis J, Gatos KG. Polymer 2003;44:3977.
[12] Liu L, Qi Z, Zhu X. J Appl Polym Sci 1999;71:1133.
[13] Kato M, Usuki A, Okada A. J Appl Polym Sci 1997;66:1781.
[14] Kornmann X, Berglund LA, Sterte J, Giannelis EP. Polym Engng Sci 1998;38:1351.
[15] Wen J, Mark JE. Rubber Chem Technol 1995;67:806.
[16] Joly S, Garnaud G, Ollitrault R, Bokobza L. Chem Mater 2002;14:4202.
[17] Arroyo M, López-Manchado MA, Herrero B. Polymer 2003;44:2447.
[18] Mousa A, Karger-Kocsis J. Macromol Mater Engng 2001;286:260.
[19] Ganter M, Gronski W, Reichert P, Mülhau R. Rubber Chem Technol 2001;74:221.
[20] Kojima Y, Fukumori K, Usuki A, Okada A, Kurauchi TJ. Mater Sci Lett 1993;12:889.
[21] Nah C, Ryu HJ, Kim WD, Chang YW. Polym Int 2003;52:1359.
[22] Chang YW, Yang Y, Ryu S, Nah C. Polym Int 2002;51:319.
[23] LeBaron PC, Pinnavaia TJ. Chem Mater 2001;13:3760.
[24] Kong D, Park CE. Chem Mater 2003;15:419.
[25] López-manchado MA, Arroyo M, Herrero B, Biagiotti J. J Appl Polym Sci 2003;89:1.
[26] Montserrat S, Málek J. Thermochim Acta 1993;228:47.
[27] Ding R, Leonov AI, Coran AY. Rubber Chem Technol 1996;69:81.
[28] Ding R, Leonov AI. J Appl Polym Sci 1996;61:455.
[29] Borchardt HJ, Daniels FJ. J Am Chem Soc 1956;79:41.
[30] Ŝesták C, Berggren G. Thermochim Acta 1971;3:1.
[31] Kissinger HE. Anal Chem 1957;29:1702.
[32] Ozawa T. Bull Chem Soc Jpn 1965;38:1881.
[33] Yehia AA, Stoll B. Kauts Gummi Kunsts 1987;40:950.
[34] Parks CR, Brown RJ. Rubber Chem Technol 1976;49:233.
[35] Paciorele KL, Mitchell LC, lenk C. J Polym Sci 1960;146:405.
[36] Viton Technical Information Brochure, DuPont Dow Elastomers, Wilmington, USA, Rev.3; February 2002.