IN-SITU MONITORING OF CURING OF POLYSILOXANE/ORGANOCLAY NANOCOMPOSITES, BASED ON ADDITION TYPE ELASTOMERS

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Abstract

A study of the vulcanization mechanism and the related kinetics in montmorillonite/vinyl terminated polysiloxane nanocomposites was carried out. Commercial unmodified and organically modified montmorillonites under the trade names: Nanofil 116, Cloisite 20A and Cloisite 30B were used as reinforcing nanofillers. The vulcanization reaction was monitored by isothermal differential scanning calorimetry experiments. The Cloisite 20A/PDMS systems have increased the reaction rate at the early stages and then, a slow rate and extension of the curing time were observed, in comparison with pure PDMS. Cloisite 30B decreases the curing rate of PDMS during the whole process, whereas significant increase was recorded in the case of unmodified clay/PDMS nanocomposites. Physicochemical interactions between the crosslinking system and organoclays are responsible for the observed behaviour.

1 Introduction

Polydimethylsiloxane (PDMS) elastomers have been recognized as the rubber of a broad spectrum of applications. These materials present a wide service temperature range, good optical clarity, weather resistance, low chemical reactivity and low toxicity [1]. They are made by vulcanization (cure) process converting low-molecular weight linear polydimethyl-siloxanes to a three dimensional network which is elastomeric in character. Its inherent mechanical weakness is overcome by reinforcement with some particulate fillers, such as silica and titania [2]. Alternatively, fillers having large specific area and aspect ratio, such as clay nanoplatelets, could bring better mechanical properties at much lower filler content, keeping the material transparent and lightweight.

Chemically, silicone is typically cured or crosslinked by addition, condensation or free radical reaction. The vulcanization process is determined by the end groups of PDMS. Vinyl terminated PDMS are crosslinked by an addition type curing reaction, involving the addition of a silicon hydrogen to the vinyl bond. Three regions are observed in an addition type curing reaction between the compounding ingredients and a vinyl terminated PDMS. An induction time, which the most of the accelerator reactions occur. The curing time which the network structure is formed and the final step involves the formation of additional crosslinking leading to over curing [3].

Several articles on the kinetics of vulcanization of various rubbers are available in the literature and especially in silicone rubbers which is the material under study in this work. Nevertheless, there are few data in the literature related with vulcanization kinetics of rubber nanocomposites and especially PDMS clay nanocomposites. Vulcanization reaction is of great interest, because the performance of the final material is determined by the chemical structure of the elastomer and the interactions among the curing agent, clay and polydimethylsiloxane. If the mechanism of curing reaction could be well understood and controlled, the properties of the prepared PDMS clay nanocomposites should be improved, according to the requirements of final application. The addition of filler makes the curing process more complicated because clay particles interact physically or chemically with PDMS chains or with the components of curing system.

Mathew et al. [4] used differential scanning calorimetry for monitoring curing reaction of ethylene acrylate rubber nanocomposites. For the kinetic study an autocatalytic model was selected to simulate the process. It is observed that the introduction of clay in base material decreased the curing time and lowered activation energy for reaction as it calculated from the autocatalytic model.

The effect of unmodified and organically modified clays on the vulcanization reaction of natural rubber was analyzed by cure-meter and thermal analysis under isothermal and dynamic conditions by Lopez-Manchado et al. [5]. They observed that the clay hardly affected the crosslinking reaction of the rubber, but a strong vulcanizing effect was observed when the octadecylamine modified clay was added to the rubber, which was attributed to a synergistic effect between filler and amine.

The vulcanization kinetics of fluoroelastomer (FKM) filled with unmodified and organo-modified clay were studied by Kader and Nah [6], with both oscillating disc rheometer and differential scanning calorimetry under isothermal and dynamic conditions. The organo-modified clay enhanced the curing procedure through the accelerating effect of quarternary ammonium salt used in the clay modification, while the unmodified clay showed cure retardation due to absorption of curative clay for in situ clay modification. 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 result indicated that the organoclay was efficient in reducing the energy requirement for the cure process.

2 Materials and testing methods

2.1 Raw Materials

Vinyl terminated PDMS - grade DMS-V31 (Gelest Inc.) with molecular weight of 26,000 g/mol was the silicone base elastomer used in this work. The vulcanization reaction system was tetrakis(dimethylsiloxy)silane as a cross-linker and platinumdivinyl-tetramethyldisiloxane complex in xylene as catalyst. Commercial montmorillonite clays under the trade name Nanofil 116 (Nan16), Cloisite® 30B (Cl30B) modified with methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium and Cloisite® 20A (Cl20A) modified with dimethyl, dehydrogenated tallow, quaternary ammonium surfactant, supplied by Rockwood Clay Additives GmbH, were used as reinforcing nanofiller.

2.2 Blending of clay/PDMS composites

Efficient dispersion of nanoparticles was achieved by sonicating the PDMS and the appropriate amount of clay, with an ultrasound probe for 6 min, at room temperature. The

cross-linking agents were then added and dispersed into the mixture and the samples were cast into molds for subsequent cure at room temperature for 1 hour.

2.3 Differential Scanning Calorimetry (DSC)

DSC measurements were run in a DSC 1 model Mettler Toledo differential scanning calorimeter. All runs were conducted under nitrogen flow of 20cm^3/min in order to limit thermo-oxidative degradation. The isothermal curing was carried out at 60, 70 and 80°C for pure PDMS and 2, 5 and 8 phr Cloisite 20A and Cloisite 30B nanocomposites. In the case of 2 and 5 phr Nanofil 116/PDMS hybrids, isothermal experiments were performed at 40, 50 and 60°C.

2.4 Curing kinetics based on isothermal experiments

DSC is an important analytical tool 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 and is proportional to the extent of the reaction. Therefore, the degree of curing (α) can be calculated from the heat-flow peak of *a* DSC curve by the following equation:

$$a = \frac{\Delta H_t}{\Delta H_\infty} \tag{1}$$

where ΔH_t is the accumulated heat evolved at time *t* of the vulvanization process, and ΔH_∞ is the total amount of the reaction heat.

The dynamics of the vulcanization reaction can be modeled by means of a differential equation with regard to time, where the influence of the temperature and vulcanization rate are seperated. Thus, the equation governing the vulcanization rate may be written as folllows:

$$\frac{da}{dt} = K(T) * f(a) \tag{2}$$

where *t* is the time, *T* is the temperature and *K* is the kinetic constant.

The function *K(T)* is related to the activation energy by the Arrhenius expression:

$$K(T) = K_0 * \exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

where K_0 is the pre-exponential factor, E_a is the activation energy and *R* is the universal gas constant.

For solid-state transformations, combination of Eqs. (2) and (3) gives:

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

In curing reaction the function *f(α)* may obtain different forms depending on the reaction mechanism. In this work, a model suitable for autocatalytic reaction, known as Sestak-Berggren equation, was used to simulate vulcanization process:

$$f(a) = a^m * (1-a)^n \tag{5}$$

where *m* and *n* denotes the reaction order.

By substitution of equation (5) in (4), the change of degree of conversion *da/dt* with temperature is given by

$$\frac{da}{dt} = K_0 * \exp\left(-\frac{E_a}{RT}\right) * a^m * (1-a)^n \tag{6}$$

Parameters of curing process such as *K(t)*, *m and n* were calculated with non-linear regression analysis plots of *da/dt* versus *a*. Activation energy was calculated graphically, from the Arrhenius expression (Eq. 3), from the slope *(-E$_a$/R)* of linear regression of ln*K* versus *1/T*:

$$\ln(K(T)) = \ln(K_o) + \left(-\frac{E_a}{R}\right) * \frac{1}{T} \tag{7}$$

3 Results and Discussion

As stated above, the vulcanization of vinyl terminated PDMS was carried out with a platinum-catalyzed hydrosilylation reaction. The formation of a three dimensional network in the elastomer proceeds by the opening of double bond through an addition exothermic reaction. Therefore, the degree of vulcanization can be related to the heat released during the reaction. The energy released in the exothermal reaction is proportional to the formation of cross-links, as can be assumed that each bond releases the same amount of energy. The amount of heat released during the cure reaction was determined by integrating the area of exothermic peak emerged in the plot heat flow vs time. Therefore, monitoring the vulcanization reaction of vinyl-terminated PDMS hybrids was performed by isothermal DSC runs. In Figure 1a, the heat flow curves of pure PDMS versus reaction time in different temperatures were presented.
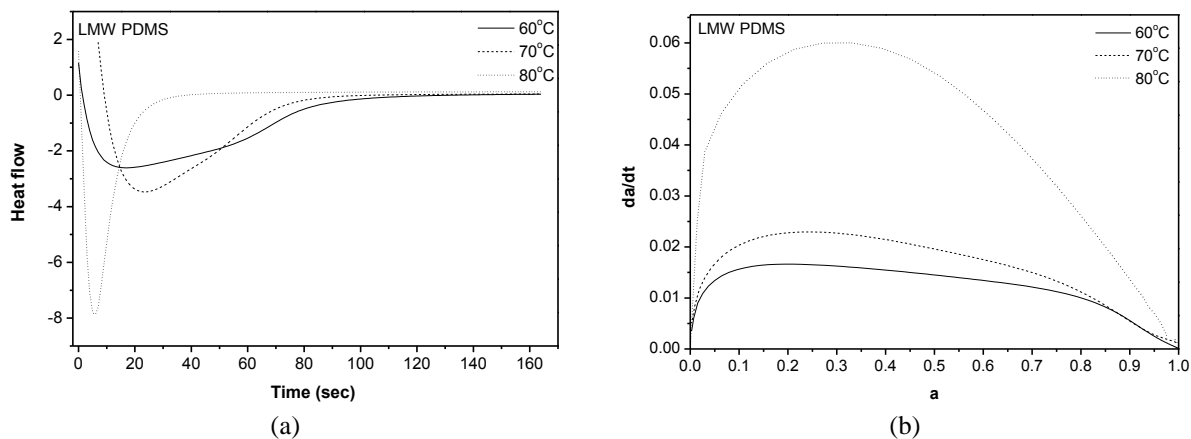
Figure 1. Isothermal DSC curves versus time (a) and vulcanization rate (*dα/dt*) versus conversion (*α*) (b), during vulcanization at 60, 70 and 80°C for pure vinyl terminated PDMS.

As the temperature of vulcanization increases, the curing rate was also increased as can be seen by the shifting of the exothermic peak to the lower time (Table 1). Furthermore, the shape of the peak became narrow and vulcanization was completed within a shorter time period.

Plots of the rate of conversion (*dα/dt*) versus the degree of conversion (*α*) of PDMS (calculated using eq. 1), at three different temperatures obtained from the DSC heat release

curves, are presented in Figure 1b. It can be seen that the shape of the conversion curve is dependent on temperature. At low temperature the change in conversion is more gradual, as the temperature increases the peak height of the conversion rate curve was also increased with a shift of the peak position to higher values. The reaction rate was found to increase rapidly and after reaching a maximum it gradually slows down toward zero. The same trend was observed for all the examined PDMS hybrids as can be seen in Table 1.

|	60°C		70°C		80°C	
	t_{max} (s)	t_f (s)	t_{max} (s)	t_f (sec)	t_{max} (s)	t_f (s)
PDMS	22.8	128.4	23.4	105	13.2	60.0
Cl20A/PDMS						
2phr	22.2	244.2	28.2	111.6	15.6	66.0
5phr	19.8	284.4	28.0	139.2	17.4	75.0
8phr	25.8	180.0	28.8	177.0	15.0	78.6
Cl30B/PDMS						
2phr	28.2	165	20.4	108	10.2	72.0
5phr	31.8	294.6	19.2	171	20.4	85.2
8phr	22.2	397.8	25.2	219.6	26.4	91.2
Nan116/PDMS	**40°C**		**50°C**		**60°C**	
2phr	17.4	101.4	15.0	46.2	15.0	45.6
5phr	15.0	94.2	13.2	37.2	7.2	28.8

Table 1. Maximum vulcanization reaction rate time (t_{max}) and time of completion of rection (t_f), for clay/vinyl terminated PDMS hybrids.

The incorporation of organoclay nanoparticles in the PDMS matrix affects the vulcanization reaction of the elastomer. The heat flow during vulcanization of vinyl terminated PDMS reinforced with different amounts of Cloisite 20A at 60°C are presented in Figure 2. As the organoclay load increases, the time required for the completion of vulcanization increases, in comparison with the same parameter in unfilled PDMS. The curing reaction rate for the Cloisite 20A/PDMS systems is high at the beginning of vulcanization. A second stage is observed, where the crosslinks formation proceeds with a lower rate in comparison with the pure elastomer, as shown in Figure 2b. Therefore, an inhibition of the curing reaction during the second stage of the process, might be possible due to oorganoclay nanoparticles, which is responsible for the higher time required for vulcanization.
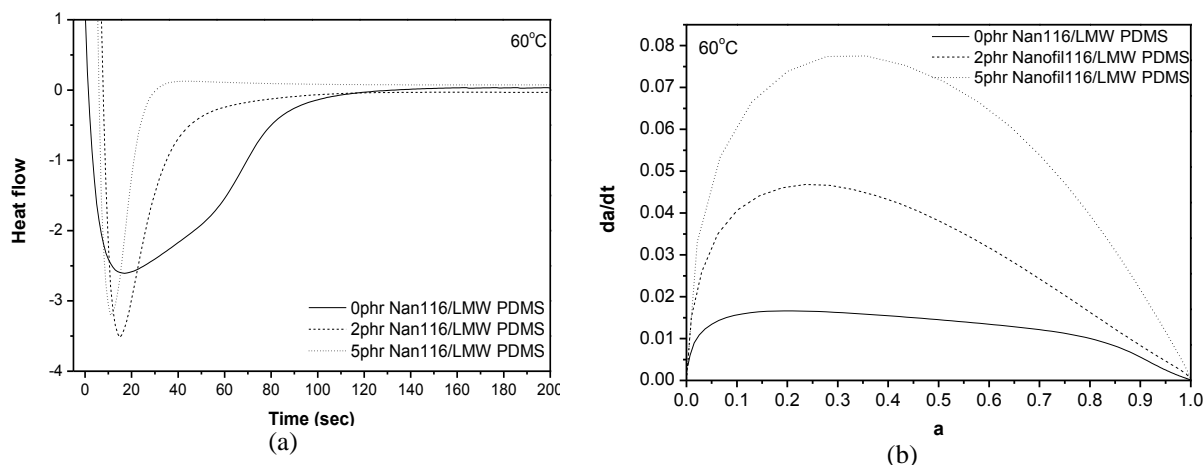

(a)   (b)
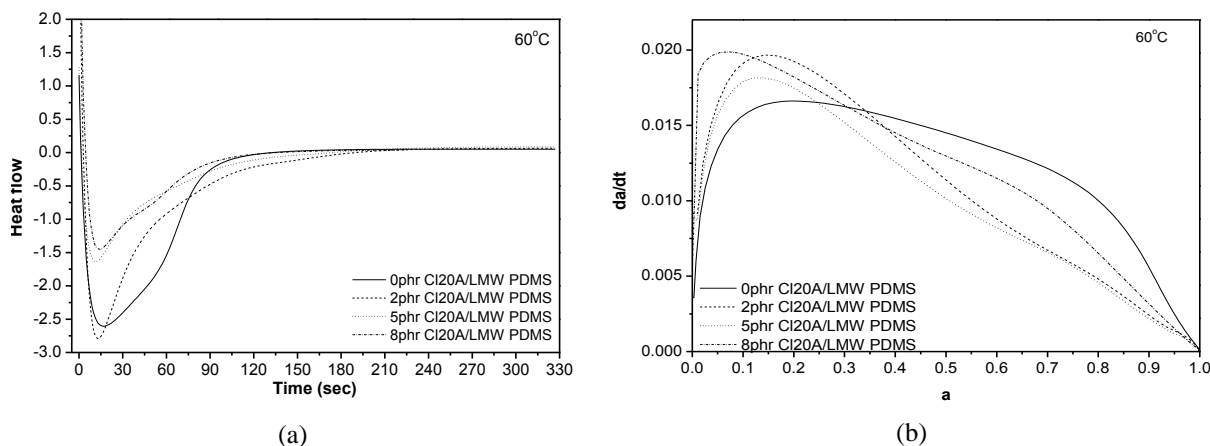
Figure 2. Isothermal DSC curves versus time (a) and vulcanization rate ($d\alpha/dt$) versus conversion (α) (b), during vulcanization at 60°C of 0, 2, 5 and 8 phr Cloisite 20A/PDMS nanocomposites.

A stronger effect on the curing time was observed for PDMS nanocomposites reinforced with Cloisite 30B organoclay, where a significant delay in vulcanization rate was observed especially for hybrids reinforced with 5 and 8 phr loading (Figures 3a&b). From the results of Table 1 it is obvious that this type of reinforcement, containing hydroxyl groups in the intercalation agent, seems to increase to a higher extent the curing reaction time.

(a)   (b)
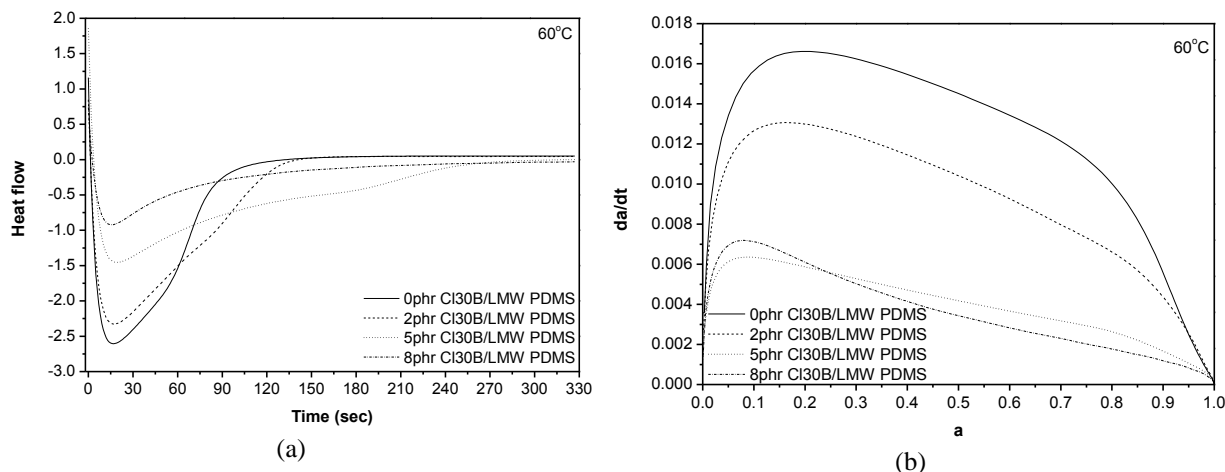
Figure 3. Isothermal DSC curves versus time (a) and vulcanization rate ($d\alpha/dt$) versus conversion (α) (b), during vulcanization at 60°C of 0, 2, 5 and 8 phr Cloisite 30B/PDMS nanocomposites.

In order to elucidate the effect of the intercalation agent used for the organic modification of clay nanoparticles on the curing mechanism of vinyl terminated PDMS/organoclay hybrids, unmodified montmorilinite (Nanofil 116) was also included studied as reinforcement. From Figure 4, a significant acceleration of curing rate can be observed as the load of the unmodified montmorillonite increases.


(a)   (b)

Figure 4. Isothermal DSC curves versus time (a) and vulcanization rate ($d\alpha/dt$) versus conversion (α) (b), during vulcanization at 60°C of 0, 2 and 5 phr Nanofil 116/PDMS nanocomposites.

From the comparative study of the examined montmorillonite reinforcements in the elastomeric matrix (Table 1, Figure 5), it was observed that Cloisite 30B increases significantly the vulcanization time of vinyl terminated PDMS, followed by Cloisite 20A. However, the opposite effect was observed for the unmodified reinforcement where the reaction was completed in shorter time and the maximum rate was achieved earlier, than the corresponding for pure elastomer.

Curing retardation can be attributed to interactions between the catalyst system and organic moiety (quaternary ammonium compound) of the modified clay, which inhibits catalytic

action. In addition to the above, the consumption of a part of the cross-linker by chemical interaction with the active sites of the intercalation agent might be possible and this, would lead to a decrease of the extent of curing reaction especially at high loadings. Moreover, absorption of the cross-linking system by the montmorillonite nanoparticles would reduce the concentration available for the cure reaction. However, the unmodified montmorillonite seem to have a catalytic effect on the vulcanization process of the examined vinyl terminated PDMS leading to faster cure.
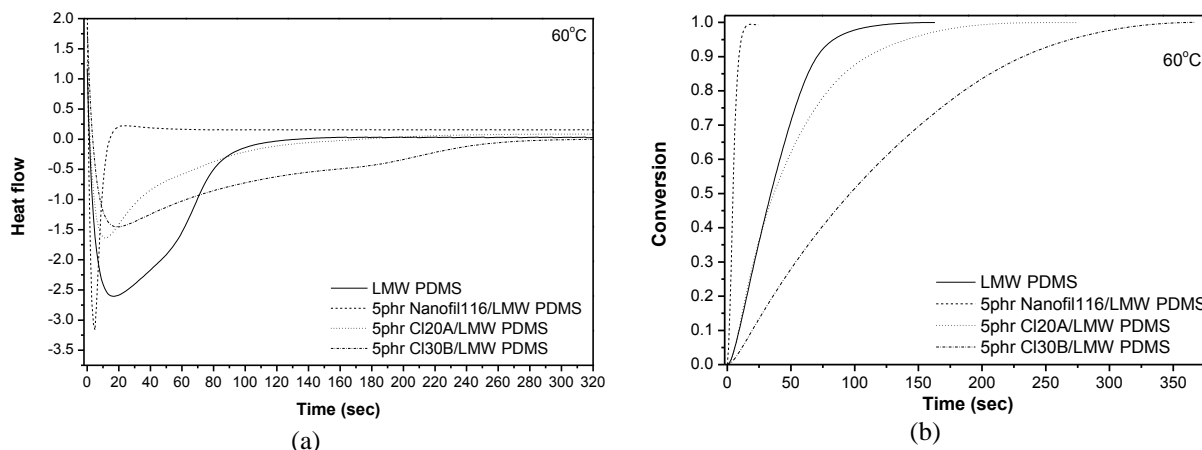
Figure 5. Isothermal DSC curves (a) and conversion (b) versus time during vulcanization at 60°C, for pure PDMS and its nanocomposites loaded with 5 phr Nanofil 116, Cloisite 20A and Cloisite 30B.

The kinetic analysis of cure reaction of vinyl terminated PDMS filled with clay reinforcement using the autocatalytic model showed good agreement with the experimental results. The kinetic parameters of vulcanization, such as the temperature dependent specific rate constant $K(T)$, were determined from the kinetic model expression of eq. 7, by means of non-linear regression analysis using ORIGIN 8.0 computer software. The activation energy E_a, related to the ease of crosslinking process, was calculated from the slope of K versus $1/T$ and the obtained values are given in Table 2. Cloisite 20A loading of 2 and 5 phr do not significantly affect the activation energy in comparison with unfilled PDMS. However, organoclay loadings of 8 phr seemed to increase the activation energy, due to inhibition of curing reaction. For Cloisite 30B/PDMS hybrids, the activation energy increases from 2 phr filler concentration, which means that cure inhibition, in that case, starts from lower clay loadings in comparison with Cloisite 20A. On the other hand, unmodified montmorillonite decreases the activation energy of curing reaction for the examined vinyl terminated PDMS.

Clay loading in PDMS	E_a (kJ/mol)		
	Cloisite 20A	Cloisite 30B	Nanofil 116
0 phr		70.82	
2 phr	76.08	80.02	67.96
5 phr	68.99	80.92	66.31
8 phr	102.31	90.98	-

Table 2. Activation energies of vulcanization of clay filled vinyl terminated PDMS, obtained from isothermal DSC experiments using eq. 7.

4 Conclusions

Clay/vinyl terminated PDMS nanocomposites were prepared by sonication mixing and the study of vulcanization process of the above systems was performed by isothermal DSC experiments. The incorporation of clay reinforcement modified the PDMS curing mechanism by altering the rate of cure. Cloisite 20A enhances the reaction rate at the beginning of curing

and then slows down the reaction rate and extends curing time, in comparison with pure PDMS. Cloisite 30B shifts the exotherm peak towards higher times and decreases the curing rate through the whole process. The opposite effect was recorded in the case of unmodified clay/PDMS nanocomposites, where curing reaction was accelerated as the clay loading increases. Physicochemical interactions between the crosslinking system and the intercalation agent of organoclay reinforcement are responsible for the observed characteristics of the curing process of vinyl terminated PDMS. The autocatalytic model showed good fitting with the experimental results. The calculated activation energies based on the above model indicated that the organoclay significantly increases the energy requirements for PDMS curing, whereas the opposite effect was observed for unmodified clay reinforcement.

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