EFFECTS OF OV-POSS NANOPARTICLES ON THE VULCANIZATION KINETICS OF NATURAL RUBBER COMPOUNDS

VPLIV OV-POSS NANODELCEV NA KINETIKO VULKANIZACIJE NARAVNIH SPOJIN GUME

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Polyhedral oligomeric silsesquioxanes (POSSs) are new-generation additives, which can provide improved properties of polymer matrices due to physical and/or chemical interactions between the polymer molecules and their reactive sites. In the case of rubber-based polymeric systems, POSSs are also able to accompany a vulcanization reaction. This study aimed to investigate the effect of octavinyl functionalized POSS (OV-POSS) on the sulphur vulcanization of a model natural rubber (NR) based compound. The reaction kinetics was studied using various kinetic approaches based on moving die rheometry and differential scanning calorimetry. Rheometric data was evaluated using a common non-linear cure kinetic model, called the Isayev and Deng Model. The Kissinger, Flynn-Wall-Ozawa and Crane Models were used to evaluate the thermal data for curing reactions. All the models were found to be able to analyze the vulcanization kinetics of OV-POSS containing NR-based rubber compounds as well as the effect of the OV-POSS incorporation.

Keywords: natural rubber, POSS, rheology, vulcanization kinetics

Poliedrični oligomerni silseskvioksani (POSSs) so nova generacija dodatkov, ki zagotavljajo izboljšanje lastnosti polimernih matric s fizikalno in/ali kemijsko interakcijo med polimernimi molekulami in njihovimi reaktivnimi položaji. V primeru polimernih sistemov na osnovi gume se lahko POSSs združujejo med reakcijo vulkanizacije. Avtorji so v študiji raziskovali vpliv z oktavinilom funkcializiranega POSS (OV-POSS) na žveplovo vulkanizacijo modelne spojine na osnovi naravne gume (NR). Opisana je kinetika reakcij z uporabo različnih kinetičnih pristopov, ki temeljijo na reometriji materiala oz. študiji tečenja in deformacije snovi v gibljivem orodju ter diferencialne vrstične kalorimetrije (DSC). Reometrični podatki so bili ovrednoteni z uporabo splošnega kinetičnega nelinearnega vulkanizacijskega modela, ki se imenuje Isayev-Deng Model. Modele po Kissingerju, Flynn-Wall-Ozawi in Craneu so uporabili za procesiranje termičnih podatkov vulkanizacijskih reakcij. Ugotovljeno je bilo, da se lahko s pomočjo vseh izbranih modelov analizira kinetika vulkanizacije spojin na osnovi naravne gume z dodatkom OV-POSS. Prav tako se lahko analizira tudi vpliv dodatka (vgradnje) OV-POSS v NR.

Ključne besede: naravna guma, POSS, reologija, kinetika vulkanizacije

1 INTRODUCTION

Vulcanization is the reaction between rubber and curing agents at a high temperature, which makes rubber compounds irreversibly cross-linked, highly elastic and strong. After vulcanization, permanent deformation and hysteresis decrease; the tensile strength, tear strength, hardness and modulus values of the compound increase remarkably. The overall properties of vulcanized rubber strongly depend not only on the type of rubber but also on the compound composition and the amount of additives such as fillers, process aids, stabilizers and curatives. Natural rubber (NR) is the most widely used rubber in the manufacturing of various rubber-based materials, particularly in the tire industry. A typical NR compound formulation includes natural rubber, a considerable amount of reinforcing fillers and process oils, stabilizers and, most likely, a sulphur crosslinking system.

Polyhedral oligomeric silsesquioxanes (POSSs) are new-generation additives and provide outstanding properties of plastics and rubber-based materials. They may have various functional (R) groups, which can interact with polymer molecules physically and/or chemically to modify the polymer structure. Hence, POSSs can modify the mechanical and thermal properties of polymers as well as their dimensional stability by reducing the chain mobility.[1] In the literature, most of the studies on the POSS incorporation into rubber are focused on silicone rubber-based matrices.[2–6]

On the other hand, there is a limited number of studies investigating the effects of POSS on NR-based composites/nanocomposites. Zhao et al. studied NR/octavinyl POSS (OV-POSS) composites.[7] Co-crosslinking

reaction between NR and OV-POSS was investigated using moving die rheometry (MDR), magnetic resonance spectroscopy (MR) and Fourier-transform infrared spectroscopy (FTIR). NR vulcanizates were found to have improved mechanical properties in the presence of OV-POSS. It was stated that OV-POSS slightly increased the glass transition temperature (Tg) of the rubber matrix. Besides, NR/OV-POSS composites exhibited improved thermal stability. Somasekharan et al. studied POSS and multi-walled carbon-nanotube hybrid filler-based NR nanocomposites prepared using a simple two-roll mill.[8] Filler-polymer interactions were examined with a dynamic-mechanical analysis (DMA). Cure characteristics of the nanocomposites indicated a positive effect of the nanofillers on the vulcanization reaction and network structures. Improved mechanical properties of the nanocomposites were also attributed to a significant level of the reinforcement provided by the hybrid filler in the NR matrix. In a recent study conducted by our research group, mechanical, thermal, and rheological properties of NR/OV-POSS composites were studied.[9] The adhesion of NR/OV-POSS composites to textile cords was evaluated with H-stripping tests. OV-POSS was found to retard the curing reaction and decrease the crosslink density. However, the OV-POSS incorporation into a model NR compound significantly improved the thermal stability and interfacial adhesion between NR and the fabric cords.

Vulcanization kinetics is a favorable tool used to better understand reaction mechanisms by correlating the kinetic parameters with the process conditions and mechanical properties of vulcanizates. Several mathematical models have been developed for vulcanization-kinetic calculations. These models are mainly classified into two main groups: mechanistic models and empirical (phenomenological) models. In mechanistic models, the amount of consumed and produced species during a vulcanization reaction is used for the calculation, whereas in empirical models, vulcanization experimental data obtained from a rheometer curve is fitted into linear or non-linear equations. All the empirical models focus on the reaction extent correlating with the reaction temperature and instant reaction time. One or more reaction rate constants and the order of reaction can be calculated by solving empirical equations.[10]

Based on empirical kinetic models, the state of cure is determined using the specific-torque values from the rheometer curve. The state of cure α of a rubber compound at a specific time t is calculated with Equation (1):

$$\alpha = \frac{M_t - M_L}{M_H - M_L} \qquad (1)$$

where M_t is the torque value measured at time t, M_L and M_H are the minimum and maximum torque values, respectively. As the easiest model for investigating vulcanization kinetics, linear or first-order reaction kinetics assumes the cure extent changes to be completely linear with the reaction time taken. The linear kinetic model is given by Equation (2). It is more practical to use it in another form – in Equation (3) after the integration.[11]

$$\frac{d\alpha}{dt} = k(T) \qquad (2)$$

$$\ln(\alpha) = k(T)t \qquad (3)$$

Torque values from the rheometer curve are used to derive α values in accordance with Equation (1) for every single reaction time, t. From the linear correlation given with Equation (3), the vulcanization rate constant can be calculated for an individual isothermal-test temperature. This methodology is applied to at least three temperatures and the vulcanization activation energy can be calculated in accordance with the very well-known Arrhenius expression, given below. Here, A is the frequency factor, E_a is the activation energy and R is the universal gas constant.

$$k(T) = Ae^{\frac{E_a}{RT}} \qquad (4)$$

The nth-order vulcanization-kinetic approach (Isayev and Deng Model) is the most common non-linear kinetic model, given in Equation (5). This model considers the curing region of the cure curve (between the minimum and maximum torque values) and correlates the total vulcanization reaction rate with the isothermal reaction temperature and instant vulcanization time:[11]

$$a = \frac{\{k(t - t_0)\}^n}{1 + \{k(t - t_0)\}^n} \qquad (5)$$

where α is the state of cure, k is the reaction rate constant (min^{-1}), t is the instant time (min), n is the reaction order, and t_0 is the induction time in minutes. In this model, it is assumed that the vulcanization rate is maximum at the beginning of the reaction.[12] Calculated k values for various reaction temperatures are used to determine the activation energy (E_a) using the Arrhenius equation. The reaction order does not depend on the vulcanization temperature; it is varied only by the compound formulation.

Khang and Ariff studied the vulcanization reaction kinetics of a NR vulcanization accelerated with tetrametiltiuram disulfide (TMTD) using the Isayev and Deng Model.[13] They fitted the rheometer curves obtained at (160, 170, 180) °C to the model and investigated the effects of the accelerator, sulphur and filler, concentration on vulcanization characteristics. The cure extent was assumed to vary with the compound composition but not with the curing temperature. The reaction order was found to be higher at higher accelerator concentrations when the sulphur level was kept constant. On the other hand, a high sulphur concentration increased the reaction order at a constant accelerator concentration. Silica was also found to increase both the reaction order and activation energy. This was simply attributed to the high thermal conductivity of silica; in other words, the heat was assumed to be absorbed by silica earlier than by natural rubber.

The other kinetic approach based on a thermal analysis, highlighting the vulcanization kinetics, is the differential scanning calorimeter (DSC) analysis. In this approach, the first step is obtaining DSC thermograms with different heating rates. The activation energy and reaction order for vulcanization can be calculated by fitting the DSC curves to common thermal kinetic models such as the Kissinger, Flynn-Wall-Ozawa and Crane Models. According to the basic approach, the reaction rate can be expressed as in Equation (6).[14]

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{6}$$

In Equation (6), t is the instant reaction time, $k(T)$ is the rate constant and $f(\alpha)$ is the instant conversion representing the cure extent. An integrated form of Equation (6) for $n \neq 1$ is in Equation (7).

$$g(\alpha) = \int_o^\alpha \frac{d\alpha}{f(\alpha)} = \frac{(1-\alpha)^{1-n} - 1}{n-1} = k(T)_t \tag{7}$$

The rate constant can again be calculated using the Arrhenius expression.

In the Kissinger Model, $d^2\alpha/dt^2$ is zero for the constant heating rate and it is expressed with Equation (8):[14]

$$\ln\left(\frac{\beta}{T_p^2}\right) = \left(\frac{A \cdot R}{E_a}\right) - \frac{E_a}{R \cdot T_p} \tag{8}$$

where β is the heating rate and T_p is the peak temperature. Hence, the plotting of $\ln(\beta/T_p^2)$ versus $1/T_p$ gives E_a and A from the slope and intercept of the line, respectively.

The Flynn-Wall-Ozawa Model correlates the apparent activation energy with the heating rate and isoconversion temperature as given in Equation (9), where E_a and A can be obtained from the $\ln(\beta)$ versus $1/T_p$ plot.[14]

$$\lg\beta = \lg\left(\frac{A \cdot E_a}{R}\right) - 2.315 - 0.4567\frac{E_a}{R \cdot T_p} \tag{9}$$

The Crane equation (Equation (10)) was developed, assuming that $d^2\alpha/dt^2 = 0$ at the peak exotherm[14] and $E_a/(nR) > 2T_p$:

$$\frac{d(\ln\beta)}{d(1/T_p)} \approx -\frac{E_a}{nR} \tag{10}$$

In this study, the effect of OV-POSS on the vulcanization kinetics of a reference natural rubber-based rubber compound was investigated. The Isayev and Deng, Kissinger, Flynn-Wall-Ozawa and Crane Kinetic Models were used to comparatively evaluate the kinetic parameters.

2 EXPERIMENTAL PART

2.1. Materials

Natural rubber (CV 60) used in this study was supplied from Baria Rubber Co. (Vietnam). Carbon black (ISAF N220) was supplied from OMSK (Russia), whereas naphthenic oil was from Petroyağ (Turkey). Octavinyl polyhedral oligomeric silsesquioxane (OV-POSS) was purchased from Hybrid Plastics Inc. (USA). Other compound components were commercially available elsewhere. The properties of the above materials are given in **Table 1**.

Table 1: Descriptions of the main compound components

Material	Manufacturer	Description
NR (CV60)	Baria Rubber Co., Vietnam	Mooney viscosity: (60 ± 5) MU [ML[1+8]@100 °C] Plasticity-retention index: 82 Dirt content: 0.019 %
OV-POSS	Hybrid Plastics Inc., USA	Solvent: THF
CB (ISAF N220)	OMSK, Russia	Average primary-particle diameter: (21 ± 9) nm Iodine-absorption number: 121 g/kg
Naphtenic oil (N418)	Petroyag, Turkey	Viscosity: 22 mm²/s Density: 902 kg/m³

2.2. Method

2.2.1. Compounding

Rubber compounds were prepared using an internal mixer with a gross volume of 300 mL and a laboratory-type two-roll mill, subsequently. In the mixer, NR was first masticated for 2 min and then CB and process oil were added to it and it was mixed for another 5 min. Other additives and, finally, sulfur and OV-POSS were added consecutively. The total mixing time was 25 min. The compound was placed onto the two-roll mill for the final homogenization. The OV-POSS loading level was selected as (1, 3, 6, 8) phr (parts per hundred rubber). All the recipes are given in **Table 2**.

Table 2: Rubber-compound recipes

Materials	REF	1 OV-POSS	3 OV-POSS	6 OV-POSS	8 OV-POSS
			Content (phr)		
Natural rubber	100	100	100	100	100
OV-POSS	0	1	3	6	8
CB	55	55	55	55	55
Naphthenic oil	11	11	11	11	11
Zinc oxide	7	7	7	7	7
Stearic acid	3	3	3	3	3
IPPD[a]	2	2	2	2	2
Cobalt naphtanate	1	1	1	1	1
Phenolic resin	2.5	2.5	2.5	2.5	2.5
HMMM[b]	2	2	2	2	2
DCBS[c]	0.7	0.7	0.7	0.7	0.7
Sulphur	3	3	3	3	3

[a] N-Isopropyl-N'-Phenyl-P-Phenylenediamine
[b] Hexa Methoxy Methyl Melamine
[c] Benzothiazyl-2-Dicyclohexyl Sulfenamide

2.2.2. Analysis of the cure kinetics

Rheological properties and optimum cure times of the compounds were obtained from their respective cure curves measured with a moving die rheometer (MDR, Alpha Technologies) in accordance with ASTM D-5289. For the kinetic evaluation, 6 different curing temperatures (140, 150, 160, 170, 180, 190) °C were selected when measuring the cure curves. Torque values from the cure curves were converted to the relative degree of cure α value between 0–1 for the respective points (time, t). The produced t-α data was processed with kinetic calculations. Non-linear curve-fitting procedures were carried out using suitable calculation software to implement the Isayev and Deng Model.

DSC thermograms for various heating rates were obtained with a Mettler Toledo DSC-1 differential scanning calorimeter. An analysis was performed under nitrogen purge between 25 °C and 250 °C, at heating rates of (1, 3, 6, 10) °C /min. Vulcanization rate and activation energy of the compounds were calculated using the Kissinger, Flynn-Wall-Ozawa and Crane Models.

3 RESULTS AND DISCUSSION

3.1. Cure characteristics

Important rheological properties such as minimum torque M_L, maximum torque M_H, scorch time t_{s2} and optimum cure time t_{90} were calculated from the cure curves obtained at 170 °C, which is the most reasonable curing temperature for the target applications. The cure extent was calculated as the difference between M_H and M_L for individual curves and can be correlated with the crosslink density. Cure rate index (CRI) values were calculated according to Equation (11).[15] Rheological parameters of the compounds are given in **Table 3**.

$$CRI = \frac{100}{t_{90} - t_{s2}} \qquad (11)$$

Table 3: Rheological properties of the compounds

Compound	t_{s2}/min	t_{90}/min	Cure extent (Nm)	CRI/min^{-1}
REF	1.03	3.89	1.443	34.96
1 OV-POSS	1.14	4.01	1.294	34.84
3 OV-POSS	0.85	3.89	1.322	32.89
6 OV-POSS	1.59	4.8	1.345	31.15
8 OV-POSS	1.52	4.81	1.369	30.39

As it is seen in **Table 3**, the cure-extent values for the OV-POSS compounds increase with the increasing OV-POSS amount even if all the OV-POSS compounds have a lower cure extent than that of the reference. The cure rate is slightly lower for the OV-POSS compounds. When these two findings are evaluated together, they suggest an altered vulcanization mechanism of the NR-based model compound in the presence of OV-POSS.

Vulcanization kinetic parameters were calculated by fitting the cure data according to the Isayev and Deng Model. Reaction order n, rate constant k and activation energy E_a values are reported in **Tables 4** and **5**.

Table 4: Vulcanization kinetic data – reaction order n

Compound	Reaction order n					
	140 °C	150 °C	160 °C	170 °C	180 °C	190 °C
REF	3.53	3.28	3.03	2.75	2.80	3.25
1 OV-POSS	3.72	3.46	3.23	2.90	2.68	3.06
3 OV-POSS	3.14	3.06	2.83	2.68	2.63	2.78
6 OV-POSS	3.42	3.51	3.21	3.28	2.96	3.25
8 OV-POSS	3.53	2.52	2.55	3.18	2.94	3.11

When the reaction order n values are evaluated, it is seen that they exhibit different variations for different curing-temperature regions as well as for different OV-POSS concentrations in the compound. Therefore, we could not define a proper relation for the reaction order. However, as an overall evaluation, n values are slightly higher for the OV-POSS-containing compounds, indicating additional species accompanying the vulcanization reaction.

Reaction-rate constants systematically increase with the increasing curing temperature, as expected. Besides, the reaction rate tends to decrease when the OV-POSS concentration reaches higher levels, providing a very good correlation with cure characteristics. In this case, similar activation-energy values for the OV-POSS-containing compounds also support the investigations on cure characteristics.

3.2 DSC analysis

Vulcanization kinetics of the reference and NR/OV-POSS compounds was also evaluated using the thermal data obtained with DSC in accordance with the common kinetic models such as Avrami, Ozawa, Flynn-Wall-Ozawa, Crane and Kissinger Models. **Figures 1** and **2** show representative DSC thermograms of

Table 5: Vulcanization kinetic data – rate constant k and activation energy E_a

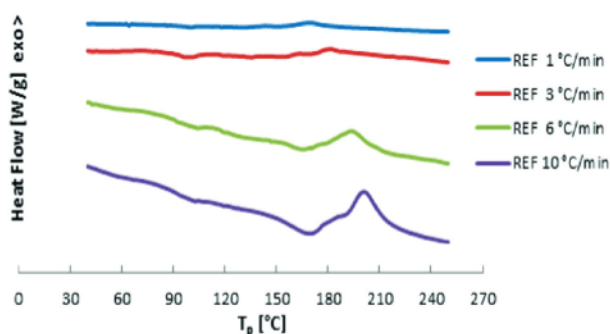| Compound	k/min^{-1}						E_a/ (kJ/mol·K)	R^2
	140 °C	150 °C	160 °C	170 °C	180 °C	190 °C		
REF	1.57×10^{-5}	1.41×10^{-3}	2.2×10^{-2}	0.20	1.36	8.53	0.41	0.99
1 OV- POSS	3.85×10^{-5}	8.48×10^{-4}	1.64×10^{-2}	0.19	1.38	7.9	0.39	0.99
3 OV-POSS	1.11×10^{-5}	4.60×10^{-4}	8.70×10^{-3}	0.14	1.32	8.39	0.40	0.99
6 OV-POSS	2.09×10^{-5}	2.94×10^{-4}	6.30×10^{-3}	0.05	0.70	5.59	0.40	0.99
8 OV-POSS	4.10×10^{-6}	2.17×10^{-3}	1.23×10^{-2}	0.06	0.73	4.05	0.40	0.98

Figure 1: DSC thermograms of REF NR compound for different heating rates

Table 6: Thermal transitions of REF and NR/OV-POSS compounds for different heating rates

Materials	β/(°C/min)	T_o/°C	T_p/°C	T_e/°C
NR(Ref)	1	154.3	169.4	178.8
	3	172.3	181.2	190.1
	6	169.9	193.3	207.9
	10	185.0	200.3	216.0
1 OV-POSS	1	165.1	168.1	172.5
	3	159.9	179.0	184.9
	6	170.4	192.6	215.2
	10	179.2	201.1	221.4
3 OV-POSS	1	159.6	167.8	185.4
	3	159.5	180.0	187.7
	6	162.2	193.9	205.9
	10	178.0	201.1	223.2
6 OV-POSS	1	161.2	168.9	180.9
	3	166.0	180.2	192.4
	6	170.4	194.8	215.2
	10	179.0	201.2	222.2
8 OV-POSS	1	156.7	169.39	178.8
	3	166.9	188.2	200.5
	6	177.2	198.7	220.5
	10	179.5	201.2	209.5

the reference and OV-POSS compounds including 1 phr OV-POSS for heating rates of (1, 3, 6, 10) °C/min. The vulcanization onset T_o, vulcanization peak T_p and vulcanization endset temperature T_e obtained from the DSC thermograms for all the compounds are listed in **Table 6**.
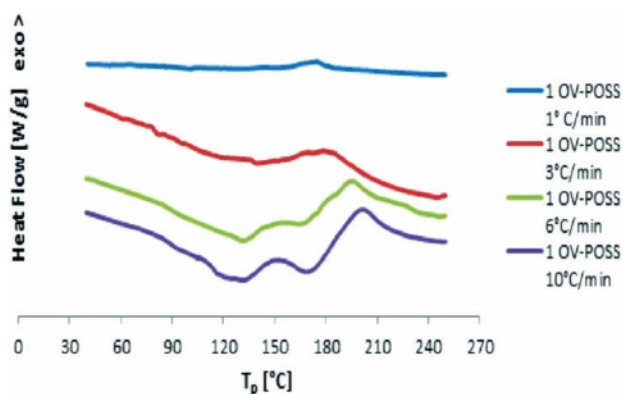

Figure 2: DSC thermograms of 1 OV-POSS compound for different heating rates

As can be seen in **Figures 1** and **2**, vulcanization started at high temperatures as the heating rate increased. Moreover, the addition of 1 phr of OV-POSS to the reference compound increased the T_o, and T_p values, especially at lower heating rate, which is in accordance with the early report by Liu et al.[15] On the other hand, it was found that the increasing OV-POSS content did not significantly affect the vulcanization onset temperature of the reference compound. However, at higher heating rate, the time required to complete the vulcanization increased in the presence of OV-POSS, as can be seen in **Table 6**, which was consistent with the CRI values obtained from rheological experiments. This can be attributed to the alteration in the vulcanization mechanism of the reference compound in the presence of OV-POSS.[9] Moreover, it was observed that the crosslinking enthalpies increased as the heating rate increased for the OV-POSS compounds as can be seen in **Figure 2**.

3.2.1 Determination of the kinetic parameters with Kissinger and Flynn-Wall-Ozawa Methods

Ln (β/T_p^2) vs. $1/T_p$ and log β vs. $1/T_p$ were plotted to investigate the linear relationships and validate the Kissinger and Flynn-Wall-Ozawa Methods up to the maximum reaction rate. Representative Kissinger and Flynn-Wall-Ozawa plots for the 3 OV-POSS compound, are given in **Figures 3** and **4**, respectively.

Kinetic parameters for all the compounds are given in **Table 7**. E_a values for NR/OV-POSS compounds were found to vary between 109.95–111.68 kJ/mol and 111.79–113.45 kJ/mol according to the Kissinger and Flynn-Wall-Ozawa Methods, respectively. Due to different kinetic approaches of the two models, the parameters found with the Flynn-Wall-Ozawa Model are slightly higher than those found with the Kissinger Model. As can be seen from **Table 7**, E_a is affected by the POSS content. E_a values first decreased with the addition of 1 phr OV-POSS to the reference compound, then increased
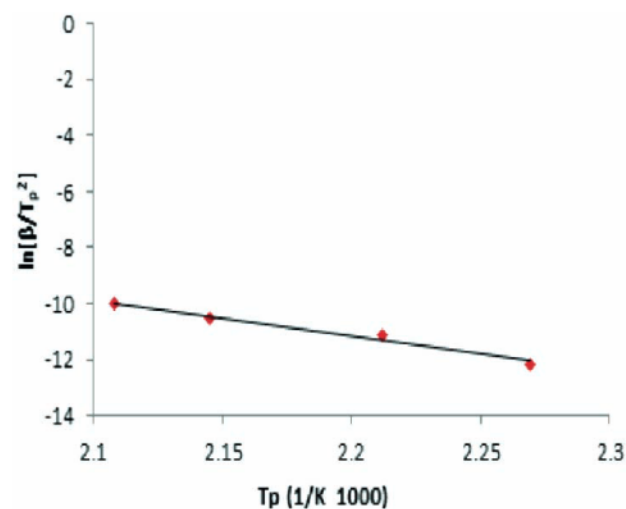

Figure 3: T_p – ln (β/T_p^2) plot (Kissinger Method) for 3 OV-POSS compound

Table 7: Kinetic parameters calculated according to Kissinger, Flynn-Wall-Ozawa and Crane Methods

	Kissinger		Flynn-Wall-Ozawa			Crane		
Compound	E_a /(kj/mol)	R^2	E_a /(kj/mol)	R^2	E_a/n	R^2	n^a	n^b
REF	119.23	0.96	120.61	0.97	126.83	0.99	0.94	0.96
1 OV-POSS	109.95	0.99	111.79	0.99	117.82	0.98	0.93	0.95
3 OV-POSS	110.22	0.99	112.04	0.98	116.85	0.99	0.94	0.96
6 OV-POSS	110.68	0.98	112.49	0.98	123.87	0.99	0.89	0.91
8 OV-POSS	111.68	0.98	113.45	0.99	119.60	0.99	0.93	0.95

[a] Using the value of E_a obtained with the Kissinger Method
[b] Using the value of E_a obtained with the Flynn-Wall-Ozawa Method

systematically as the OV-POSS content increased. The decrease in E_a in the presence of 1 phr OV-POSS can be attributed to a possible reaction between sulphur and OV-POSS, as reported in our previous study,[9] which adversely affected the crosslinking density of NR. On the other hand, for the NR compounds with a higher content of OV-POSS, higher E_a values were obtained, which was due to the contribution of OV-POSS to the crosslinking mechanism of NR via its vinyl groups. This effect was more prominent for the NR compound with 8 phr OV-POSS. Therefore, it can be concluded that more activation energy was needed to initiate the crosslinking of NR when the OV-POSS level increased.
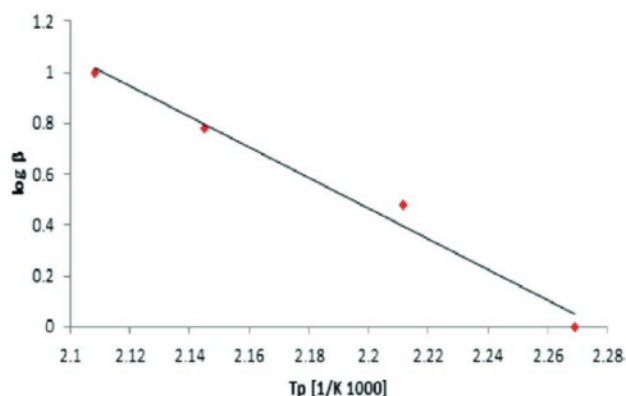

Figure 4: $\log \beta – T_p$ plot (Flynn-Wall-Ozawa Method) for 3 OV-POSS compound

Figure 5: $\ln \beta – 1/T_p$ plot (Crane Method) for 3 OV-POSS compound

3.2.2 Determination of the overall reaction order (n) with the Crane Method

The overall reaction order n can be obtained with the Crane Method, according to Equation (10). Linear relationships were obtained by plotting $\ln \beta$ vs. $1/T_p$, confirming the validity of the model. **Figure 5** shows the representative Crane curve for the 3 OV-POSS compound. The calculated reaction order based on the slope and correlation coefficients for the compounds containing different POSS amounts are given in **Table 7**. As displayed in this table, the reaction orders calculated according to both the Kissinger Method and Flynn-Wall-Ozawa Method were all close to 1. This result shows that OV-POSS makes the curing-reaction mechanism more complicated, following the first-order kinetics.

The activation-energy values calculated for different kinetic approaches (Kissinger, Flynn-Wall-Ozawa and Crane Methods) are quite similar and the OV-POSS incorporation into the reference NR compound increase the reaction activation energy. This result also coincides with the varied cure-extent values for the OV-POSS compound, representing an altered reaction mechanism.

4 CONCLUSION

In this study, the Isayev and Deng, Kissinger, Flynn-Wall-Ozawa and Crane Kinetic Models were used to investigate the cure kinetics of OV-POSS containing natural-rubber compounds. Based on the rheological analysis, the Isayev and Deng Model indicated an altered vulcanization stoichiometry in the presence of OV-POSS. Based on the DSC analysis, it was found that the increasing OV-POSS amount did not significantly affect the vulcanization onset temperature of NR, whereas the time required for the completion of the vulcanization increased in the presence of OV-POSS. Vulcanization-activation-energy values were found to be quite similar for the Kissinger, Flynn-Wall-Ozawa and Crane Models. OV-POSS led to a higher vulcanization-activation energy, which was found to be in a good correlation with the altered cure extent, measured with moving die rheometry.
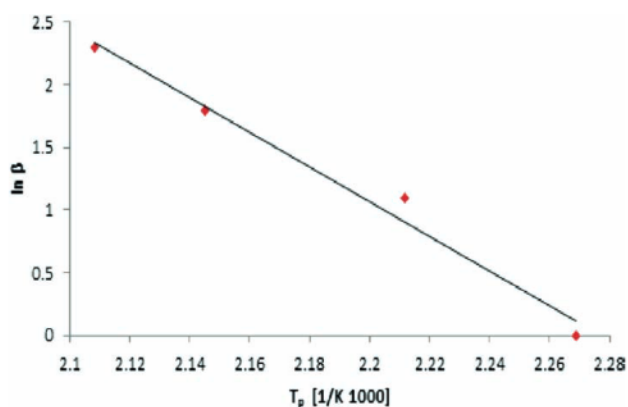
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