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Effect of co-agent type on curing kinetics of vinyl-methyl siloxane and phenyl-vinyl-methyl siloxane elastomers

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Abstract

In this study, Type I co-agents Zinc Acrylate (ZDA), Zinc Methacrylate (ZDMA) and Type II co-agents Triallyloxy-1,3,5-triazine (TAC) and 1,3,5-triallyl-1,3, the effect of 5-triazine (TAIC) on the curing kinetics of vinyl methyl polysiloxane (VMQ) and phenyl vinyl methyl polysiloxane (PVMQ) elastomers was examined. Cure rate constant (k), reaction degree (n), and activation energy (Ea) values were evaluated according to the 1st and nth cure kinetics, using the data of the cure curves obtained from the rheological analyses performed with the moving die rheometer at different temperatures. It was determined that the type of co-agent used in the preparation of the elastomer had a positive effect on the cure rate and effective cross-link formation. In addition, the effect of both

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the molecular structure of the co-agent used and the type of silicone elastomer on the cure reaction was explained. Since activation energies were calculated using the entire cure curve in the nth degree cure kinetics, higher activation energy values were obtained compared to the 1st-degree cure kinetics. While the use of co-agents has been shown to affect the curing behavior and rheology of silicone elastomers, it is clear that the elastomer components and type of coagent will affect the performance of the final product.

Keywords: Activation energy; Co-agent; Peroxide curing; Silicone elastomer.

Ko-ajan tipinin vinil-metil siloksan ve fenil-vinil-metil siloksan elastomerlerinin kür kinetiğine etkisi

Öz

Bu çalışmada Tip I ko-ajanlar Çinko Akrilat (ZDA), Çinko Metakrilat (ZDMA) ve Tip II ko-ajanlar Trialiloksi-1,3,5-triazin (TAC) ve 1,3,5-trialil-1,3 5-triazinin (TAIC), vinil metil polisiloksan (VMQ) ve fenil vinil metil polisiloksan (PVMQ) elastomerlerinin kürlenme kinetiği üzerindeki etkisi incelenmiştir. Kürleşme hızı sabiti (k), reaksiyon derecesi (n) ve aktivasyon enerjisi (Ea) değerleri, hareketli kalıp Reometresi ile farklı sıcaklıklarda gerçekleştirilen reolojik analizlerden elde edilen kürlenme eğrilerinin verileri kullanılarak 1. ve n. kür kinetiğine göre değerlendirildi. Elastomerin hazırlanmasında kullanılan ko-ajan türünün kürleşme hızına ve etkili çapraz bağ oluşumuna olumlu etkisi olduğu belirlendi. Ayrıca hem kullanılan ko-ajanın moleküler yapısının hem de silikon elastomer tipinin kür reaksiyonuna etkilediği tesbit edilmiştir. n. derece kür kinetiğinde aktivasyon enerjileri kür eğrisinin tamamı kullanılarak hesaplandığından 1. derece kür kinetiğine göre daha yüksek aktivasyon enerjisi değerleri elde edilmiştir. Yardımcı ajanların kullanımının silikon elastomerlerin kür davranışını ve reolojisini üzerindeki etkisi görülmüştür. Elastomer bileşenlerinin ve ko-ajan tipinin nihai ürünün performansını etkileyeceği açıktır.

Anahtar Kelimeler: Aktivasyon enerjisi; Ko-ajan; Peroksit kürleme, Silikon elastomer.

1. Introduction

Silicone elastomers have been used in many applications because of their chain flexibility, and thermal resistance and maintain their physical properties at a wide temperature range. Siloxane bonds (Si-O-Si) form the skeleton of the silicone structure. Silicone structures with different properties can be obtained by bonding other organic groups to the silicon atom [1]. As a result of the cross-linking of the elastomers, their physical properties and dynamic performances are significantly increased [2]. The strength and quantity of the cross-links affect the stiffness, mechanical properties, and network structure of the elastomer. Usually, organic peroxides are used for crosslinking of silicone elastomers. Organic peroxides are the structures formed by bonding at least two oxygen atoms bonded to an organic group. The peroxide decomposes with the heat to form free radicals, forming the active group on the polymer chain. Crosslinking occurs with the interaction of the active parts formed on the polymer chains. The chemical structure of the organic group attached to the oxygens in peroxides allows the peroxide to be classified as dialkyl, diacyl, peroxyketal, and peroxyester. Some peroxides in these peroxide classes, and often used with silicone elastomers have advantages and disadvantages.

Peroxyketals react more quickly due to their low half-life. Peroxyketals give a high curing reaction at low temperatures compared to diacyl peroxides. However, since peroxyketals contain both weak and strong free radicals, they show less efficient cross-linking than dialkyls [3]. Diacyl peroxides, on the other hand, form highly active free radicals when they decompose. However, they are preferred in processes that require little crosslinking because they require a high curing temperature and have a long half-life [4]. It is frequently used in co-agents in systems where silicone elastomers are cured by peroxide curing. Co-agents or accelerators are important additives as they affect the activity of crosslinking agents and the amount of crosslinking [5]. They also change processing parameters such as cure rate and cure time [6]. Co-agents used with peroxide are classified as Type I and Type II based on their contributions to cure. Type I co-agents increase both the rate and state of cure. Type II co-agents form less reactive radicals and contribute only to the state of cure [7]**.** Type I co-agents have two functional groups, and Type II has three functional groups. Type I accelerators are generally polar, multifunctional, and have low molecular weight. Type I accelerators contain acrylates, methacrylates, methacrylate esters, and dimelamides in their structure. Type II accelerators are radicals with lower activity and only increase the number of crosslinks. Type II accelerators contain allyl groups, cyanurate, isocyanurate, and phthalates.

Experimental investigations of the cure and rheology of elastomers are crucial for understanding how to achieve the highest quality components in manufacturing processes. However, this empirical approach is often complex and time-consuming. Numerical modeling and simulations offer a more cost-effective alternative, allowing for iterative studies without the need for extensive in situ trials. In addition, experimental research on the curing and rheology of elastomers can give us information about the components that the highest quality product will need, the production method, and factors affecting the performance of the end product, etc. in a production process [8].

In this study, we have investigated the effect of various co-agents on the curing kinetics of different polysiloxane elastomers at different temperatures. The impact of different co-agent types on curing was examined with 1st and nth cure kinetics models. The investigation into the effects of co-agents on the curing kinetics and cure parameters of polysiloxane elastomer reveals that, although co-agents significantly influence the curing behavior and rheology of silicone elastomers, the performance of the final product is also heavily dependent on the elastomer components and the type of manufacturing process used.

2. Materials and Methods

2.1. Materials

Phenyl vinyl methyl silicone (PVMQ) was purchased from Shin-Etsu Chemical Co. Ltd. (Tokyo, Japan). Vinyl methyl silicone (VMQ) was purchased from Wacker Co. Ltd. (USA). Co-agents, triallyl cyanurate (TAC), triallyl isocyanurate (TAIC), zinc diacrylate (ZDA), and zinc dimethacrylate (ZDMA) were obtained from Sigma-Aldrich. As crosslinker, 2,5-dimethyl-2,5-di(tertiary-butylperoxy) hexane (DBPH) with product code trigonox 101-45S and peroxide content of 44-46% was obtained from Akzo Nobel (Netherlands). The mold release agent (MRA) used to remove elastomers from vulcanization molds was purchased from SolPro Co.Ltd. (Türkiye).

2.2. Preparation of compounds and vulcanizates

In the formulations specified in **Table 1**, silicone elastomers have been prepared in the Thermo HAAKE Rheomix Mixer system at 25 ^{0}C for 20 minutes at a rate of 50 rpm. Cure characteristics at these rubber blends (etc: scorch time t_{2s}, optimum cure time t_{90}, and torque increments ΔM) were determined according to ASTM D 5289 using Alpha 2000B Moving Die Rheometer (MDR) at five different temperatures 170, 175, 180, 185 and 190 °C for 20 minutes.

Table 1. Formulations of the compounds.

	Components, phr*							
Blends Code	***VMQ***	***PVMQ***	***DPBH***	***TAC***	***TAIC***	***ZDA***	***ZDMA***	***MRA****
VMQ	100	-	0.8	-	-	-	-	1.25
VMQ-TAC	100	-	0.8	0.5	-	-	-	1.25
VMQ-TAIC	100	-	0.8	-	0.5	-	-	1.25
VMQ-ZDA	100	-	0.8	-	-	0.5	-	1.25
VMQ-ZDMA	100	-	0.8	-	-	-	0.5	1.25
PVMQ	-	100	0.8	-	-	-	-	1.25
PVMQ-TAC	-	100	0.8	0.5	-	-	-	1.25
PVMQ-TAIC	-	100	0.8	-	0.5	-	-	1.25
PVMQ-ZDA	-	100	0.8	-	-	0.5	-	1.25
PVMQ-ZDMA	-	100	0.8	-	-	-	0.5	1.25

*phr, Parts per Hundred Rubber**,** **MRA, Mould release agent

2.3. Characterization

The rheological analysis of the silicone blends has been performed using Alpha Technologies MDR 2000B rheometer according to ASTM D5289. The mechanical properties of the blends have been investigated using a Zwick/Z010 Universal Testing Machine according to ASTM D412 with a crosshead speed of 100 mm/min.

3. Theoretical Background

3.1. 1st Order Kinetic Model

Cure Rate Index (CRI) which is related to the rate of vulcanization was calculated using Equation 1 [9].

$$\mathrm{CRI} = 100/(\mathrm{t}_{90} - \mathrm{t}_{s2}) \tag{1}$$

The cure rate content and activation energy of silicone elastomers were calculated according to 1st order kinetic model. The state of cure (α) values were calculated by evaluating cure curves of VMQ and PVMQ elastomers at four different temperatures using equation 2 [10].

$$\propto (t) = (M_t - M_H)/(M_H - M_L) \tag{2}$$

Where M_H is the maximum torque, M_L is the minimum torque and M_t is the torque at the time t. k values were calculated according to 1st order kinetic model using Equation 3 by evaluating the area between α=0.25-0.45 in the cure curve.

$$\ln(\propto) = k(T).t \tag{3}$$

Activation energies of elastomers have been calculated with k values obtained at different temperatures using the Arrhenius equation.

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right) \tag{4}$$

Where Ea is the activation energy, R is the universal gas constant and T is the absolute temperature.

3.2. n nth order kinetic model

The second method for calculating k, Ea, and reaction order (n) is the nth-order kinetic model. The state of cure-time curves was evaluated using a scientific program according to Equation 5 to obtain k and n values.

$$\propto = k[(t - t_s)]^n / (1 + k[(t - t_s)]^n \qquad (5)$$

Where ts is scorch time, activation energies of elastomers have been calculated using Equation 4.

4. Results and Discussion

4.1. Cure characteristics of VMQ & PVMQ at different temperatures

Silicone elastomers are prepared according to the recipes given in **Table 1**. They were cured at 170, 175, 180, 185, and 190 °C. The cure curves of VMQ and P VMQ elastomers without co-agents at 5 different temperatures are given in **Figures 1-a** and **1-b**.

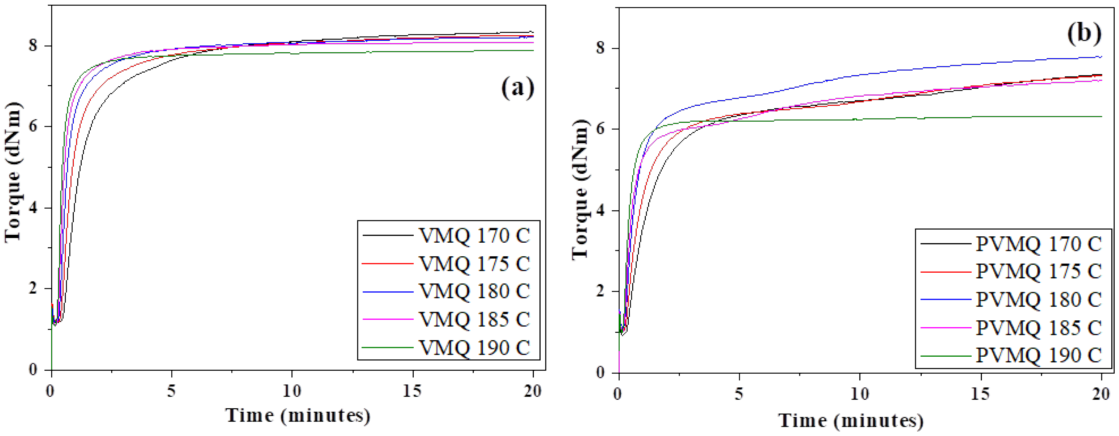

Figure 1. The cure curves of VMQ and PVMQ compounds.

The curing characteristic parameters of PVMQ and VMQ elastomers at different temperatures are presented in **Table 2** and **Table 3**, respectively.

The curing curves give valuable information into the curing behavior of elastomers. Tables 2 and 3 include parameters such as scorch time (t_{s2}), optimum cure time (t_{90}), and the cure rate index (CRI) which is a parameter that indicates the rate of the curing reaction. It is indicative of the curing performance and efficiency of the compounds. In addition, Δ_{torque}, which is the degree of cure is the difference between the minimum torque and the maximum torque. The torque difference in an MDR test is proposed to be theoretically linked to the shear dynamic modulus, and this modulus is indirectly associated with the total crosslink density in rubber compounds [16].

Table 2. Cure characteristic parameters of PVMQ.

Temperature	Cure Parameter	PVMQ	PVMQ-TAC	PVMQ-TAIC	PVMQ-ZDA	PVMQ-ZDMA
170° C	M_L *(dNm)*	0.92±0.02	0.95±0.05	0.96±0.03	1.21±0.02	1.08±0.08
	M_H *(dNm)*	7.35±0.98	12.19±1.22	12.48±1.01	11.07±0.87	11.23±0.99
	ts_2 *(min)*	0.79±0.02	0.77±0.03	0.68±0.03	0.44±0.04	0.65±0.34
	t_{90} *(min)*	10.03±0.99	3.65±0.31	3.60±0.38	3.00±0.02	3.90±0.74
	CRI(min^{-1})	10.8±0.9	34.7±2.6	34.3±4.3	39.1±2.8	30.8±1.6
175° C	M_L *(dNm)*	1.04±0.02	0.99±0.01	0.92±0.08	1.23±0.02	1.14±0.08
	M_H *(dNm)*	7.33±0.67	12.06±0.99	11.98±0.99	11.00±0.94	10.42±0.54
	ts_2 *(min)*	0.63±0.06	0.60±0.05	0.53±0.08	0.36±0.06	0.55±0.04
	t_{90} *(min)*	10.37±0.95	2.53±0.21	2.51±0.87	1.63±0.07	2.74±0.17
	CRI(min^{-1})	10.3±0.8	51.8±3.5	50.5±4.1	78.7±0.7	45.7±2.3
180° C	M_L *(dNm)*	1.11±0.02	0.99±0.04	0.98±0.08	1.10±0.65	1.19±0.21
	M_H *(dNm)*	7.79±0.79	12.41±0.95	12.18±1.00	10.40±0.09	10.61±0.84
	ts_2 *(min)*	0.48±0.03	0.46±0.02	0.43±0.03	0.31±0.02	0.43±0.03
	t_{90} *(min)*	7.94±0.98	1.81±0.32	1.77±0.87	1.19±0.09	1.86±0.06
	CRI(min^{-1})	13.4±1.2	74.1±6.5	74.6±6.9	113.6±13.2	69.9±4.3
185° C	M_L *(dNm)*	1.00±0.02	0.96±0.03	1.07±0.03	1.17±0.07	1.22±0.85
	M_H *(dNm)*	7.21±0.95	12.19±1.01	12.09±0.99	10.02±0.86	10.50±0.08
	ts_2 *(min)*	0.41±0.04	0.38±0.05	0.36±0.04	0.28±0.03	0.36±0.04
	t_{90} *(min)*	7.35±0.76	1.27±0.21	1.23±0.21	0.92±0.07	1.34±0.03
	CRI(min^{-1})	14.4±1.2	112.4±9.8	114.9±13.2	156.3±16.2	102.0±8.7
190° C	M_L *(dNm)*	1.00±0.02	1.04±0.01	0.94±0.07	1.30±0.03	1.18±0.05
	M_H *(dNm)*	6.33±0.36	12.32±0.58	11.27±0.99	10.42±0.42	9.76±0.96
	ts_2 *(min)*	0.35±0.01	0.33±0.02	0.31±0.02	0.24±0.03	0.32±0.02
	t_{90} *(min)*	1.11±0.32	0.96±0.08	0.91±0.07	0.70±0.04	1.01±0.01
	CRI(min^{-1})	131.6±11.4	158.7±13.2	166.7±14.6	217.4±15.1	144.9±9.5

Table 3. Cure characteristic parameters of VMQ.

Temperature	Cure Parameter	VMQ	VMQ-TAC	VMQ-TAIC	VMQ-ZDA	VMQ-ZDMA
170° C	M_L *(dNm)*	1.15±0.05	1.11±0.08	1.20±0.22	1.34±0.87	1.38±0.07
	M_H *(dNm)*	8.35±0.25	16.04±0.14	15.26±0.90	11.36±1.24	11.18±0.93
	ts_2 *(min)*	0.80±0.01	0.74±0.07	0.72±0.08	0.46±0.01	0.67±0.02
	t_{90} *(min)*	4.96±0.09	3.12±0.25	2.91±0.12	1.64±0.24	3.10±0.04
	CRI(min^{-1})	24.0±0.2	42.0±2.1	45.7±2.3	84.7±6.5	41.2±1.4
175° C	M_L *(dNm)*	1.17±0.11	1.14±0.04	1.18±0.41	1.39±0.08	1.32±0.08
	M_H *(dNm)*	8.26±0.32	15.70±1.02	15.02±0.51	11.01±0.99	10.75±0.87
	ts_2 *(min)*	0.62±0.02	0.57±0.03	0.55±0.02	0.39±0.01	0.54±0.04
	t_{90} *(min)*	3.68±0.08	2.15±0.32	1.96±0.11	1.14±0.02	2.22±0.87
	CRI(min^{-1})	32.7±1.9	63.3±5.8	70.9±2.3	133.3±9.8	59.5±3.8
180° C	M_L *(dNm)*	1.17±0.35	1.13±0.08	1.15±0.30	1.34±0.08	1.31±0.02
	M_H *(dNm)*	8.22±0.25	15.58±1.25	14.79±1.01	10.89±0.87	10.82±0.98
	ts_2 *(min)*	0.49±0.02	0.46±0.01	0.44±0.01	0.34±0.01	0.44±0.02
	t_{90} *(min)*	2.44±0.23	1.68±0.11	2.09±0.02	0.94±0.02	1.55±0.07
	CRI(min^{-1})	51.3±2.5	81.9±4.2	60.6±1.9	166.6±12.3	90.1±5.6
185° C	M_L *(dNm)*	1.12±0.11	1.12±0.09	1.09±0.01	1.30±0.03	1.28±0.08
	M_H *(dNm)*	8.10±0.90	15.40±1.42	14.52±0.98	10.55±0.57	10.58±0.98
	ts_2 *(min)*	0.40±0.01	0.39±0.02	0.39±0.01	0.30±0.01	0.36±0.04
	t_{90} *(min)*	1.74±0.02	1.21±0.08	1.09±0.02	0.70±0.03	1.13±0.01
	CRI(min^{-1})	74.6±3.6	121.9±8.9	142.8±7.5	250.0±18.7	129.9±8.9
190° C	M_L *(dNm)*	1.09±0.02	1.08±0.01	1.06±0.02	1.28±0.18	1.27±0.03
	M_H *(dNm)*	7.89±0.94	14.82±0.21	14.33±0.97	10.48±0.54	10.41±0.99
	ts_2 *(min)*	0.35±0.03	0.34±0.02	0.33±0.02	0.26±0.01	0.32±0.04
	t_{90} *(min)*	1.17±0.08	0.86±0.04	0.83±0.09	0.55±0.02	0.87±0.09
	CRI(min^{-1})	121.9±8.9	192.3±9.3	200±15.68	344.8±18.9	181.8±7.4

Analyzing the curing curves of these compounds, a noticeable trend emerged – the delta torque value rose with the use of co-agents. Moreover, this increase was more pronounced in blends containing Type-II co-agents compared to those with Type-I co-agents. Notably, the delta torque value of silicone elastomers also increased with the addition of accelerators. TAC and TAIC exhibited higher torque values than ZDA and ZDMA, attributed to the former's possession of an extra vinyl group [11]. Also, When the CRI values of each prepared compound were examined, it was seen that the cure reactions occurred faster with the use of co-agent compared to the reference compound which did not contain co-agents. Type I co-agents cause a faster curing reaction than Type 2 co-agents because Type I co-agents create radicals with lower molecular weight and higher reactivity [7]. In addition, ZDA, one of the Type I co-agents, has a higher CRI value than ZDMA because ZDMA forms a more stable 3° radical due to the methyl group in its structure [15]. Furthermore, the compound containing co-agents demonstrated the highest CRI value, while the blend without co-agents exhibited the lowest. Co-agents were identified to enhance the cure rate by mitigating reactions that could compete with cross-linking, such as transfer and rearrangement reactions, distinct from cross-linking reactions [12,13].

4.2 The Cure rate constant (k) and activation energy (Ea) according to the first-order kinetic model

The k values calculated with first-order curing kinetics using the data of the rheometer curves of the prepared silicone elastomer blends are given in **Table 3**.

Table 3. First-order cure rate constant (k) of silicone compounds.

Blends Code	**Cure Rate Constant. k (min^{-1})**				
	170 ^{o} C	***175 ^{o} C***	***180 ^{o} C***	***185 ^{o} C***	***190 ^{o} C***
VMQ	2.14±0.11	3.10±0.19	4.89±0.21	6.25±0.45	8.31±0.39
VMQ-TAC	1.65±0.07	2.54±0.11	3.48±0.15	5.08±0.32	7.28±0.40
VMQ-TAIC	1.89±0.10	2.95±0.11	4.14±0.22	5.65±0.27	7.81±0.35
VMQ-ZDA	3.10±0.14	4.52±0.21	6.29±0.27	8.79±0.36	11.22±0.58
VMQ-ZDMA	1.41±0.06	2.17±0.08	3.07±0.12	4.39±0.25	6.01±0.27
PVMQ	1.35±0.06	1.94±0.09	2.60±0.09	3.45±0.19	6.91±0.32
PVMQ-TAC	1.37±0.07	2.11±0.10	2.89±0.12	4.61±0.24	6.78±0.35
PVMQ-TAIC	1.53±0.08	2.21±0.09	3.39±0.17	5.11±0.25	7.13±0.29
PVMQ-ZDA	2.11±0.11	3.38±0.15	4.99±0.26	7.46±0.24	9.5±0.48
PVMQ-ZDMA	1.10±0.04	1.73±0.07	2.60±0.14	3.82±0.22	5.27±0.34

As presented in **Table 3**, it is clear that the rate constant (k) values increase with increasing temperatures in all compounds. Especially for VMQ-based elastomers, k values increased in elastomers containing TAC, TAIC, and ZDA compared to VMQ samples without coagent. At the same time, it was determined that the elastomer containing ZDMA had a lower k value compared to the k value of the reference compound without co-agent at all temperatures.

This observed decrease in k values for ZDMA can be attributed to the presence of a methyl group in its structure, which leads to steric hindrance as well as the formation of a more stable and less reactive tertiary radical. The highest k values in all compounds in the VMQ series were observed in ZDA, which is the Type I co-agent.

When elastomers prepared with PVMQ are examined, with the addition of the k-rate constant value TAC, TAIC, and ZDA, they have a higher reaction rate constant compared to the reference compound which has without co-agent. However, it is seen that the reaction rate decreases in the compound containing the Type I co-agent ZDMA. This trend can be attributed to the fact that ZDMA has a lower k value and forms a more stable 3° radical. However, it is interesting to observe that the k constant of samples prepared with VMQ is larger than those prepared with PVMQ. This difference can be attributed to the steric hindrance introduced by the phenyl group in the PVMQ structure.

Activation energies (Ea) of the elastomers were found by using the Arrhenius equation from the slope of the lines obtained by drawing ln k-1/T graphs from the k values found in the ln α - time graphs of the elastomer compounds. At high temperatures, reactants can become thermally unstable. This means that additional reactions such as dissociation or recombination of chemical species may occur. This may cause the reaction rate to be different than expected. The lnk vs. 1/T graphs drawn using the k values calculated with the first-order curing kinetics of Type I and Type II co-agent-containing elastomers of VMQ, and PVMQ elastomers are given in **Fig. 2** and **Fig. 3**, respectively.

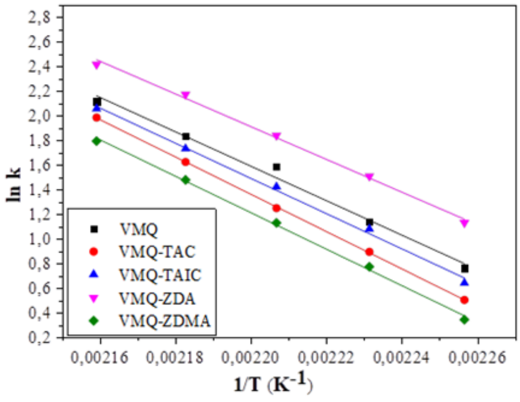

Figure 2. ln k versus (1/T) of VMQ silicone blends from Arrhenius equation at 170 ºC, 175 ºC, 180 ºC, 185 ºC and 190 ºC.

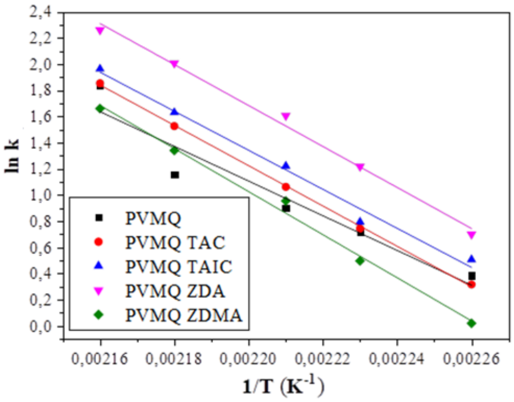

Figure 3. ln k versus (1/T) of PVMQ silicone blends. from Arrhenius equation at 170 °C, 175 °C, 180 °C, 185 °C, and 190 °C.

As shown in **Table 4** activation energy does not change significantly with co-agent addition. The main reason for this is that in first-order curing kinetics, not the entire curing curve is evaluated, but the area where the cure rate (α) of 0.25-0.45 occurs. However, the activation energies of PVMQ samples are higher than VMQ samples.

Table 4. The activation energy (Ea) of silicone blends for the first order.

Blends Code	**VMQ**	**VMQ-TAC**	**VMQ-TAIC**	**VMQ-ZDA**	**VMQ-ZDMA**	**PVMQ**	**PVMQ-TAC**	**PVMQ-TAIC**	**PVMQ-ZDA**	**PVMQ-ZDMA**
Ea (kj/mol)	116±8	126±3	119±5	111±6	123±4	129±3	136±2	134±9	130±8	135±8

4.3 The cure rate constant (k) and activation energy (Ea) according to nth order kinetic model

After completing the first-order vulcanization kinetic analysis, a subsequent examination of all curing curves was conducted using the nth-order kinetic model. This model, based on the methodology proposed by Isayev and Deng [14], involves a comprehensive analysis of the entire vulcanization curve from minimum torque (M_L) to maximum torque (M_H). The process includes the acquisition of α-time curves, representing the degree of cross-linking, and the application of Equation 5. Graphical interpretation using specialized software allows for the determination of the 'k' rate constant and 'n' reaction order values. The obtained 'k' values at different temperatures are then utilized in the Arrhenius equation to calculate the activation energy (Ea). This holistic approach provides valuable insights into the kinetics of the vulcanization reaction, offering information about the rate constant and reaction order dynamics across a range of temperatures.

According to **Equation 5**, the reaction rate constants of each blend at different temperatures "k" and the reaction rate degree "n" were determined by modeling using the Microcal Origin 7.5 software, the constants of the Deng–Isayev model were determined. **Fig. 4-a** and **4-b** present sample α-time curves for silicone elastomer compounds, with fitted curves obtained by solving these curves according to nth-order cure kinetics (depicted in red). The curves in **Fig. 4-a** correspond to VMQ blends, while those in **Fig. 4-b** represent PVMQ compound. The reaction rate constants "k" and the reaction rate "n" of the silicone compound are given in **Table 5**. As can be seen in **Table 5**, the k values of all silicon blends increased with the increase in temperature. The reason for this increase is the molecular mobility that increases with temperature. Radicals with lower stability play a crucial role in enhancing the cure rate, as they exhibit a higher propensity for reaction. The diminished rate constant values observed in Type II accelerators compared to their Type I counterparts can be attributed to the radical stability inherent in the phenyl ring within the structure of Type II co-agents. This phenomenon has been previously discussed in the literature. Additionally, the participation of TAC and TAIC in reactions situated outside the cross-linking process contributes to the delayed formation of effective cross-linking, thereby lowering the rate constant of Type II accelerators [**15**].

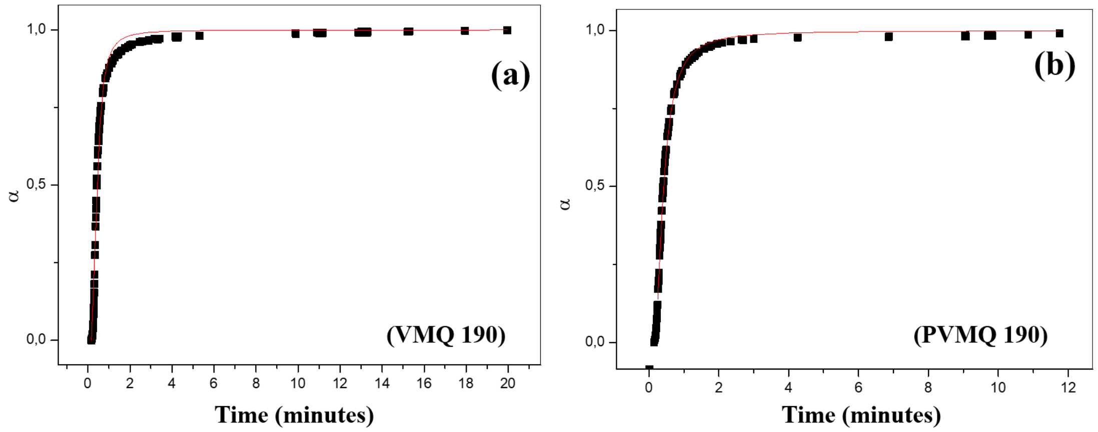

Figure 4. α-time curves of silicone elastomer blends and the curve fitted curve.

Notably, the structures of Type I accelerators, featuring acrylate and methacrylate, generate more reactive radicals, resulting in higher rate constant values when compared to their Type II counterparts. Further elucidating this trend, ZDMA exhibits lower rate constant values than ZDA, a phenomenon attributed to the formation of a more stable 3° radical due to the methyl group in its structure. As previously mentioned, the steric hindrance caused by this methyl group accounts for the observed disparity in rate constants.

Table 5. The cure rate constant (k)of silicone blends for **n**th order.

Blends Code	**Cure Rate Constant. k (min^{-1})**					**Reaction order. n**				
	170 °C	***175 °C***	***180 ° C***	***185 ° C***	***190 ° C***	***170°C***	***175°C***	***180 °C***	***185°C***	***190°C***
VMQ	2.8±0.2	3.6±0.2	4.9±0.3	6.7±0.7	9.0±0.6	0.8±0.0	0.8±0.0	0.8±0.0	0.8±0.1	0.8±0.1
VMQ-TAC	2.1±0.1	3.6±0.1	5.5±0.3	9.2±0.7	17.8±0.9	1.5±0.1	1.4±0.1	1.30±0.1	1.3±0.1	1.4±0.1
VMQ-TAIC	2.6±0.1	4.5±0.2	4.8±0.2	11.6±1.0	18.1±1.0	1.3±0.1	1.3±0.0	1.08±0.0	1.3±0.1	1.3±0.1
VMQ-ZDA	5.9±0.4	9.7±0.9	12.6±0.8	23.0±0.4	38.1±0.7	1.3±0.1	1.3±0.1	1.20±0.1	1.3±0.1	1.4±0.1
VMQ-ZDMA	2.2±0.1	3.5±0.2	6.1±0.5	9.0±0.9	15.6±0.4	1.3±0.1	1.2±0.1	1.4±0.1	1.3±0.1	1.3±0.1
PVMQ	1.9±0.1	2.2±0.2	2.6±0.1	3.2±0.2	9.1±0.16	0.6±0.1	0.5±0.1	0.6±0.0	0.6±0.0	0.8±0.1
PVMQ-TAC	1.9±0.1	3.2±0.2	4.9±0.3	8.3±0.8	13.4±0.5	1.3±0.1	1.2±0.1	1.3±0.1	1.2±0.1	1.3±0.1
PVMQ-TAIC	1.9±0.1	3.3±0.2	5.7±0.4	8.4±0.6	13.1±0.2	1.1±0.1	1.2±0.1	1.1±0.1	1.2±0.1	1.2±0.1
PVMQ-ZDA	2.9±0.3	5.2±0.4	8.2±0.6	10.9±0.6	17.5±0.5	1.0±0.4	1.1±0.1	1.1±0.1	1.0±0.1	1.2±0.0
PVMQ-ZDMA	1.6±0.1	2.7±0.1	4.5±0.2	7.3±0.8	10.3±0.4	1.3±0.1	1.1±0.1	1.3±0.1	1.2±0.1	1.1±0.1

The degree of reaction is associated with molecularity in simple chemical reactions [7]. In simpler terms, the degree of reaction is linked to the number of molecules that must collide at the appropriate geometry and energy for the chemical reaction to occur. As depicted in **Table 5**, the reaction degree of silicone elastomer without an accelerator is approximately 0.8. However, with the use of an accelerator, it is evident from the table that the 'n' value of the blends increases to an average of 1.2. This outcome signifies that accelerators are employed to enhance molecularity by altering the mechanism of the cross-linking reaction. The **n**th cure rate content and activation energy of silicone elastomers are further detailed in **Table 6**.

The k rate constant values of VMQ polymer show that the increase in k constant with temperature for TAC (from 2.1 min^{-1} to 17.8 min^{-1}) and TAIC (from 2.6 min^{-1} to 18.1 min^{-1}) is comparable. However, the results obtained for ZDA and ZDMA were found to be different. ZDA showed an increase in rate constant k from 5.9 min^{-1} to 38.1 min^{-1}, but ZDMA showed an increase from 2.2 min^{-1} to 15.6. min^{1}. As mentioned before, steric hindrance of ZDMA is assumed to be responsible of this difference. Nevertheless, the k rate constant values do not vary much with the accelerator when the PVMQ polymer.

Table 6. The activation energy (Ea) of silicone blends for nt **n**th h order.

Blends Code	**VMQ**	**VMQ-TAC**	**VMQ-TAIC**	**VMQ-ZDA**	**VMQ-ZDMA**	**PVMQ**	**PVMQ-TAC**	**PVMQ-TAIC**	**PVMQ-ZDA**	**PVMQ-ZDMA**
Ea (kj/mol)	217±8	281±6	308±6	308±9	255±8	171±8	254±4	258±6	233±7	225±8

It can be seen in **Table 5**; that the reaction rate increases with the increase of temperature for all samples. Reaction order and rate constants values are higher than first order because **nth** order calculation comprises all curves. The highest k-constant values were observed in samples containing ZDA. In comparison, the lowest k values were observed in samples containing ZDMA. As shown in Table 6, the calculated activation energies from the nth **nth** order are also higher than the first order. Activation energy values obtained from compounds containing Type II co-agents were found to be higher than the activation energy values obtained from compounds containing Type I co-agents.

It has been found that the reaction rate constants in the nth **nth** -order cure kinetics of most prepared elastomers are higher than those in the first-order cure kinetics. This indicates that co-agents increase the cure rate by mitigating transfer and rearrangement reactions that compete with cross-linking reactions. The PVMQ, and VMQ elastomers without co-agents, however, have lower rate constants because they do not exhibit this effect. For example, in Table 3, the reaction rate constants for VMQ and VMQ-ZDA elastomers at an optimal cure temperature of 180°C were found to be 4.9±0.3 min^{-1} and 6.3±0.3 min^{-1}, respectively, in first-order cure kinetics calculations. Additionally, the reaction rate constants for PVMQ and PVMQ-ZDA were 2.6±0.1 min^{-1} and 5.0±0.3 min^{-1}, respectively. In the **nth** -order cure kinetics calculations given in Table 5, the reaction rate constants at 180°C for the VMQ and VMQ-ZDA compounds were 4.9±0.3 min^{-1} for the VMQ compound without co-agents, showing no significant change, while the VMQ-ZDA compound had a rate constant of 12.6±0.8 min^{-1}, approximately two times higher. The reaction rate constant for PVMQ was 2.6±0.1 min^{-1}, and for PVMQ-ZDA it was found to be 8.2±0.6 min^{-1}, which is approximately 65% higher. The primary reason for this is that in the first-order cure kinetics, the cure state (α) values in the range of 0.25-0.40 are considered, whereas in the nth **nth** -order cure kinetics, the entire cure curve is included in the calculation. As previously stated, in the first-order cure kinetics, the reaction order (n) was assumed to be 1. However, in the nth **nth** -order cure kinetics, the reaction orders for VMQ and PVMQ without co-agents were found to be 0.80±0.01 and 0.70±0.01, respectively. Additionally, the reaction order values for all compounds containing co-agents were found to be approximately 1.2 on average. This indicates the positive effect of co-agent usage on cross-linking reactions. The activation energy values in Table 6 are higher than those given in Table 4 because the Ea values in Table 6 are obtained by evaluating the entire cure curves. The Ea values of PVMQ and VMQ compounds containing co-agents were found to be approximately 40% higher than those of the compounds without co-agents. The Δtorque value, which is a measure of cross-link density, increased by approximately 61% with the use of co-agents.

Comparative activation energy bar graphs of silicone elastomer blends found using 1st and nth-order curing kinetic models are given in **Fig. 5**.

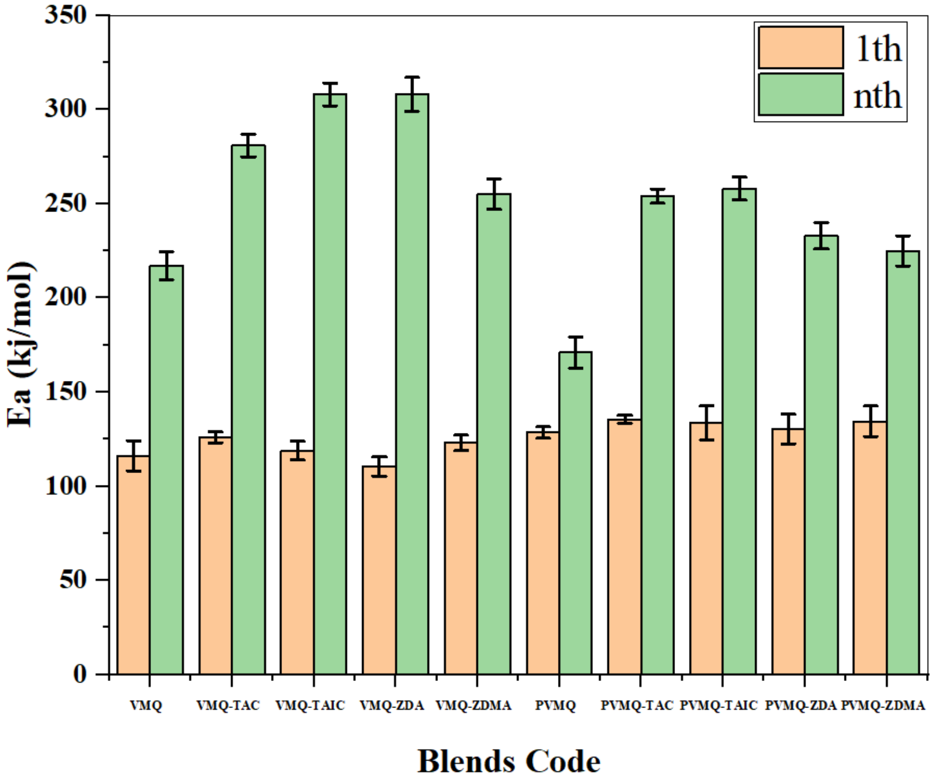

Figure 5. Comparative activation energy bar graphs of silicone elastomer blends.

As can be seen in **Fig. 5**, the activation energies found at n order were higher than the activation energies found at 1 order. This is because the 0.25/0.40 range of the α (degree of crosslinking value) is used in calculations from 1st , while the entire cure curve is used in nth cure kinetics.

5. Conclusion

It has been observed that the use of co-agents increased the curing reactions and efficiency of the state of cure value in silicone elastomers cured with peroxide. Because co-agents prevent reactions other than cross-linking, such as transfer and rearrangement, that compete with the cross-linking reaction. It was observed that the activation energy values obtained with the nth **nth** kinetic model were higher than the values obtained with the first-order kinetic model, since they were the values obtained by using the cure reaction or the entire cure curve. For this reason, it is necessary to use the nth kinetic model to find the activation energy. When the 1st degree activation energies are examined, it is seen that the activation energies obtained for PVMQ are higher than the activation energies obtained for VMQ. This is thought to be due to the steric hindrance of the phenyl group in the structure of the PVMQ elastomer. When the n^{th} activation energies are examined, it is seen that the activation energies obtained for VMQ are higher than the activation energies obtained for PVMQ. This is because VMQ has a higher degree of reactivity, so more molecules must cross the energy barrier for the cross-linking reaction. While the use of co-agents has been shown to affect the curing behavior and rheology of silicone elastomers, it is clear that the elastomer components and type of manufacturing process will affect the performance of the final product.

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