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Research Article

ACCUMULATION OF RECYCLED WASTE TYRE WITHIN DIFFERENT RUBBERS: A KINETIC STUDY

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ABSTRACT

Waste tyres around the world are increased severely in the last century. The accumulation of waste tyre within poly dimethyl siloxane (silicone) and ethylene–propylene–diene monomer rubber (EPDM) rubbers were examined. The moving die rheometer were used for the kinetic analysis of the samples. The MDR results showed that the silicone sample that has 5% waste tyre content has the better rheological results. Kinetic study examination of both EPDM and silicone rubber were done according to non-linear curve fitting model. The fitting model were conducted as Kamal-Sourour Model. In addition, the fitted model was corrected with fourth order Runge-Kutta model. Moreover, activation energy of both samples were calculated from Arrhenius plot for both rubbers. For EPDM case, it was found 99 kJ/mole and 66 kJ/mole for m^{th} order and n^{th} order, respectively. For silicone case, it was found to 87 kJ/mole for n^{th} order. The results were hearting enough to pursue the accumulation of waste tyre on other rubbers.
Keywords: EPDM, silicone, waste tyre, vulcanization, kinetic.

1. INTRODUCTION

The automotive technology has improved profoundly in the last century. The parts used in automotive industry are changed severely. Therefore, the wastes of this industry are also changed in this regard. The less changed part of the automotive industry is tyres [1]. Unfortunately, the tyres can degrade over hundreds of years. This can lead to massive tyre dumps all around the world. The waste tyre could a good waste for rubber industry. One of the main usage of the tyre wastes is combustion material. Unfortunately, this can lead to environmental problems in the long periods [2].

The amounts of waste tyre has shown an increase temporarily which is around 325 million tyres per year [3]. A temporary solution to this problem was storage. However, this is not the appropriate way to solve the problem. Recently, a massive event in Castilla-La Mancha end-of-life tyre site forced 9000 people to be evacuated from their homes in May of 2016 [4]. The tyre dump site contained around 100,000 tons of end-of-life tyres and the fires was continuing for

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several days. This devastating event should unveil the efforts taken upon to a solution of waste tyre management.

In the last decade, a number of studies have been done to use the massive amount of waste tyres around the globe. There are processes that had been suggested to decrease the effect of increasing amount of waste tyre [5], [6]. One of the accumulation ways is rubber compounding. This way, rubber companies can reach the waste tyres easily. Moreover, the blending of rubbers would be better than other materials. Polymer miscibility is an important point in preparing rubber composites. The waste tyre contains SBR and NR. It is well known that silicone, EPDM, SBR and NR have close Hildebrand solubility constants [7].

Ethylene–propylene–diene monomer rubber (EPDM rubber) is a widely used synthetic rubber with a very loading capacity. EPDM has very unique properties like high temperature resistance and good electric insulator. It is clear that EPDM rubber is extensively used for its excellent properties and economic price [8]. Silicone rubber, with the repeat structure of -SiRR′-O-, is one of the inorganic elastomers. Silicone rubber has a variety of unique properties such as dielectric capacity, chemical resistance, UV and mechanical stabilities [9].

There are limited use of waste tyre within rubber blends in the literature. Moreover, there is no study for kinetic parameters and silicone rubber. Formela et al. studied the mechanical and morphology properties of butyl rubber (BR) with ground tire rubber (GTR). Different range of GTR was studied and the best resulting sample was determined as 30 phr GTR content. The microstructure of optimum sample has a strong interaction with filler and rubber matrix [10]. Lu et al. studied GTR with different thermoplastic vulcanizates blends. The results showed that the particle size has a dramatic effect for properties all thermoplastic blends. Moreover, thermal analysis showed that the addition of GTR increase the thermal stability [11]. Datta et al. studied recycled polyethylene/ground tyre rubber/thermoplastic poly(ester-urethane) blends. The results showed that materials break at interface between filler and rubber matrix for static tensile test. The prepared polymer blends show best results for 40% GTR content in mechanical and abrasion tests [12]. Yasin et al studied the properties of styrene butadiene rubber containing GTR. The radiation cured samples showed better thermal stability compared to sulphur curing. Optimum GTR content were found to be 10 phr according to mechanical and swelling data [13].

In this study, waste tyre particles were added into the matrixes of EPDM and Silicone Rubber and the vulcanization process were analysed with kinetic parameters. Moving die rheometer were used for kinetic analysis of the compounds. The kinetic data were fitted with non-linear curve fitting method. Moreover, the fitted data were compared with the experimental data to understand the kinetic values. Activation energy of the vulcanization process for EPDM and Silicone rubbers were calculated from the obtained kinetic values.

2. MATERIAL & METHOD

Waste tyre was kindly gifted from İzmit Pirelli factory. EPDM/waste tyre composite were prepared with KELTAN 9650Q, carbon black (N330), zinc oxide, mineral oil, stearic acid, TAC/S 50, and Perkadox 14–40. The ground waste tyre used in the experiment contains natural rubber (NR) and styrene butadiene rubber (SBR), and has 30 phr carbon black content. The waste tyre content was optimised at 15% in a different study [3]. All chemicals were used as received.
Silicone rubber were prepared with Polydimethyl siloxane, crosslinker cc6 and the same waste tyre used in the EPDM making. All chemicals list is given in Table 1.

The materials were placed to a kneader type mixer and the materials were mixed at 50 rpm and 65 °C. Then, the prepared composite transferred to two-roll mill and the non-vulcanized rubber was prepared with a thickness of 2 mm. The prepared rubbers were cured in a MonTech 3000 basic model MDR. The MDR test results were evaluated in MonControl™ software.

Table 1. Rubber formulates us ed in the experiments

Materials	Function	(phr)
KELTAN 9650Q	Synthetic Polymer	100
Carbon Black	Filler	30
Zinc Oxide	Activator	1.5
Mineral Oil	Lubricant	32
Stearic Acid	Activator	1
TAC 50	Coagent	1
Perkadox 14-40	Vulcanization Agent	5
Waste Tyre	Filler	30 (15%)
PDMSQ	Synthetic Polymer	100
Crosslinker CC6	Vulcanization Agent	3
Waste Tyre	Filler	5.5 (5%)

Reaction degree values was calculate to obtain the kinetic parameters and the activation energy, reaction degree (α) is defined as follows [14]:

$$\alpha = M_t - M_L / M_H - M_L \quad (1)$$

Where M_H and M_L defines the maximum and minimum torque and M_t defines the torque at a given time.

Kamal-Sourour model is a used for kinetic model for the curing process of rubbers. This model is given in Equation 2 where α defines reaction degree, n and m define the reaction order [15].

$$d\alpha/dt = (k_1 + k_2 * \alpha^m) * (1 - \alpha)^n \quad (2)$$

k_1 is related to the catalytic n^{th} order reaction rate constant and k_2 is related to the autocatalytic m^{th} order reaction rate constant. k_1 and k_2 could be calculated using the Arrhenius Equation, given in Equation 3, where A, R, T and E_a are represent the Arrhenius coefficients, universal gas constant, temperature and activation energy, respectively.

$$k = A * \exp(-\frac{E_a}{RT}) \quad (3)$$

The reaction orders higher than 2 is uncommon for silicone vulcanization, therefore, silicone data were calculated as the modified Kamal-Sourour model [16].

$$d\alpha/dt = k\alpha^{2-n}(1 - \alpha)^n \quad (4)$$

3. RESULTS & DISCUSSION

3.1. EPDM/Waste Tyre Samples Kinetic Test Results

MDR test results of EPDM/Waste Tyre samples are given in Figure 1. It was seen that at 170 °C, the EPDM sample could not finished the vulcanization reaction. Even though the lowest t_{90} value is belong to the sample cured at 200 °C, the low value of scorch time makes this sample unfavourable in the regards of curing reaction. Moreover, due to quick crosslinking occurred within matrix of the sample cured at 200 °C, uncured locations were occurred that leads to decrement of M_H value. This results showed that due to high M_H value and low scorch time, the sample cured at 180 °C gives the best results.

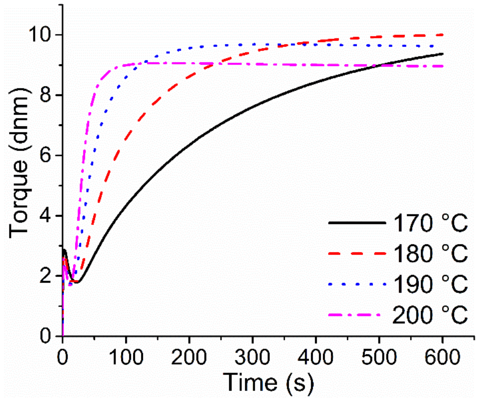

Figure 1. MDR test results of EPDM/Waste Tyre Samples

The cure kinetic study for EPDM/Waste Tyre samples were carried out using MDR data and obtained results are given in Figure 2. In addition, the obtained results for the vulcanization parameters are given in Table 2. As the vulcanization temperature increased, the maximum dα/dt value increased, which means that vulcanization reaction rate is also increased, can be seen in Figure 2.

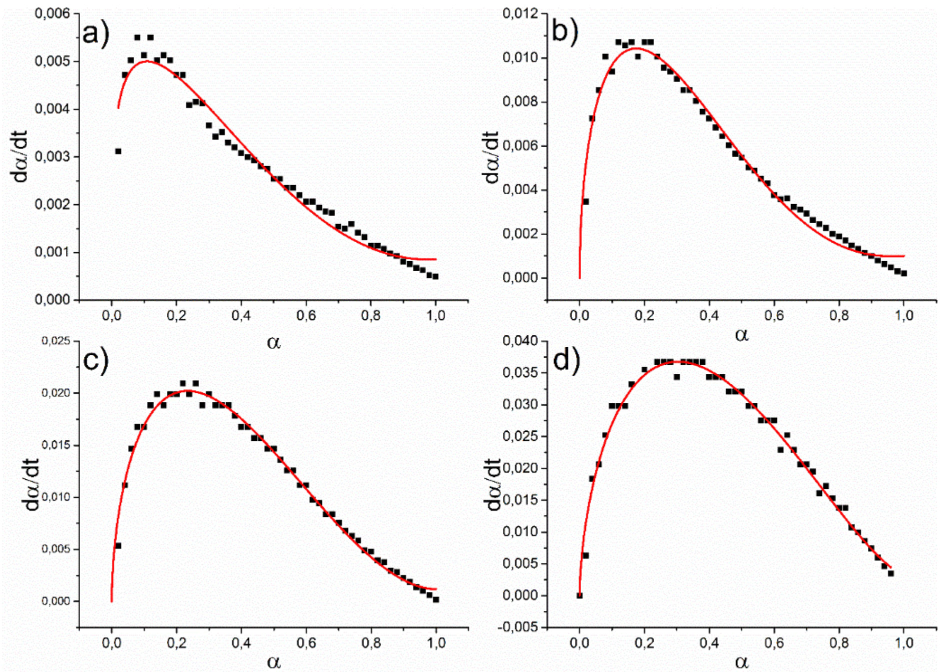

Figure 2. Experimental and fitted data for EPDM/Waste Tyre at (a) 170 ˚C (b) 180 ˚C (c) 190 ˚C (d) 200 ˚C (Black dot: Experimental data; Red curve: Fitted data)

The kinetic values of EPDM/Waste Tyre composite were calculated using Origin™ Software via Equation 2. The calculated parameters are given in Table 2. The values of m increased with increasing of cure temperature, whereas the values of n decreased with the increasing of cure temperature. These results show that the autocatalytic reactions are dominant. The reaction rate constants are increased with the increasing cure temperature as expected. The bigger increase in k_2 compared to k_1 also proves the autocatalytic reactions. These results were in line with MDR analysis as expected for which the best resulting sample is the sample cured at 180 ˚*C* in terms of fitting with Kamal-Sourour Model.

Table 2. Kinetic parameters of Kemal-Sourour Model of EPDM/Waste Tyre Samples

Cure Temperature	**n**	**m**	$\mathbf{k_1}$	$\mathbf{k_2}$
170 ˚*C*	2.16	0.24	0.0008	0.0098
180 ˚*C*	2.51	0.51	0.0010	0.0396
190 ˚*C*	1.86	0.55	0.0012	0.0722
200 ˚*C*	1.43	0.59	0.0033	0.1204

To compare the calculated cure reaction constants in Equation 2, the parameters also calculated with numerical solution using the 4th order Runge & Kutta method. The resulting data are presented in Figure 3. This figure shows that the numerical calculation could be used in all temperatures range which was used in the experiment.

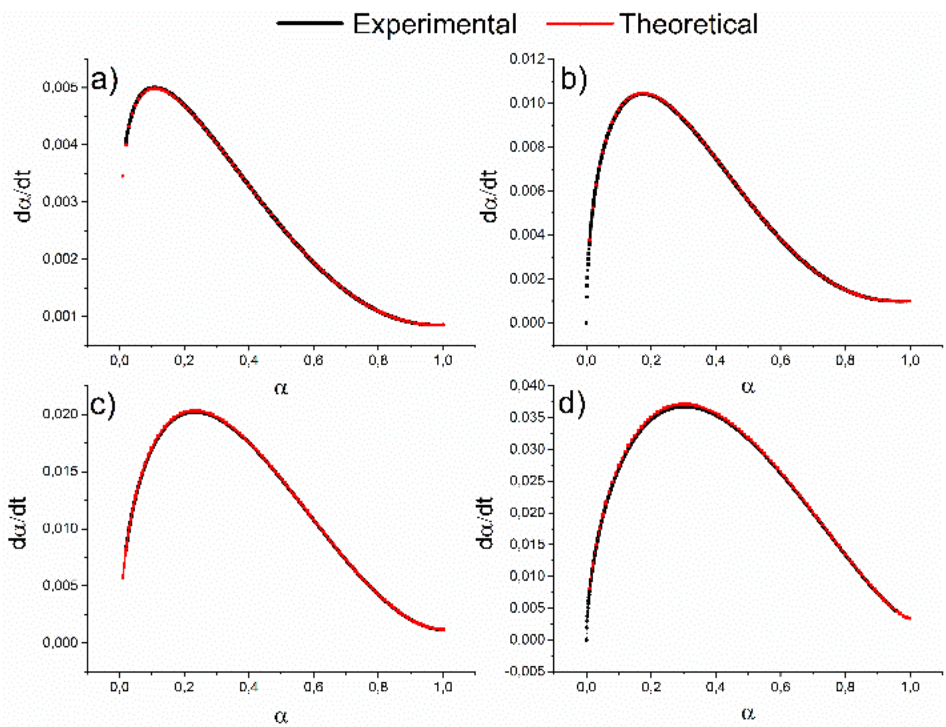

Figure 3. Comparison of experimental data and numerical solution for EPDM at (a) 170 ˚C (b) 180 ˚C (c) 190 ˚C (d) 200 ˚C

Figure 4 shows the activation energy calculation and regression values of EPDM/Waste tyre samples. The activation energy data calculated as 99 kJ/mole for m-th order and 66 kJ/mole for n^{th} order. This results were in line with theoretical calculations.

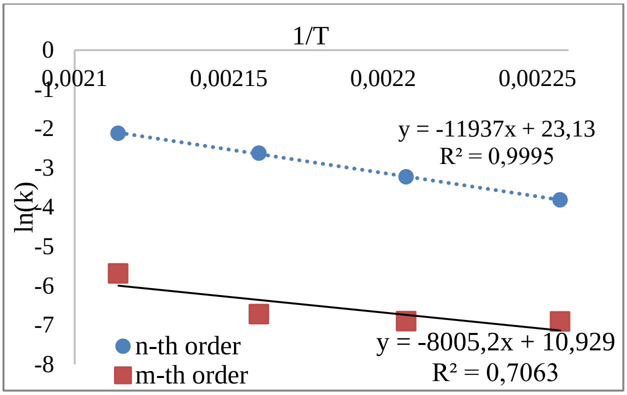

Figure 4. Activation energy calculation and regression values of EPDM/Waste Tyre Samples

3.2. Silicone/Waste Tyre Samples Kinetic Test Results

MDR test results of Silicone/Waste Tyre samples are given in Figure 4. It was seen that sample that has 5% WT has the lowest t_{90} value. Moreover, scorch time of all samples is adequate and similar. Therefore, it can be thought that waste tyre could be used as a filler for silicone. To kinetic calculations, EPDM with 5% WT was used because it gives the best results. The increase in cure temperature increased the torque values whereas it decreased the scorch time. It seems that curing temperatures above 180 ˚C diminishes the vulcanization reaction which can be seen with the torque curves with overcure at 190 and 200 ˚C.

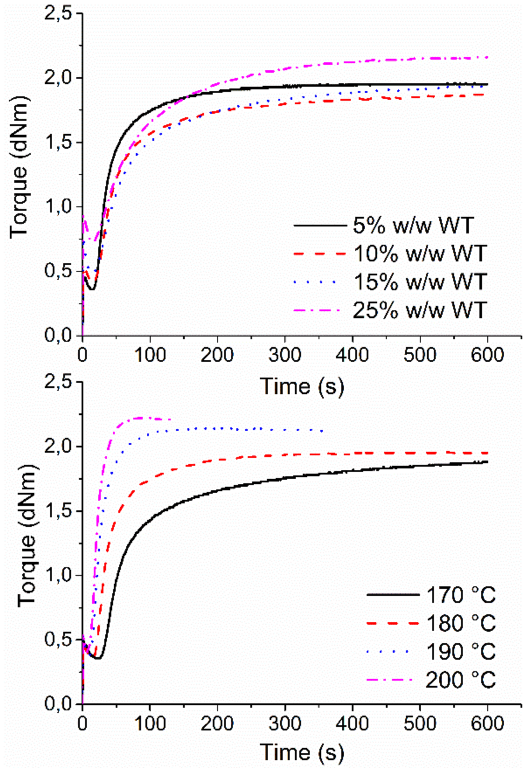

Figure 5. Torque graphs of Silicone/Waste Tyre composites

Table 3 shows the MDR test results of Silicone/Waste Tyre samples, it can be seen from the table that the sample that has 5% WT content has the highest CRI value. Even though the sample that cured at 200 °C has the lowest t_{90} value, low scorch time would limit its mould motions. The results showed that the sample that has 5% WT and cured at 180 °C is the best resulting sample.

Table 3. MDR test results of Silicone/Waste Tyre samples

Samples	M_L	M_H	t_{s2}	t_{90}	CRI
Silicone with 5% WT	0,36	1,96	0,44	2,00	82,16
Silicone with 10% WT	0,41	1,88	1,07	3,09	74,43
Silicone with 15% WT	0,49	1,94	1,37	4,06	71,24
Silicone with 25% WT	0,73	2,16	1,56	4,05	69,55
Silicone at 170 °C	0,36	1,88	1,25	4,24	65,43
Silicone at 180 °C	0,36	1,96	0,44	2,00	78,56
Silicone at 190 °C	0,38	2,14	0,27	0,59	56,51
Silicone at 200 °C	0,40	2,22	0,22	0,41	54,88

The cure kinetic study for Silicone/Waste Tyre samples were carried out using MDR data and obtained results are given in Figure 6. In addition, the obtained results for the vulcanization parameters are summarized in Table 4. The increase of the curing temperature, increased the maximum dα/dt value which means that the reaction rate of auto acceleration increased as shown in Figure 6. This results also in line with MDR torque results.

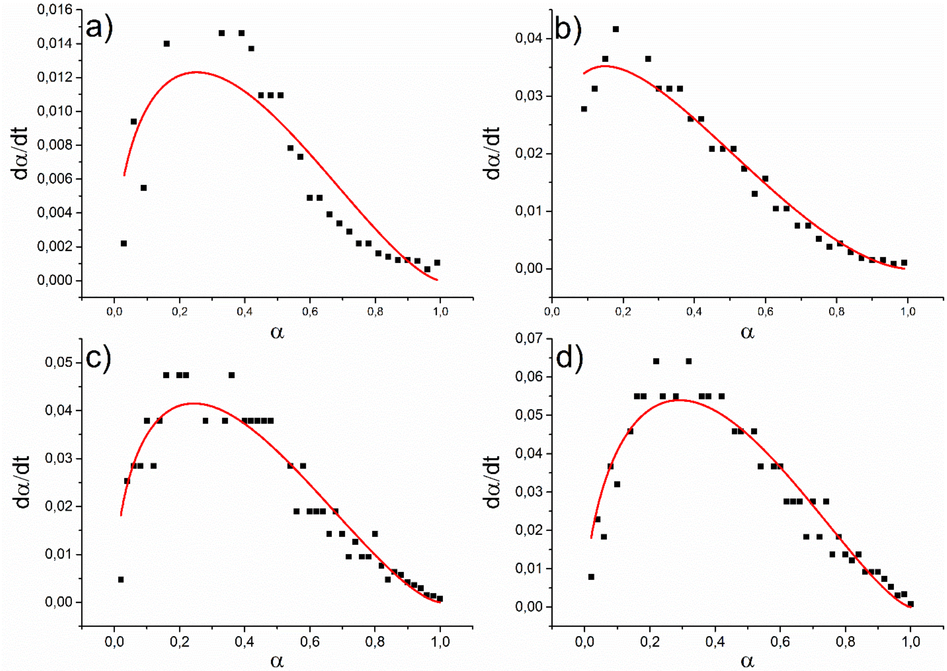

Figure 6. Experimental and fitted data for Silicone/Waste Tyre at (a) 170 ˚C (b) 180 ˚C (c) 190 ˚C (d) 200 ˚C (Black dot: Experimental data; Red curve: Fitted data)

Table 4. Kinetic parameters of Kemal-Sourour Model of Silicone/Waste Tyre Samples

Cure Temperature	n	k_1
170 ˚C	1.49	0.038
180 ˚C	1.7	0.086
190 ˚C	1.51	0.012
200 ˚C	1.42	0.018

To compare the calculated cure reaction constants in Equation 4, the parameters also calculated with numerical solution using the 4th order Runge & Kutta method. The resulting data are presented in Figure 7. This showed that the suggested model nearly covers the whole curing reaction. The reaction order of sample cured at 200 °C is the lowest along all samples. Even though it is the best fitted curve, highest reaction degree is preferred. Therefore, the fitting data is in line with kinetic study.

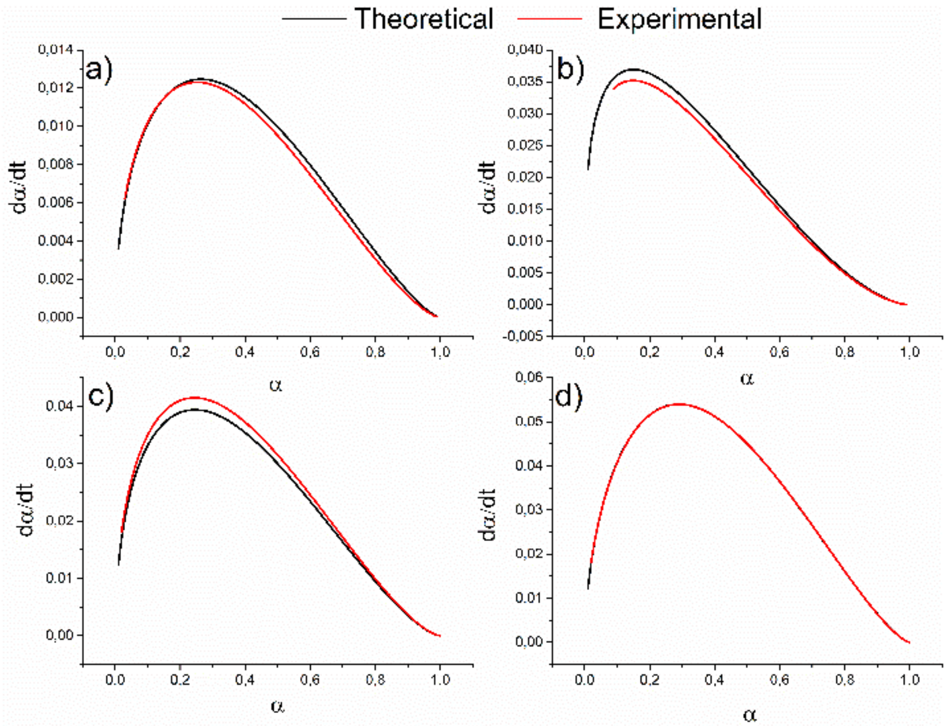

Figure 7. Comparison of experimental data and numerical solution for EPDM at (a) 170 ˚C (b) 180 ˚C (c) 190 ˚C (d) 200 ˚C

Figure 8 shows the activation energy calculation and regression values of Silicone/Waste tyre samples. The activation energy data calculated as 87 kJ/mole for nth order reaction system. This results were in line with theoretical calculations.

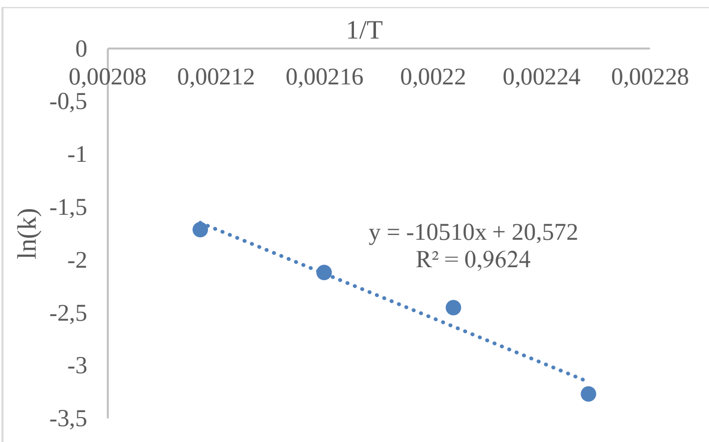

Figure 8. Activation energy calculation and regression values of Silicone/Waste Tyre Samples

4. CONCLUSION

The rubber vulcanization could be affected from the cure kinetics. Moreover, a good kinetic evaluation leads to more economic and fasten production. Waste tyre addition to rubbers could diminished a waste problem, but it should be harmonious to not affect the vulcanization process. To understand this case, non-linear curve fitting was applied. Moreover, the fitting was controlled with fourth order Runge-Kutta method. The results showed that the EPDM showed autocatalytic reactions rather than non-autocatalytic reactions. The bigger increase in k_2 compared to k_1 also proves the autocatalytic reactions. For silicone case, firstly content of the rubber compound was selected and the selected content were evaluated via kinetically. The results showed that curing temperature above 180 ˚C diminished the reaction rate. The activation energy of the samples was calculated. For EPDM case, it was found 99 kJ/mole and 66 kJ/mole for m^{th} order and n^{th} order, respectively. For silicone case, it was found to 87 kJ/mole for n^{th} order. The activation energy results were in line with the composite literature.

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