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Kinetics of Powder-Free Laboratory Examination Gloves at 323°C and 408°C by Thermogravimetric Analysis

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

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ABSTRACT

At two isotherm temperatures, 323°C and 408°C, and two thermal scans the kinetics of thermolysis of powder-free laboratory safety gloves (LG) was studied by thermogravimetric analysis. Three methods was used to determine the fraction of reactants and hence the related kinetics parameters. The results of the study indicated that the kinetics parameters depended on the method of calculation the fraction of reactants. The experimental data at the isothermal temperature 323°C fitted in zeroth, first and second order reaction, and the kinetics of pyrolysis at the isotherm temperature 408°C fitted into first order and second order, depending on the definition of the fraction of reactants. Moreover, the reiteration method was used to find the best value of n and k for thermolysis at both temperatures; the best order for the thermolysis found to be 1.78, and 1.93 at 323 and 408°C, respectively. The activation energy of thermalizes was estimated by two methods: thermal scans, and the plot of k values obtained from five isotherms versus the invers of corresponding temperatures. The value of activation energy for the process at lower temperatures was near to activation energy corresponds to evaporation of volatiles, and at higher temperatures the activation energy was below constituents' chemical bond energies but it was higher than the reported activation energy for decomposition of polymethyl methacrylate and it was lower than activation energy for decomposition of rubber in tires.

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1. INTRODUCTION

1.1 Waste Plastics and Related Problems

The kinetics of decomposition of waste plastics are of interest from different points of view including evolution of harmful substances during fires or waste incineration, recovery of chemical raw materials from waste plastics and design of a practical recycling procedures. Neoprene or polychloroprene ($-\text{CH}_2-\text{CCl}=\text{CH}-\text{CH}_2-$)_n that is the subject of this study, is a member of family of synthetic rubbers that are produced by free-radical polymerization of 2-chlorobutadiene ($\text{CH}_2=\text{CCl}-\text{CH}=\text{CH}_2$) [1]. Neoprene exhibits good chemical stability, and maintains flexibility over a wide temperature range. It is used in a wide variety of applications, such as gloves, laptop sleeves, orthopedic braces (wrist, knee, etc.), electrical insulation, liquid and sheet applied elastomeric membranes or flashings, and automotive fan belts [2]. The waste plastics contrary to the other household waste are not consumed by micro-organism in landfill, water, and surface. Their incineration in landfills neither contribute to energy gain nor to environmental benefits [3]. Therefore, energy recovery by step-by-step thermolysis [4] which converts waste to the valuable petrochemicals must be considered [5,6] as an alternate treatment.

To simulate the condition of waste plastics thermolysis, researchers focused the thermal degradation of plastic blends such as polystyrene (PS) mixtures with other materials and their mutual interactions [7-9]. The decomposition of pure, freshly prepared polymeric materials, has been of interests to scientists since the applied knowledge of polymeric materials gained relevance [10-12]. The decomposition kinetics of poly ethylene (PE) [13,5] and the mechanism of decomposition have been studied by many researchers [14,15]. Some widely used polymeric materials such as poly(methyl methacrylate) (PMMA), upon heating, decomposed to original monomers [16] likewise PS to styrene [17-19]. However, poly(vinyl chloride) (PVC), and neoprene resins thermolysis [20] took a different route than the above mentioned polymers. These polymers decomposed to hydrogen chloride and other fragments upon heating. Thus the World Health Organization (WHO) is opposed to land filling or incineration of these wastes. Processing techniques such as energy recovery including

plastics-derived fuel have been proven successful [21-25]; however, polycyclic aromatic hydrocarbons (PAHs) evolved from rubber resins [26] and hydrogen chloride from wastes based on PVC [27,28] and neoprene [29] resins in the combustion process are obstacles in the application.

It is noteworthy that most of the well documented investigations were done on pure polymers with known molar mass distribution or clean materials provided directly by manufacturers [30,31] on a micro-scale analysis. The researchers were presented several detailed kinetic models describing the polymer degradation [32-36]. These kinetics models can be useful in the study and analysis of the role of mixing in the thermal degradation of polymer blends. Therefore, the knowledge of decomposition of waste plastics and their condition and the product of decomposition remains of interests [37]. Study on kinetics properties of pyrolysis of medical wastes including absorbent cotton, medical respirator, bamboo sticks and cotton gauges, packaging boxes, capsule plates and transfusion tubes are paving the road for recycling medical wastes [38].

Based on our previous experiments [39,40] and the results reported by other researchers, one possible process for recovering valuable chemical and petrochemical products from chlorine-resin based waste plastics is the stepwise thermal degradation. In theory, this process allows step-by-step separation of the different product fractions generated by degradation of the waste plastics blend [41]. In this paper we report the effect of temperature on kinetics of thermolysis of powder-free latex gloves (LG), the ones made of chloroprene as rubber ingredient. The LG was thermalized in five consecutive steps: a fast increase of temperature to initial decomposition temperature (323°C), followed with a 90 min isothermal step at this temperature; sequenced with another linear thermal scan from 323°C to 408°C, succeeding by another isotherm at the same temperature for 30 min. The last thermal scan to 853° led to full degradation of LG.

1.2 The Theory of Kinetics of Pyrolysis

The rate of a chemical reaction, including pyrolysis, is a function of temperature, pressure,

and the concentration of the various species in the reaction. Also, catalyst and inhibitors effects the rate of a reaction, but they may not appear in the overall reaction. For a simple gas-phase reaction:



$$\text{Rate} = r = -\frac{dw}{adt} = kW^n \quad (2)$$

where w is the activity of reactant A at time t , " a " is the stoichiometric coefficient of the balanced chemical reaction equation, n is the order of reaction at the slowest step, and k is the rate constant of the reaction. In a multiple phase reaction where solids, liquids, and-gases are presented as reactants and products such as thermolysis of LG the rate of reaction usually is expressed in terms of the fractional conversion of reactants, α . There are several manner to evaluate the value of α . In this work the kinetic parameters of LG was evaluated with three methods as following:

1. The fractional conversion of reactants α defined in terms of the actual, final, and initial mass of sample, w , w_f , and w_i , in each step of pyrolysis, respectively:

$$\alpha = \frac{w_i - w}{w_i - w_f} \quad (3A)$$

The rate of conversion, $d\alpha/dt$, in relation to the amount of reactants, $(1-\alpha)$, can be expressed as:

$$\text{Rate} = r = \frac{d\alpha}{dt} = -\frac{d(1-\alpha)}{dt} = ak(1-\alpha)^n \quad (4A)$$

Rearranging Eq (4) results:

$$\frac{d\alpha}{(1-\alpha)^n} = -akdt \quad (5A)$$

Integration of Eq (5) for the values of $n = 0, 1,$ and 2 results:

$$n \neq 1, (1-\alpha)^{1-n} = -(1-n)akt + c \quad (6A)$$

$$n = 0, (1-\alpha) = -akt + (1-\alpha)_0 \quad (7A)$$

$$n = 1, \text{Ln}(1-\alpha) = -akt + \text{Ln}(1-\alpha)_0 \quad (8A)$$

$$n = 2, (1-\alpha)^{-1} = akt + (1-\alpha)_0^{-1} \quad (9A)$$

2. The fractional conversion of reactants α' defined in terms of the actual, final (mass at the end of thermolysis process), and

initial (mass of sample at very begging of thermolysis), w , w_f , and w_i , respectively.

$$\alpha' = \frac{w_i - w}{w_i - w_f} \quad (3B)$$

The kinetics equations remain similar as Eq(4A) to Eq(9A) as followings:

$$\text{Rate} = r = \frac{d\alpha'}{dt} = -\frac{d(1-\alpha')}{dt} = ak(1-\alpha')^n \quad (4B)$$

Rearranging Eq (4) results:

$$\frac{d\alpha'}{(1-\alpha')^n} = -akdt \quad (5B)$$

Integration of Eq (5B) for the values of $n = 0, 1,$ and 2 results:

$$n \neq 1, (1-\alpha')^{1-n} = -(1-n)akt + c \quad (6B)$$

$$n = 0, (1-\alpha') = -akt + (1-\alpha')_0 \quad (7B)$$

$$n = 1, \text{Ln}(1-\alpha') = -akt + \text{Ln}(1-\alpha')_0 \quad (8B)$$

$$n = 2, (1-\alpha')^{-1} = akt + (1-\alpha')_0^{-1} \quad (9B)$$

3. The fractional conversion of reactants α'' defined in terms of the actual, and initial mass of sample, w , and w_i , respectively:

$$\alpha'' = \frac{w}{w_i} \quad (3C)$$

The rate of conversion, $d(1-\alpha'')/dt$, in relation to the fraction of reactants, α'' , can be expressed as:

$$\text{Rate} = r = -\frac{d\alpha''}{dt} = ak(\alpha'')^n \quad (4C)$$

Rearranging Eq (4C) results:

$$\frac{d\alpha''}{(\alpha'')^n} = -akdt \quad (5C)$$

Integration of Eq (5C) for the values of $n = 0, 1,$ and 2 results:

$$n \neq 1, \alpha''^{(1-n)} = -(1-n)akt + \quad (6C)$$

$$n = 0, \alpha'' = -akt + \alpha''_0 \quad (7C)$$

$$n = 1, \text{Ln}\alpha'' = -akt + \text{Ln}\alpha''_0 \quad (8C)$$

$$n = 2, (\alpha'')^{-1} = akt + (\alpha''_0)^{-1} \quad (9C)$$

2. MATERIALS, INSTRUMENTATION AND METHODS

A Perkin-Elmer (USA) thermogravimetric analyzer (TGA-7) was used to perform the step-by-step pyrolysis of LGs at two isothermal and two scans in between the isotherms. The atmosphere was fluxed with argon (flow rate of 10 mL min⁻¹). The heating rate in all dynamic experiments was kept at the maximum capacity of the TGA instrument, 200°C min⁻¹. The initial sample weight was 6.319 mg; however, in calculations, the weight was normalized to weight percentage of the samples. The LG was thermolysis in six steps: first, the sample was rapidly heated up to 323°C (The calculated average heating rate in this step was 79.8°C/min.) and then the temperature was kept constant for 90 min at 323°C (Fig. 1). In succession, the temperature was rapidly increased (The calculated average heating rate in this step was 21.1°C/min.) to the second isothermal step (408°C) and maintained there for 30 min; successively, the temperature was rapidly increased to 853°C which led to the complete degradation of the organic substances. The fast temperature ramps to the isothermal conditions did not show more than 1°C overheating.

The experimental data, such as time (min), sample temperature (°C), weight percentage, and derivative of weight loss over time (dw/dt), were downloaded from a Pyris program to Microsoft Office for calculation, graphing, and word processing.

3. RESULTS AND DISCUSSION

3.1 Thermograms Analysis

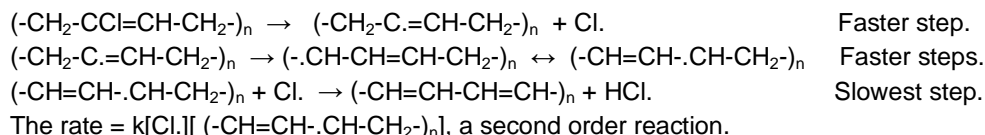
Table 1 summarizes the main points of thermolysis of the LG. Thermal scan from room temperature to 323°C caused about 2.67% of LG weight loss (Fig. 1, Table 1). During 87.32 min at

323°C about 21.95% of the LG was volatilized. A pure sample of neoprene, (-CH₂-CCl=CH-CH₂-)_n, contains 40.08% Cl and 41.21% HCl. In the case of step-by-step decomposition, if all primary volatiles would be HCl, then a weight loss of 58.79% was expected. The actual weight loss at the end of 91 min was 75.35% which is 15.4% less than the expected weight loss. Therefore, at this stage not all HCl were detached from LG.

During the fast heating from 323°C to 408°C (21.1°C/min) about 4.02% of weight loss occurred, and 21.88% of weight loss followed when the sample was held at 408°C for 30 min. 8.86% of material volatilized during the scan from 408°C to 853°C where the organic components of the sample was consumed completely. The leftover ashes (about 8.77%) has white color, soluble in hot water, the solution has strongly basic (pH > 10) property.

3.2 Kinetics of Pyrolysis

1. The plots of Figs. 2 (a, b, and c) show the treatment of the experimental data of weight loss over time obtained for LG at 323°C and 408°C according to the Eq (7A), to Eq (8A) for integer order of reactions, saying, zeroth, first and second. The examination of the resulted curves indicated that the experimental data did not fit into zeroth, first, and second order reactions, at both isotherm temperatures.
2. Figs. 3 (a, b, and c) show the treatment of the experimental data of weight loss over time obtained for LG at 323°C and 408°C according to the Eq (7B), to Eq (8B). The experimental data at 323°C fitted better to a second order reaction based on the value of R² (Table 2). Postulating a second order reaction for the first step radical decomposition of neopren is quite rational based on the following chemical reaction equations:



The experimental data at the isotherm temperature 408°C also fitted into a first order reaction. In this case the slowest step can be the scissoring of polymeric chain under high temperature by itself to volatile chemicals.

Table 1. Pyrolysis steps of LG, including initial time (t_i), final time (t_f), duration of the process (Δt), initial and final weight loss ($w_i\%$, $w_f\%$) and the amounts of weight loss (Δw), initial and final temperatures (t_i and t_f) and the range of temperature (ΔT) °C

Steps	t_i (min)	t_f (min)	Δt (min)	$w_i\%$	$w_f\%$	$\Delta w\%$	t_i (°C)	t_f (°C)	ΔT (°C)	$\Delta T/\Delta t$
1	0.00	3.72	3.72	99.98	97.31	2.67	27	324	297	79.8
2	3.73	91.05	87.32	97.30	75.35	21.95	324	323	-1	0.0
3	91.07	95.08	4.02	75.35	39.57	35.77	323	407	85	21.1
4	95.10	120.68	25.58	39.51	17.63	21.88	407	409	2	0.1
5	120.70	126.00	5.30	17.63	8.77	8.86	409	853	444	83.8

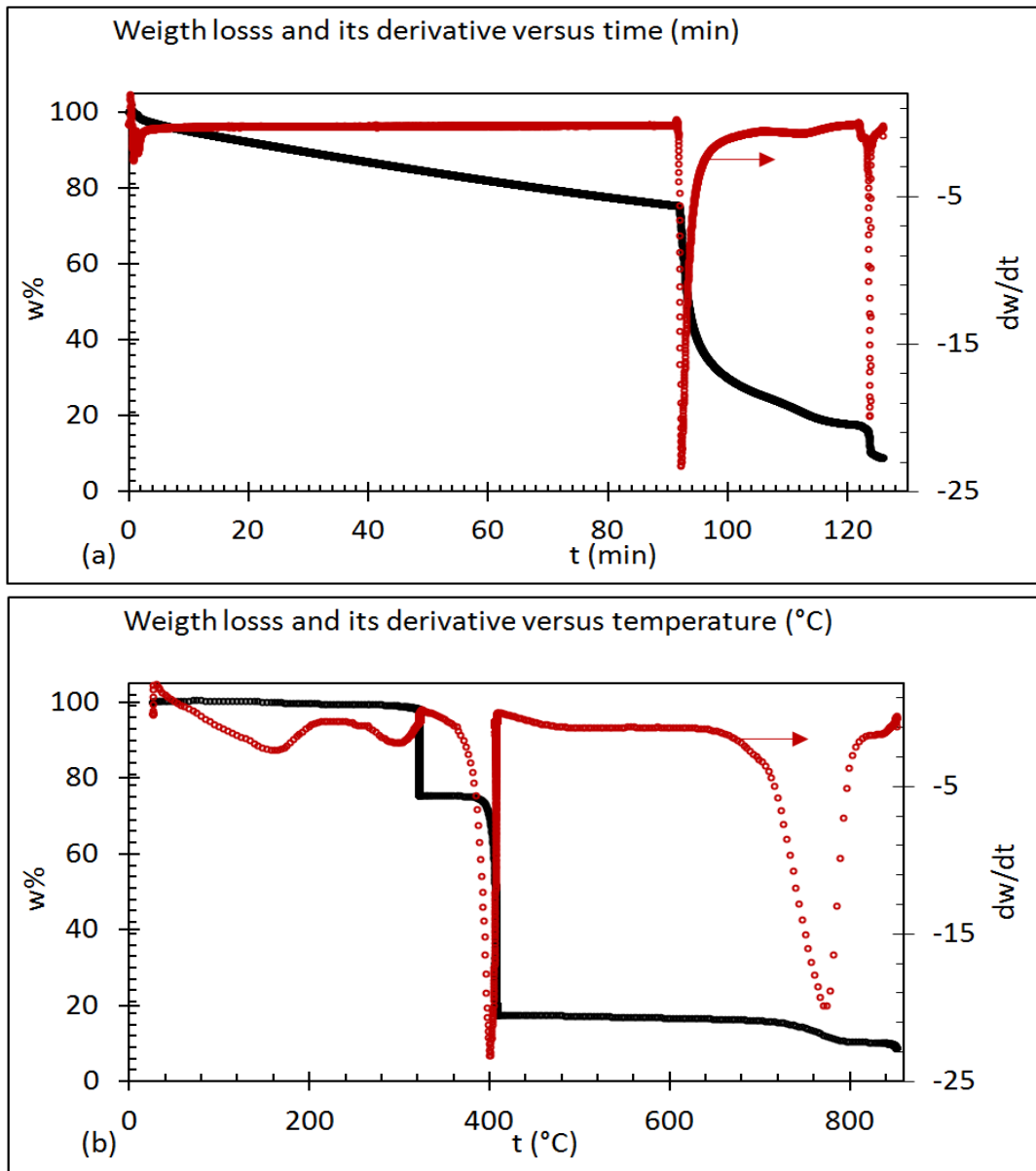


Fig. 1. The thermogram of LG sample: (a) weight loss versus time and derivative of weight loss (dw/dt) by time and (b) weight loss versus temperature and dw/dt versus temperatures

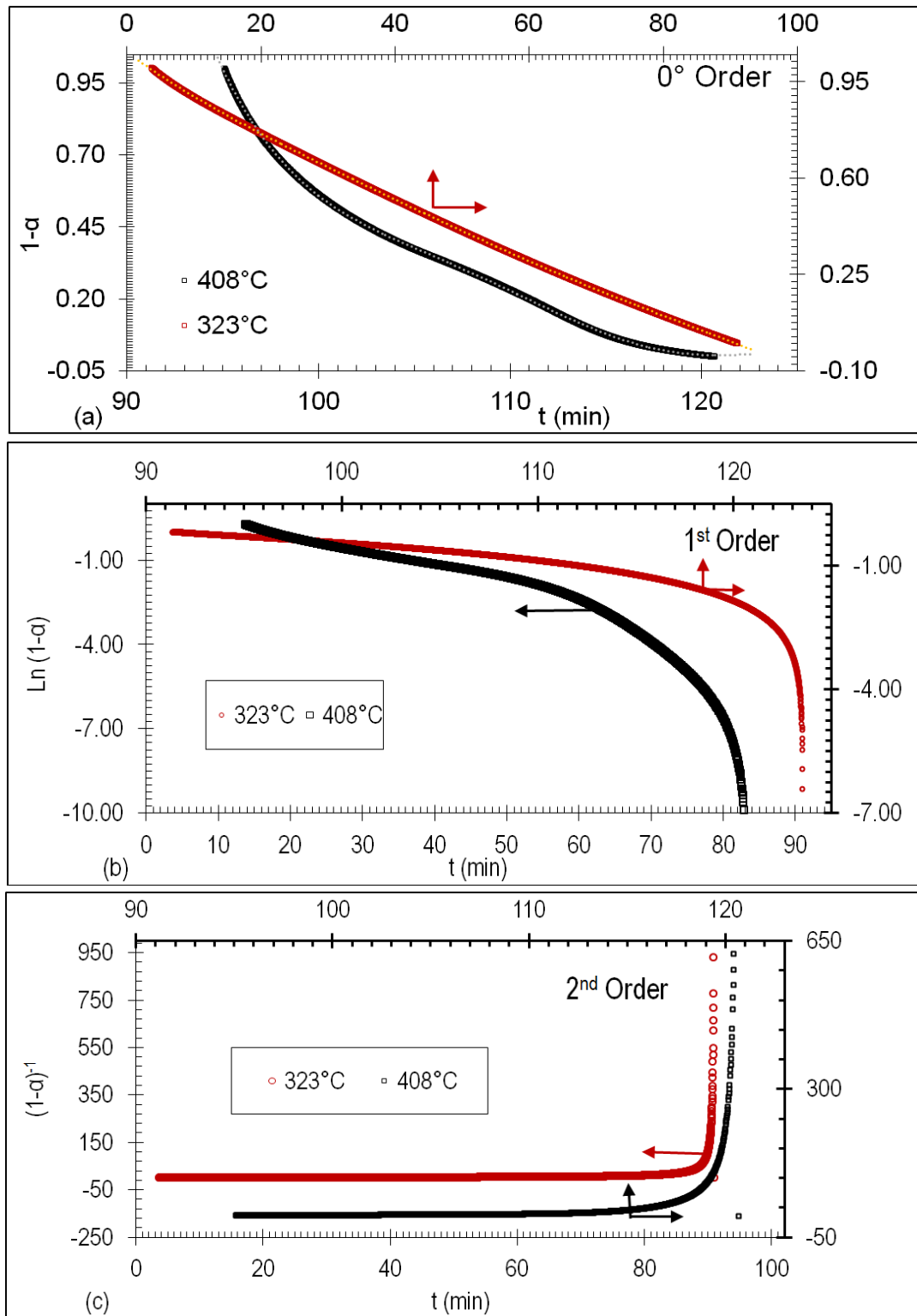


Fig. 2. Isothermal curves corresponding to degradation of LG at the indicated temperatures based on Eq(7A), Eq(8A) and Eq(9A) for (a) zeroth, (b) first and (c) second order reactions at 323°C and 408°C, respectively

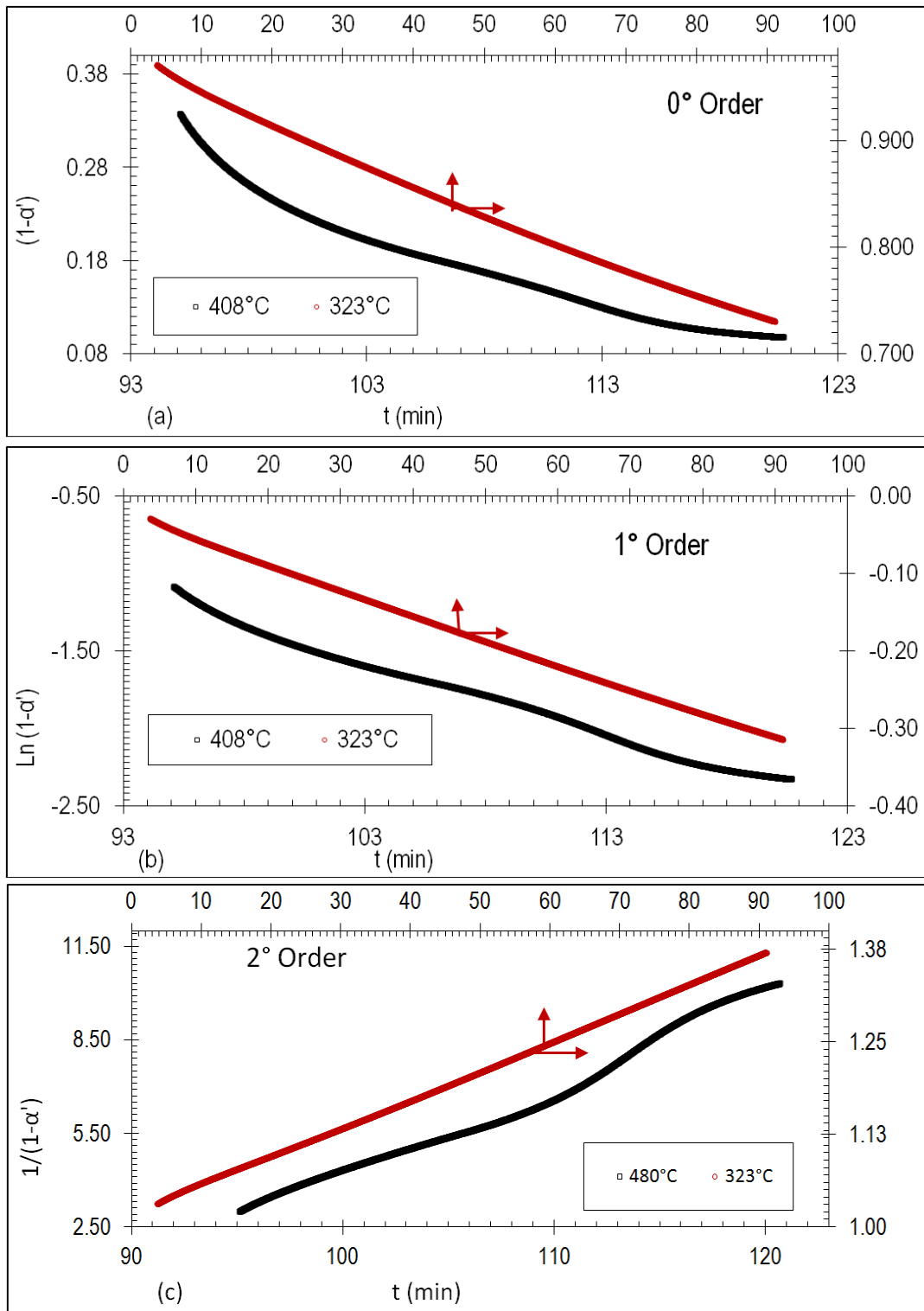


Fig. 3. Isothermal curves corresponding to degradation of LG at the indicated temperatures based on Eq(7B), Eq(8B) and Eq(9B) for (a) zeroth, (b) first and (c) second order reactions at 323°C and 408°C, respectively

3. Figs. 4 (a, b, and c) show the treatment of the experimental data of fraction of reactants over time for LG at 323°C and 408°C according to the Eq (7C) to Eq(9C) relationships. The experimental data at 323°C apparently fitted well into zeroth, first and second order. But the most suitable fit, based on the highest value of R^2 , was the second order reaction (Table 2). The experimental data at the isotherm temperature 408°C poorly fitted into the second order reaction. Postulating a second order reaction for the first step radical decomposition of neopren is quite rational based on the mechanism proposed in 2. for dehydrochlorination of neoprene.

The obtained values of k are small, due to the retardant material that manufactured had added to the neoprene in time of pressing. However, they are in the range of $k = 0.0047$ 1/min reported for polytetrafluoroethylene (PTFE) at lowest decomposition temperature, 480°C [42].

3.3 Reaction Order by Reiteration Methods

The value of n in Eq(6A), 6(B) and Eq(6C) can be determined by reiteration method. In this method, a plot of corresponding reactant fraction $(1-\alpha)^{(1-n)}$ or $(1-\alpha')^{(1-n)}$ or $\alpha''^{(1-n)}$ versus t (min) for each value of n was constructed from experimental data. Then, the correlation coefficient (R^2) value of each trial was plotted versus corresponding (1-n) value (Fig. 5 (a), Fig. 6 (a) and Fig. 7 (a)). The n corresponding to the largest R^2 value represents the best straight line, and the best reaction order. The slope of the plot

of $w^{(1-n)}$ versus t (min) (Fig. 3 (b)), Fig. 6 (b) and Fig. 7 (b)) represents ak , after it is divided by (n-1). These results are summarized in Table 3 assuming a = 1.

The obtained n and k values depended on the definition of fraction of reactants, α , α' and α'' . The most suitable fit of experimental data was corresponded to α'' that had highest correlation coefficient at both temperatures (Table 3 7th column). The k values of thermolysis at 323°C obtained based on α' and α'' models are in the range of k value obtained for pyrolysis of PTFE at lower temperature, 480°C. Similarly, the values of k obtained from model related to α'' for LG thermolysis at 408°C is in the range of k value reported for thermolysis of PTFE at 500°C [42]. Other k values of the Table 3 are larger than the reported values of PTFE. Also, the above values are in the same range of $6.8 < 1000k$ (min^{-1}) < 23 for pyrolysis of lignin with $134 < E_a$ (kJ/mol) < 172 [43]. The reported Arrhenius k values, 8.32×10^{-5} and 2.34×10^{-6} for slow pyrolysis of enzymatic hydrolysis of lignin [44] are considerably lower than the values estimated by above methods for pyrolysis of neoprene.

As the temperature of pyrolysis was increased the value of k also increased which was within expectations based on Arrhenius relationship, Eq (11), for a given reaction at two temperatures.

It is instructive to mention that most of researchers assumed a first order reaction rate for thermolysis [e.g.42]. The methods for evaluation of reaction order using thermogravimetric data [e.g.45] did not worked for LG degradation. Therefore, the reiteration method was used.

Table 2. The reaction order (n), rate constant (k) and correlation coefficient (R^2) of isothermal decomposition of LG at 323, and 408°C according to three definition of pyrolysis conversion. The best n and k values showed by bold faces

Model	n	323°C		408°C	
		$10^3 k$	R^2	$10^3 k$	R^2
α	0	11.3	0.997	33.9	0.951
	1	37.3	0.780	174	0.816
	2	704	0.0129	7770	0.04
α'	0	2.71	0.997	8.12	0.951
	1	3.23	0.9995	46.7	0.993
	2	3.86	0.9997	290	0.981
α''	0	2.47	0.997	7.41	0.951
	1	2.89	0.9993	29.6	0.985
	2	3.40	0.9999	122	0.995

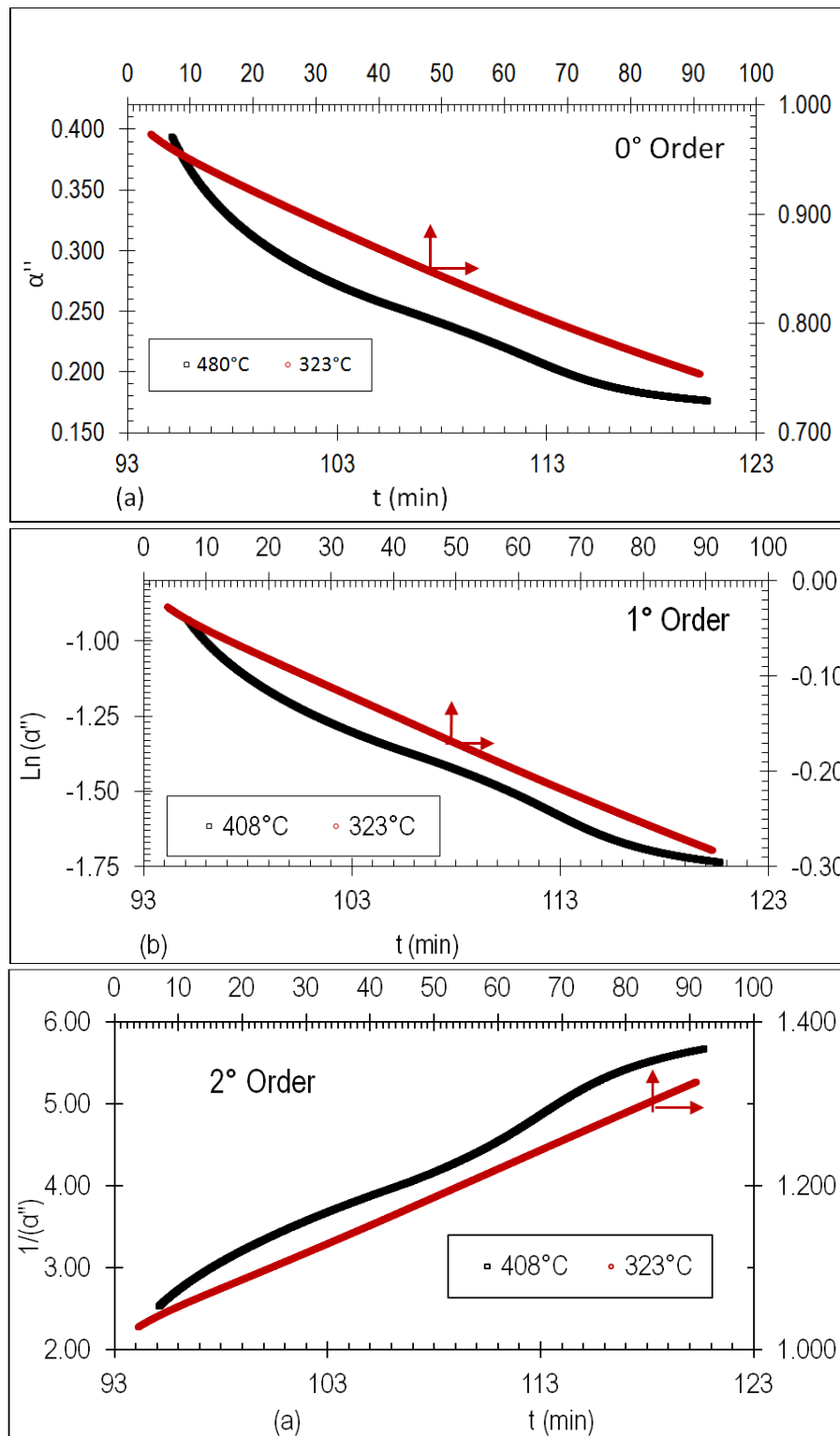


Fig. 4. Isothermal curves corresponding to degradation of LG at the indicated temperatures based on Eq(7C), Eq(8C) and Eq(9C) for (a) zeroth, (b) first and (c) second order reactions at 323°C and 408°C, respectively

Thermolysis weight loss reactions occurs either in solid or liquid state where a typical reaction order of zero for just vaporization of degraded products, one when the macromolecule by itself undergo scissoring to produce volatiles, and second order when a radical produced reacts with the substrate to produce another volatile. Fractional order are observed for many complex consecutive radical reactions. For example, the kinetic law for the hydrogen-bromine reaction is complicated; the reaction order with respect to concentration of bromine was established to be $\frac{1}{2}$. The obtained order by reiteration methods for pyrolysis of LG at 323 and 408°C (Table 3) $0.18 < n < 1.93$ also are fractional which are the indication of complex reactions. Moreover, the value of n depended on the chosen model (α , α' , α'') and the temperature of the isotherm. The reaction order $n = 1.78$ and 1.93 for the thermolysis of LG at temperatures 323 and 408°C, respectively, were near to 2. But the fractional numbers were fitted better to the experimental data indicating that the thermolysis process is a set of complicated reaction rather than a simple decomposition reaction. The pyrolysis of neoprene at higher temperatures also showed fractional rate order. For example, rate equation of $r = k[LG]^{0.49}$ and $r = k[LG]^{0.83}$ were obtained for decomposition of LG at 346 and 405 °C, respectively also were related to complex pyrolysis reactions [46].

3.4 Reaction Order from Rate of Pyrolysis

The logarithmic form of Eq(2) relates the rate of thermolysis, r , to the fraction of reactants, $(1-\alpha)$, $(1-\alpha')$, and α'' :

$$\ln r = \ln ak + n \ln(1 - \alpha). \quad (10A)$$

$$\ln r = \ln ak + n \ln(1 - \alpha'). \quad (10B)$$

$$\ln r = \ln ak + n \ln(\alpha''). \quad (10C)$$

For a simple one step reaction the slope of the variation of $\ln r$ versus the fraction of unreacted reactants ($\ln(1-\alpha)$, $\ln(1-\alpha')$, $\ln\alpha''$) yields the order of reaction and the intercept is a combination of stoichiometric coefficient of the reactants and rate constant (ak). Figs. 8 (a) to 8 (c) depicted such a plots for both isotherm temperatures. The graph of experimental data appear that the initial reaction order gradually decreases to lead to a plateau with zeroth order. However, the expansion of Figs. 8 for isotherm at 323°C indicated that there must be occurrence of many simultaneous zeroth order reactions with their proper k values (intercept) rather than one simple reaction.

The existence of many parallel chemical reactions resulting from thermal decomposition of LG also could be confirmed by referring to a previous work, where total ion chromatogram (TIC) obtained by gas chromatography mass spectrometry (GC-MS), of any samples of LG pyrolysis, showed over 150 chemicals [39,40]. When many simultaneous zero order reactions are taking place, the reaction order from double logarithmic plot of rate of reaction and fraction of reactants will be inaccurate as it is visible with the values of n tabulate in the Table 4.

The experimental data at 408°C, however, shows an initial straight line which reaches to a minimum then increased to a plateau at maximal. The initial rate order varies with respect to the method of calculation of the fraction of reactants (Table 4). The values of reaction order estimated by this method (Table 4) are larger than the corresponding values from previous method (Table 3).

Table 3. Kinetics parameters of LG at the isotherms temperatures 323 and 408°C corresponding Figs. 4 -7. The PTFE data are included for comparison [42]

t (°C)	Model	1-n	10 ³ slope	n	10 ³ k	R ²
323	α	0.82	-10.94	0.18	13.34	0.9786
	α'	-0.68	2.48	1.68	3.64	0.9972
	α''	-0.78	2.56	1.78	3.28	1.0000
408	α	0.585	-34.5	0.42	58.99	0.9927
	α'	-0.23	16.3	1.23	70.73	0.9950
	α''	-0.93	10.3	1.93	11.03	0.9954
480	PTFE			1	4.70	1.000
500	PTFE			1	16.0	0.999

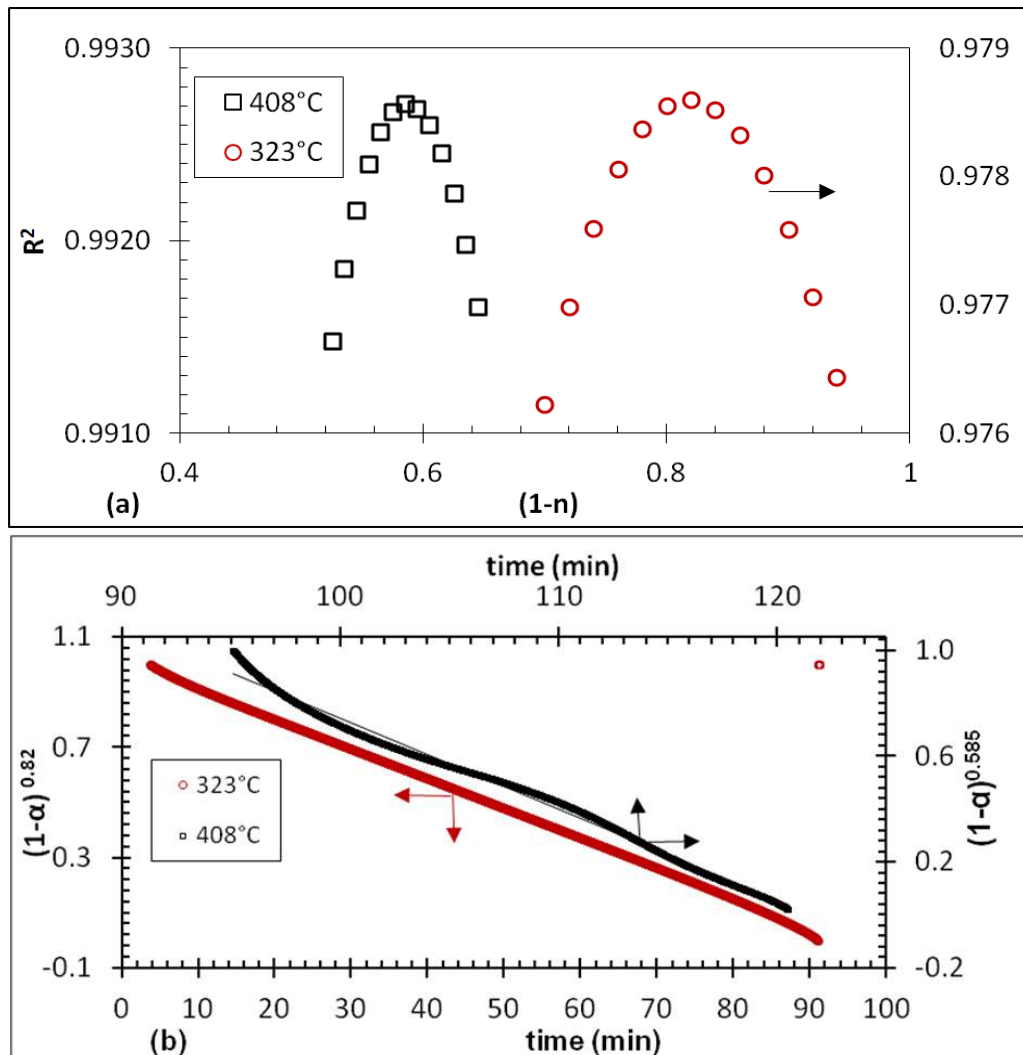


Fig. 4. Treatments of the isothermal data at temperatures 323 and 408°C to estimate the kinetics parameters of pyrolysis of LG: (a) the plot of R^2 versus reiterated values of $(1-n)$; (b) the plot of $(1-\alpha)^{(1-n)}$ versus t (min) according to Eq (6A) for the best n value obtained from max of Fig. 5 (a)

Table 4. The initial values of slopes (n) and k (EXP(intercept)) assuming $a=1$ for LG at 323 and 408°C based on relationships Eq (10A) to Eq (10C)

Model α	Isotherm at 323°C		Isotherm 408°C	
	n	k	n	K
1	3.64	0.451	1.73	3.20
2	15.3	0.713	2.96	86.3
3	16.8	0.713	4.14	167.

The plots on Fig. 9 shows the variation of double logarithmic values of the rate of reaction and the fraction of reactants where the rate of reaction was calculated using experimental values of

$(1-\alpha)$, $(1-\alpha')$, and α'' at the corresponding time, $R = \Delta(1-\alpha)/\Delta t$, $\Delta(1-\alpha')/\Delta t$, and $\Delta\alpha''/\Delta t$, instead of the rate obtained by TGA driving program (Pyris). In these plots, the zeroth order reactions can be observe, easier. For example, five zeroth order parallel reaction with their proper values of k at 323°C and 26 concurrent zeroth order reactions with proper k values at 408°C (Table 5) were identified from Fig. 9 (a).

Theoretically, occurring many simultaneous reactions at high temperatures is within expectation [14,47,48]. For example, Kruse et al. [32] presented a detailed mechanism of PS

pyrolysis based on population balance equations and the method of the moments in which up to 93 species and 4500 reactions were used to describe product distribution and average molecular weight. Similarly, detailed kinetics models of PE, polypropylene (PP) and PS pyrolysis were presented and discussed by other researchers [7-9]. The reported results of thermal degradation of plastic blends and their mutual interactions do not completely agree since each research group depending on their particular interests focused on different effects. The researchers who studied the decomposing of polymer mixtures discovered that the pyrolysis of a particular polymer in a polymeric mixtures behaves quite similarly to the pyrolysis of a pure polymer by step-by-step pyrolysis [14-15]. Thus, the additive rule was applicable to the pyrolysis of a mixture of polymers. Therefore, the pyrolysis of LG, which made of a mixture of many

chemical, will be similar to pyrolysis of each individual ingredient resulting in many simultaneous concurrent reactions.

3.5 Evaluation of E_a from Thermal Scans

Arrhenius relationship (Eq 11) relates the rate constant, k , to the activation energy of reaction E_a , the absolute temperature of the reaction T , the ideal gas constant, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and another constant such as z to describe the efficiency of the molecular collisions in a chemical reaction.

$$k = ze^{\frac{E_a}{RT}} \quad (11)$$

Combining Eq (2) and Eq (11) results:

$$r = ze^{-E_a/RT}(1 - \alpha)^n \quad (12)$$

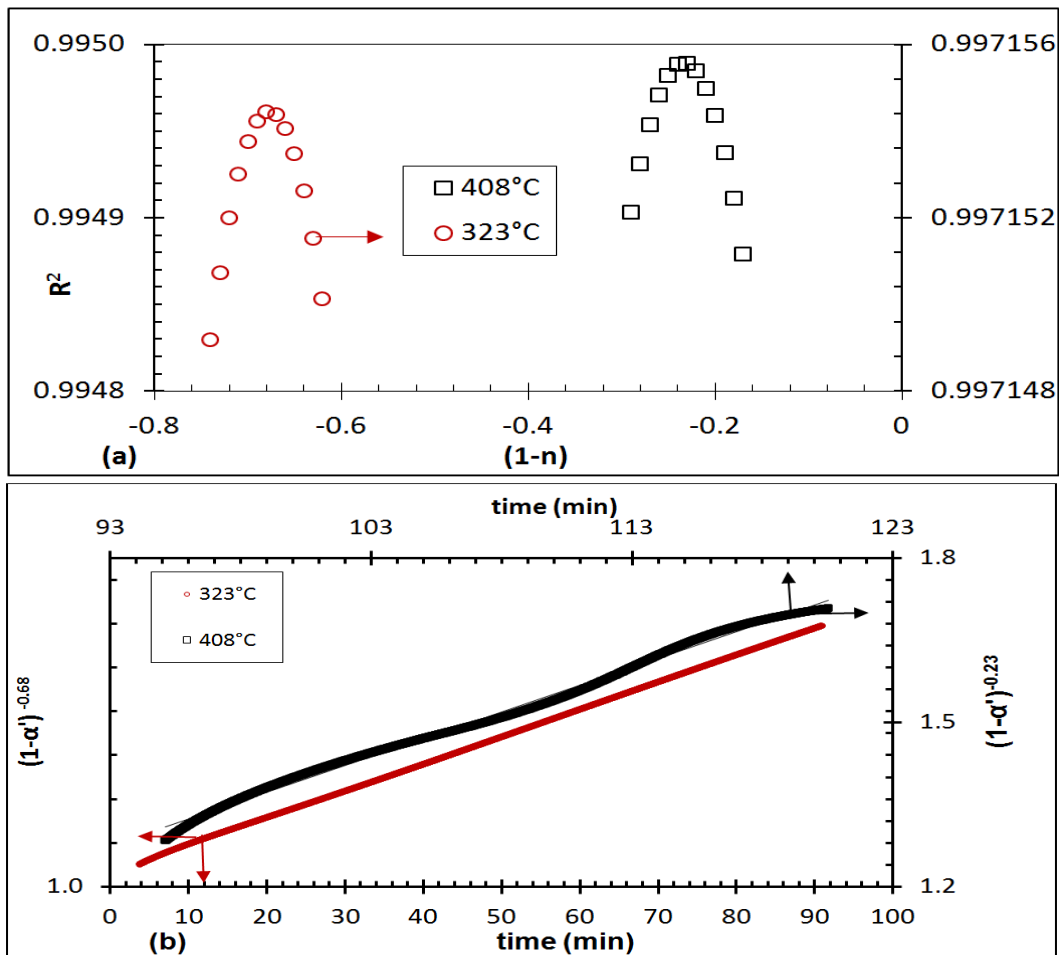


Fig. 5. Treatments of the isothermal data at temperatures 323 and 408 °C to estimate the kinetics parameters of pyrolysis of LG: (a) the plot of R^2 versus reiterated values of $(1-n)$; (b) the plot of $(1-\alpha')^{(1-n)}$ versus t (min) for the best n value obtained from max of Fig. 6 (a)

The logarithmic form of Eq (12), linearly relates $\ln r$ to the inverse of temperature, $1/T$ (K):

$$\ln r = \ln z(1 - \alpha)^n - E_a/RT \quad (13)$$

Fig. 10 represents the application of Eq (13) to the experimental data covering a wide range of temperatures (50-409°C) including the isotherm at 323°C. Six steps are visible in the graph. Three steps with positive values of E_a and three steps with negative values of E_a (Table 6). The positive E_a values can be related to the minimum energy required to disassociate a physical bond to release a volatile from a solid such as evaporation of moisture from reactants and the decomposition of chemical bonds within LG. Neoprene contains bonds between carbon and

hydrogen, carbon and chlorine and carbon and carbon. The bond energy for radical decomposition (homolytic bond cleavage) of Cl-C bond = 331, C-C single bond = 346, C=C double bond = 620, and C-H bond = 413 all in kJ/mol under standard thermodynamic conditions (one atmosphere pressure and at 25°C). Therefore, the expected E_a value must be near to the bond energy value under the same conditions. The obtained E_a (Table 6) are below the amount of standard bond energies of C-Cl, C-H, and C-C. Since those reactions occurred at higher temperatures lower E_a required. The negative E_a value are related to the exothermic process including crystallization of melted chemical, and recombination of chemically active specimen resulted from decomposition reactions.

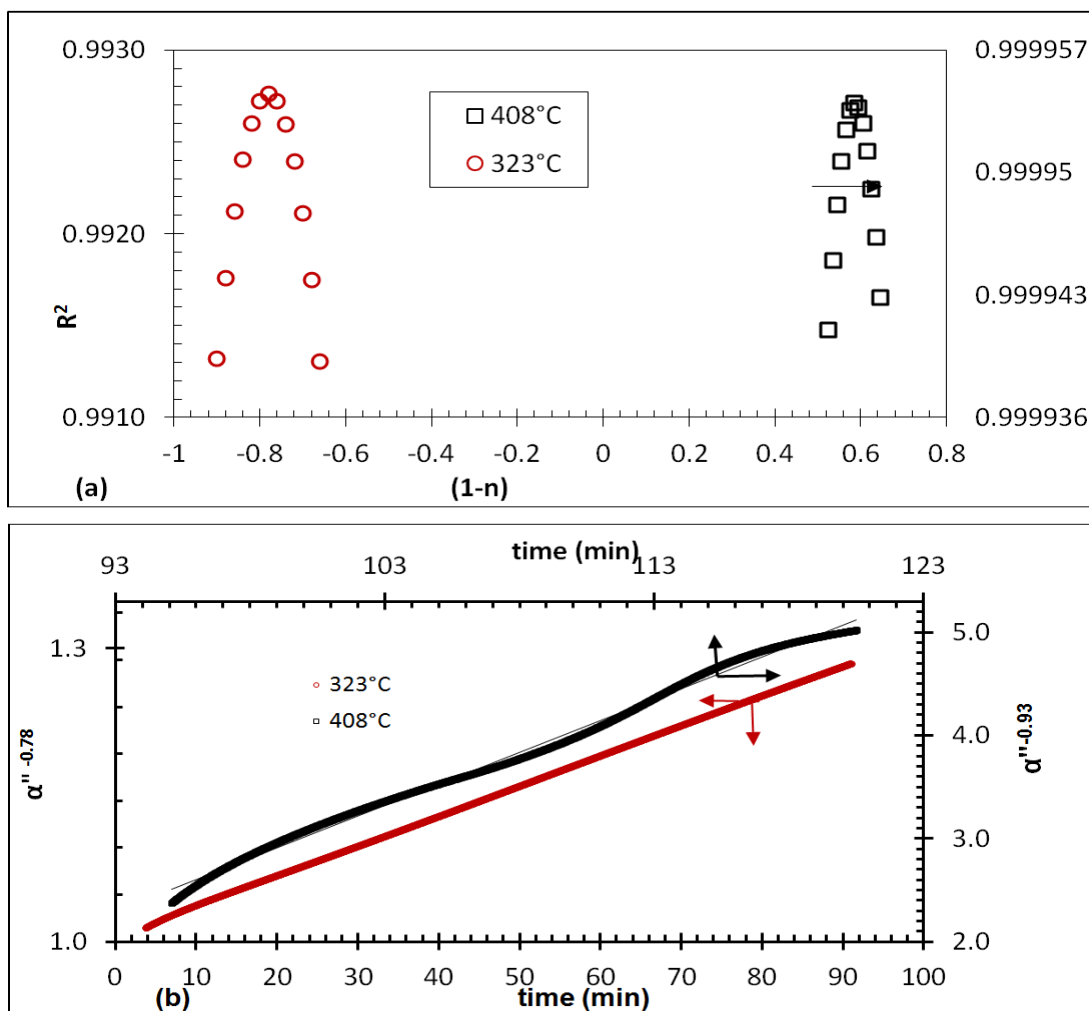


Fig. 6. Treatments of the isothermal data at temperatures 323 and 408 °C to estimate the kinetics parameters of pyrolysis of LG: (a) the plot of R^2 versus reiterated values of $(1-n)$; (b) the plot of $\alpha^{n-0.78}$ versus t (min) according to Eq (6C) for the best n value obtained from max of Fig. 7 (a)

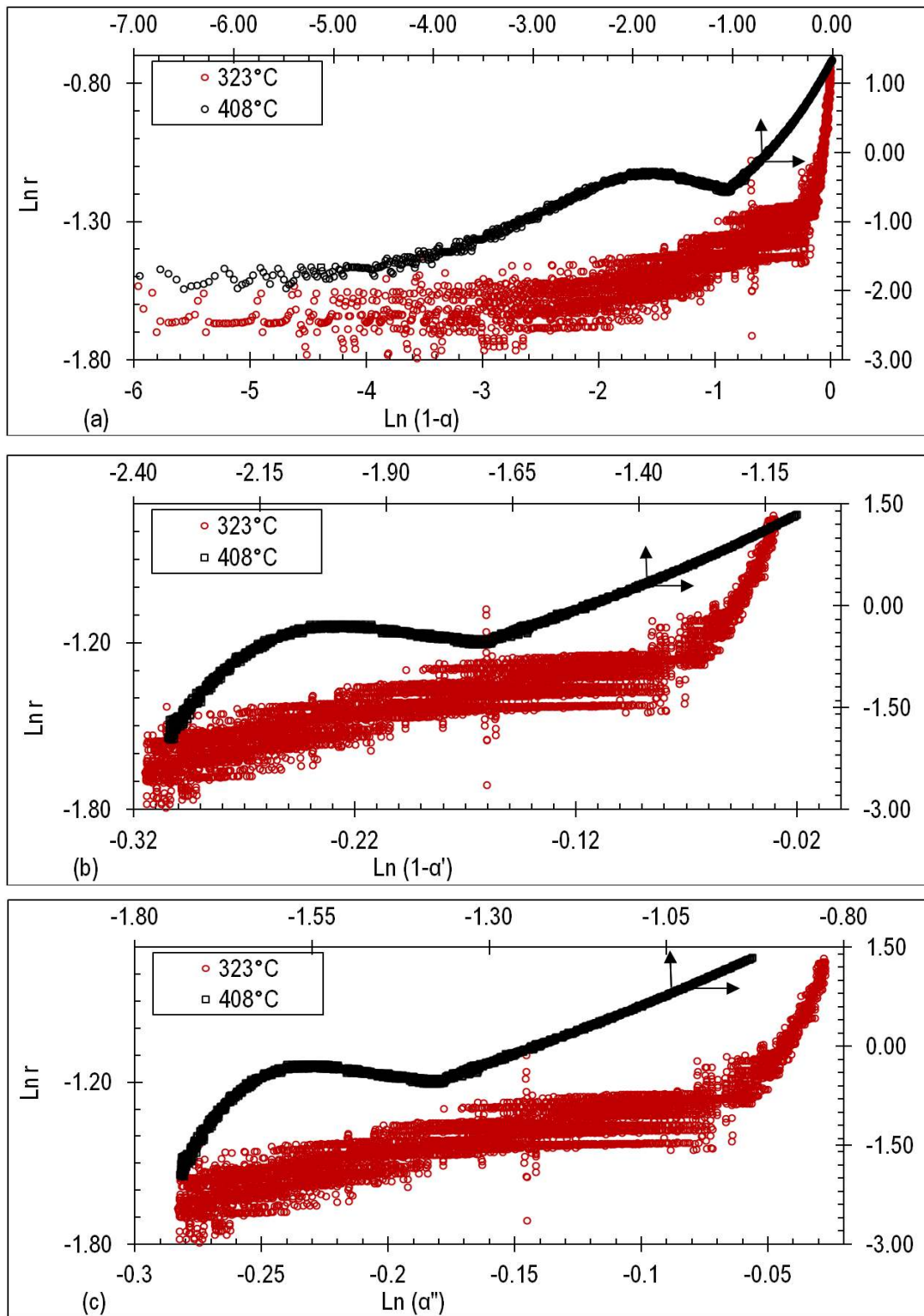


Fig. 7. Double logarithmic variation of rate ($-dw/dt$) obtained by Pyris versus the fraction of unreacted LG according to: (a) Eq (10A), (b) Eq (10B), (c) Eq (10c)

The calculated $E_a = 25.0$ kJ/mol at temperature range of 90-161°C (Table 6) could be related to vaporization of volatile and moisture within LG, plus physical changes including melting and some fundamental chemical changes in the structure of reactants. This value is in the range of reported $16.2 < E_a$ (kJ/mol) < 27.0 E (Table 6) for dehydration of bituminous coal over a temperature range from 35 – 115°C [49]. The $E_a = -63$ shows the crystallization of melted materials including combination reaction of melts in the temperature range of 170 – 215°C. The $E_a = 58$ kJ/mol at temperature range of 237-293°C (Table 6) is around the E_a related to unzipping of some well know polymers such as polymethylmethacrylate (PMMA). For example, E_a for unzipping PMMA radicals was evaluated to be 60 kJ/mole [50] by radical process. Likewise, the values of $24.6 < E_a$ (kJ/mol) < 64.0 related to various thermolysis reaction of LG similar to reactions involved in thermolysis of glucose based carbohydrates [51]. These reported E_a are considerably lower than involved standard bond energies of original reactants. In the temperature range of 310-324°C (Table 6) the exothermic recombination reactions in the liquid phase occurred with a very high $E_a \approx -299$ kJ/mol. These combination and decomposition reactions continued during the isotherm at 323°C. The $E_a = 284$ kJ/mol at temperature range of 337-402°C related to depolymerization of LG. Thought, it is smaller than standard bond energies, however, it is in the rage of E_a reported for the thermolysis of other organic resins.

3.6 Evaluation of E_a from isotherms

The plot of $(1-\alpha)^{(1-n)}$ versus reaction time, according to Eq(6) for six isotherms were constructed based on the experimental data at

temperatures 308, 313, 323, 333, 336 and 346°C, similar to the Fig. 8 (b) which was built for temperatures 323°C and 408°C. The values of k were calculated from the slope of each plot at a given isotherm (Fig. 11 (a)). Then, a plot of $\ln k$ versus invers of temperature according to Eq (13) was built (Fig. 11 (b)). Considering the data obtained from six isotherms, the value of $E_a = 117$ kJ/mol with $z = 3.22 \times 10^{12}$ obtain from slope and the intercept of Fig. 11 (b), respectively, which is not in agreement with the one obtained in the previous section. However, a close inspection of Fig. 11 (b) indicated that the isotherms at lower temperatures (first four isotherms) may have a different E_a than the isotherm at higher temperatures. Therefore, $E_a = 317$ kJ/mol with $z = 4.4 \times 10^{29}$ (Table 7) was calculated from slope and the intercept of the data at higher temperatures (Fig. 11 (b)), respectively. This value is in the range with the values of E_a reported for pyrolysis of rubbers in car tires [21,52], and it is closer to the values of the bond energies. It is higher than $E_a = 261$ kJ/mol for decomposition of PTEE, and the $134 < E_a$ (kJ/mol) < 172 of lignin at temperature rang 500-800°C [42].

The $E_a = 2.7$ kJ/mol (Table 7) obtained from isotherms at lower temperatures is not in agreements with the E_a values calculated by previous method; and it is lower than E_a of vaporization of moisture from coal [49]. Therefore, it is related to volatilization of volatile organic compounds from LG structure. The thermolysis E_a according to Sanchez-Jimenez et al is independent of the kinetic model to be used [53], however, the value of z heavily depends on the kinetic model. Therefore, it will be hard to do any comparison of the z values.

Table 5. The values of $\ln k$ for the zeroth ordered reactions identified in Fig. 8 (b)

Reaction no.	$\ln k$ at 323°C	$\ln k$ at 408°C	Reaction no.	$\ln k$ at 408°C
1	0	-1.745	14	-2.403
2	-3.958	-1.783	15	-2.476
3	-3.945	-1.823	16	-2.556
4	-4.35	-1.863	17	-2.644
5	-5.043	-1.906	18	-2.739
6		-1.95	19	-2.844
7		-1.997	20	-2.962
8		-2.046	21	-3.098
9		-2.097	22	-3.251
10		-2.151	23	-3.434
11		-2.209	24	-3.657
12		-2.269	25	-3.943
13		-2.333	26	-4.351

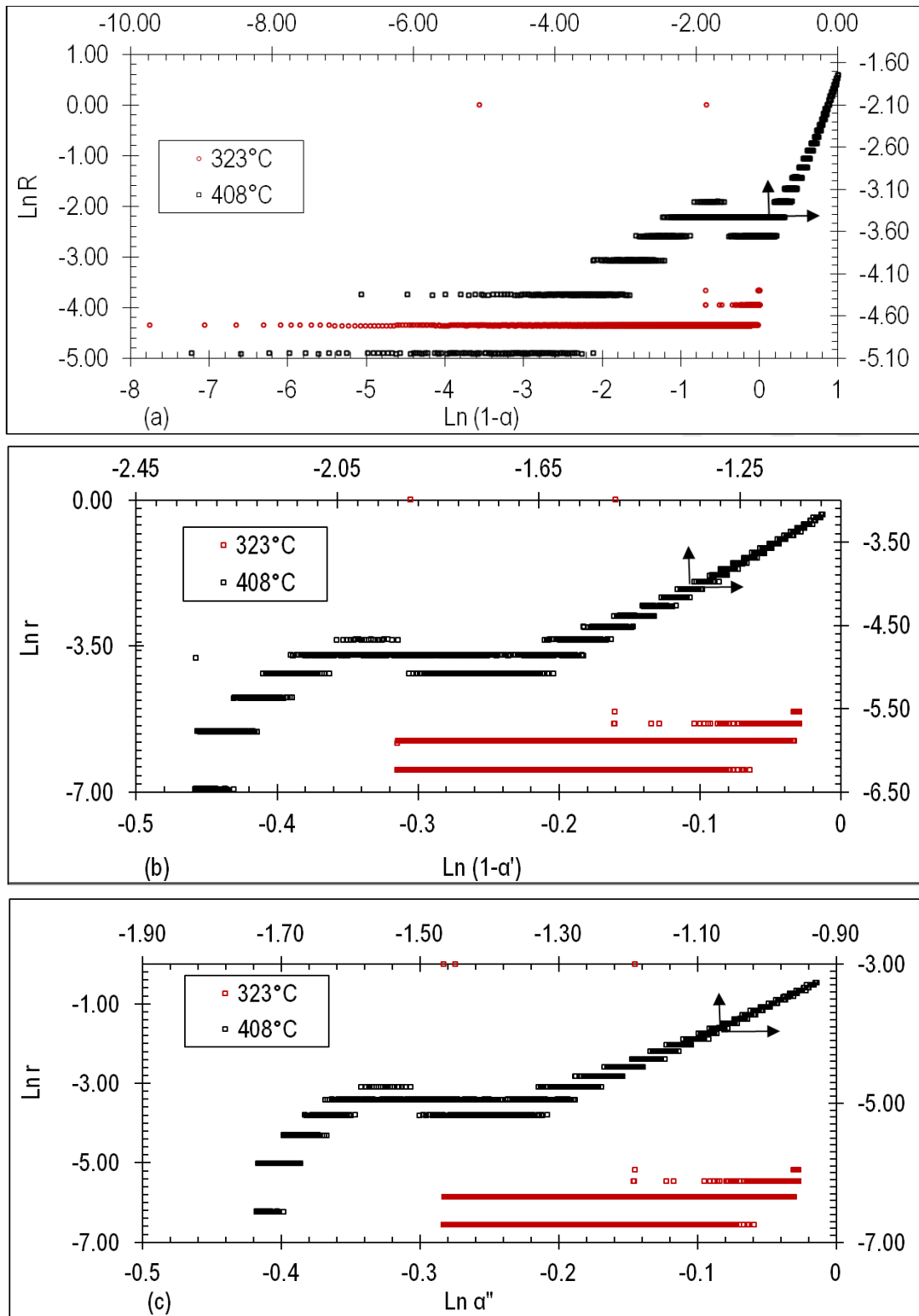


Fig. 9. Double logarithmic variation of calculated rate ($R = -\Delta(1-\alpha)/\Delta t$) versus the fraction of unreacted LG: (a) Eq (10A), (b) Eq (10B), (c) Eq (10c)

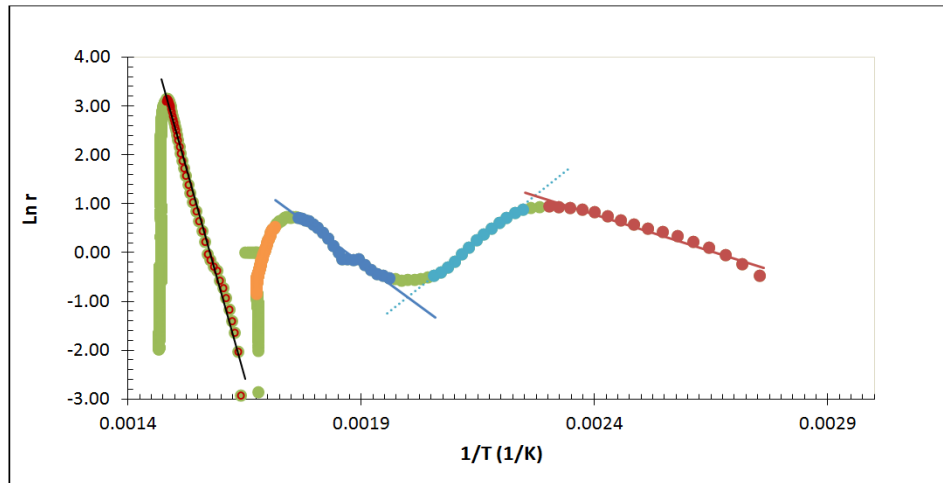


Fig. 10. Variation of logarithm of rate of decomposition of LG versus inverse of temperature

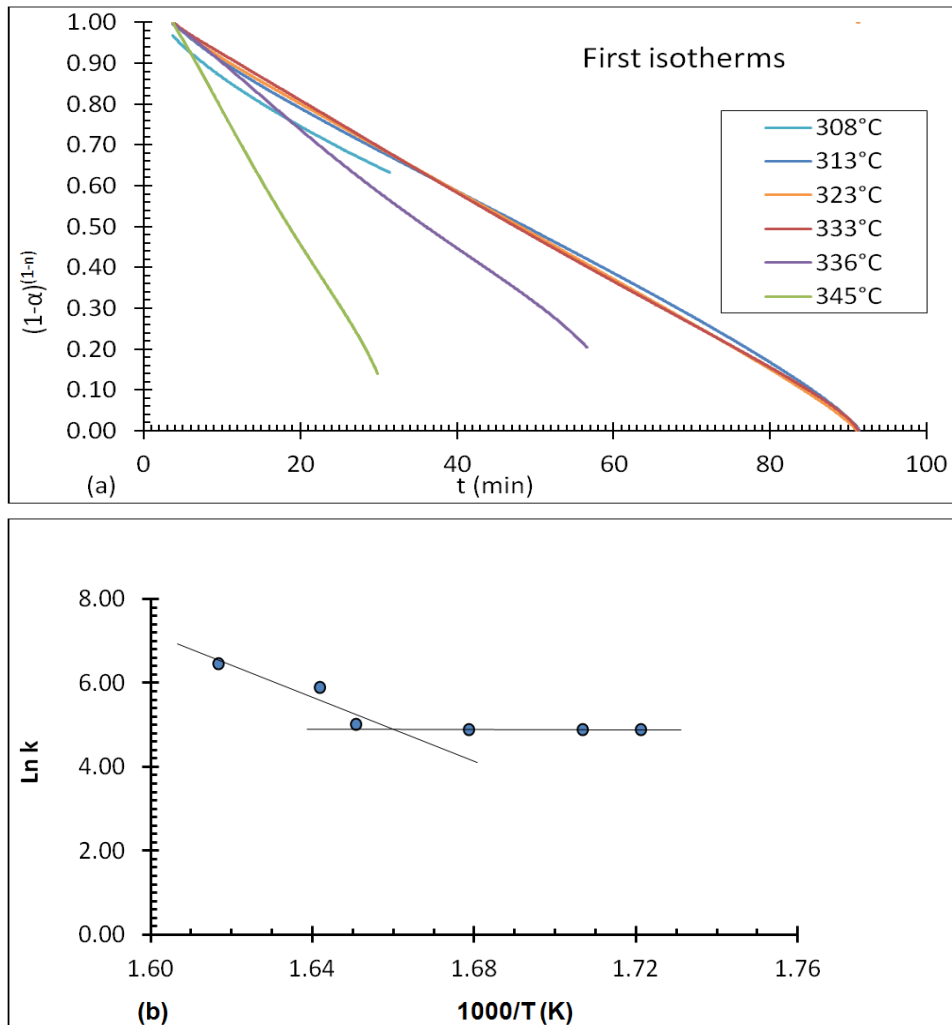


Fig. 11. (a) Isothermal curves corresponding to the thermolysis of LG, recorded at 308, 313, 323, 333, 336 and 346°C. (b) Plot of the values of Ln k obtained from the slope of isotherms of Fig. 11 (a) versus corresponding invers temperature

Table 6. Kinetics parameters of the thermolysis of LG, initial and final weight loss (w_i , w_f) and the amounts of weight loss (Δw), initial and final temperatures (t_i and t_f), and the range of temperature (ΔT), average heating rate and the activation energy

Steps	t_i (min)	t_f (min)	Δt (min)	$w_i\%$	$w_f\%$	$\Delta w\%$	t_i (°C)	t_f (°C)	ΔT (°C)	$\Delta T/\Delta t$	Ln Z	E_a (kJ/mol)
Initial	0.62	0.87	0.25	100.36	99.91	0.45	90	161	71	285.1	8.01	25.0
Heating	0.92	1.12	0.20	99.78	99.51	0.27	172	213	41	205.5	-16.2	-63.5
	1.23	1.53	0.30	99.44	99.08	0.36	237	293	56	186.7	13.0	58.0
Heating between	1.75	3.72	1.97	98.65	76.12	22.53	310	324	13	6.8	-61.0	-299.4
	91.62	92.38	0.77	75.30	67.23	8.07	337	402	66	85.8	53.9	284.4
Isotherms	92.42	120.68	28.27	66.50	17.63	48.87	403	409	6	0.2	-592	-3350

Table 7. Arrhenius constant of thermolysis of LG

	E_a	Z
LG all points	117	3.22×10^{12}
LG High T	317	4.36×10^{29}
LG Low T	2.72	2.31×10^2

4. CONCLUSIONS

The results obtained showed that the kinetics parameters depended on the form of extent reaction (α). The experimental data showed fractional reaction order for the both isotherm temperatures. The double logarithmic variation of rate of reaction ($\ln r$) and unreacted fraction of reactants showed that the order of thermolysis reaction was zero at the both isothermal temperatures while many parallel concurrent reactions were occurred simultaneously with proper k values. Therefore, the detailed description of the overall degradation of a LG sample which is made up of a large number of chemicals, mainly, neoprene, plasticizers, minerals and fragrant, is quite a complex process which involves a large number of chemical reactions, and intermediate species. The decomposition of neoprene was compared to the pyrolysis of similar materials including the decomposition of rubber in car-tire and PTFE.

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COMPETING INTERESTS

Author has declared that no competing interests exist.

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