

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

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ABSTRACT

At two consecutive temperatures, 323°C and 408°C as well the two thermal scans in between these two temperatures the kinetics of thermolysis of powder-free laboratory safety gloves (LG) was studied by thermogravimetric analysis (TGA). Three models were used to evaluate the kinetics parameters related to the decomposition of LG at both isotherms. The results of the study indicated that the kinetics parameters depend on the model to choose. The experimental data at the isothermal temperature 323°C fitted in zeroth, first and second order depending on the definition of extent of reaction. The pyrolysis at the isotherm temperature 408°C fitted into first order and second order depending on the definition of extent of reaction. Also, 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 (E_a) was estimated by thermal scans, and isotherms at 308, 313, 323, 333, 336, and 345 °C. The value of E_a for the process at lower temperature was near to E_a corresponding to evaporation of volatiles, and at higher temperatures E_a was below constituents' chemical bond energies but it was higher than the reported E_a for decomposition of polymethylmethacrylate and it was lower than E_a for decomposition of rubber in tires.

Keywords: Kinetics, thermogravimetric analysis, powder free examination gloves, safety gloves, latex gloves, pyrolysis of gloves, neoprene, thermalizes.

1. INTRODUCTION

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 [7,8,9]. The decomposition of pure,

freshly prepared polymeric materials, has been of interests to scientists since the applied knowledge of polymeric materials gained relevance [10,11,12]. 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 [17,18,19]. 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 [21,22,23,24,25]; 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 [32,33,34,35,36]. 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 six 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 860°C tailed to a short isotherm (2 min) led to full degradation of LG.

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 846°C and maintained there for 2 min 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, $(-\text{CH}_2-\text{CCl}=\text{CH}-\text{CH}_2-)_n$, 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 846°C and holding there for 2 min 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.

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)	$\Delta T(^{\circ}\text{C})$	$\Delta T/\Delta t$
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&6	120.70	126.00	5.30	17.63	8.77	8.86	409	853	444	83.8

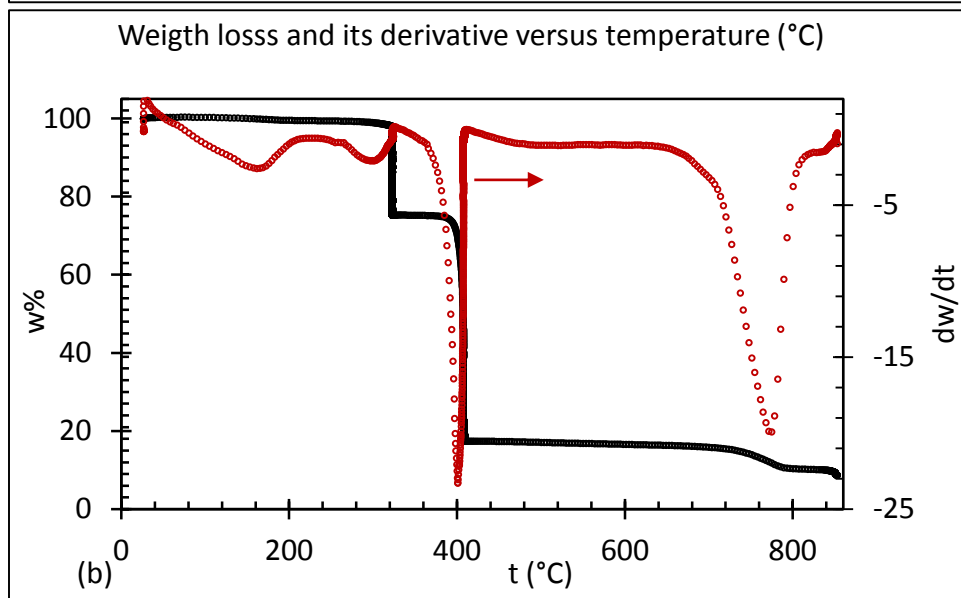
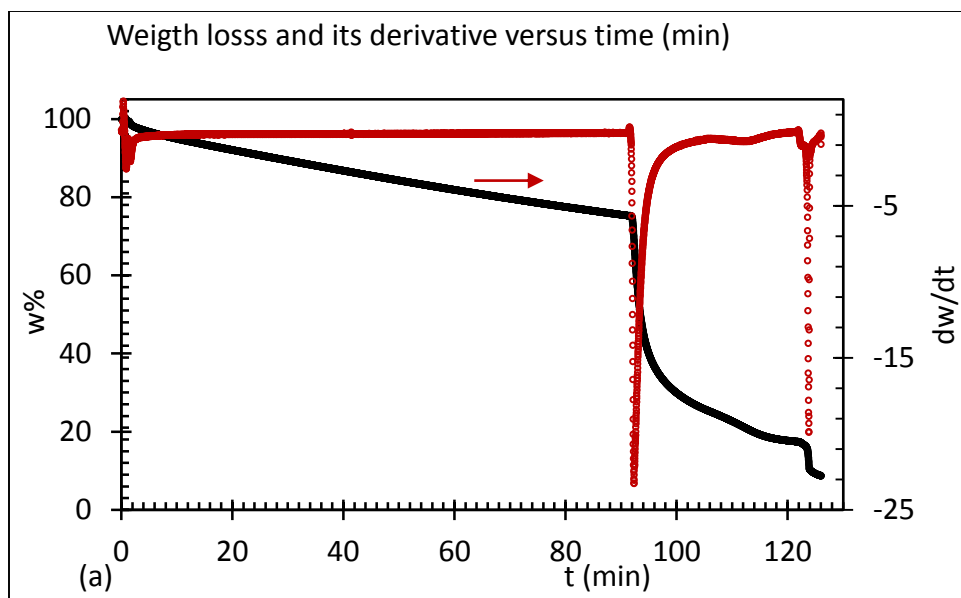


Fig 1. The thermogram of LG sample: (a) weight loss versus time and derivative of weight loss (dw/dt) by time, and (b) weight loss versus temperature and dw/dt versus temperatures.

3.2. 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, da/dt , in relation to reactants, $(1-\alpha)$, can be expressed as:

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

Rearranging Eq (4) results:

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

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

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

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

$$n = 1, \ln(1-\alpha) = -akt + \ln(1-\alpha)_0 \quad (8)$$

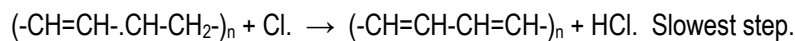
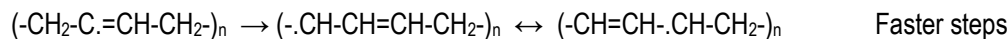
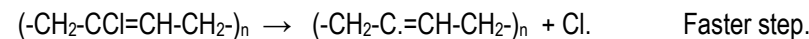
$$n = 2, (1-\alpha)^{-1} = akt + (1-\alpha)_0^{-1} \quad (9)$$

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 above relationships. The experimental data do not fit into zeroth, first, and second order reactions, at both temperatures.

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 themolysis), 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(4) to Eq(9). **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 above relationships. The experimental data at 323°C fitted better to a second order reaction based on the value of R_{sq} (**Table 2**). Postulating a second order reaction for the first step radical decomposition of neopren is quate rational based on the following chemical reaction equations:



The rate = $k[Cl.] [(-CH=CH-CH-CH_2)_n]$, a second order reaction.

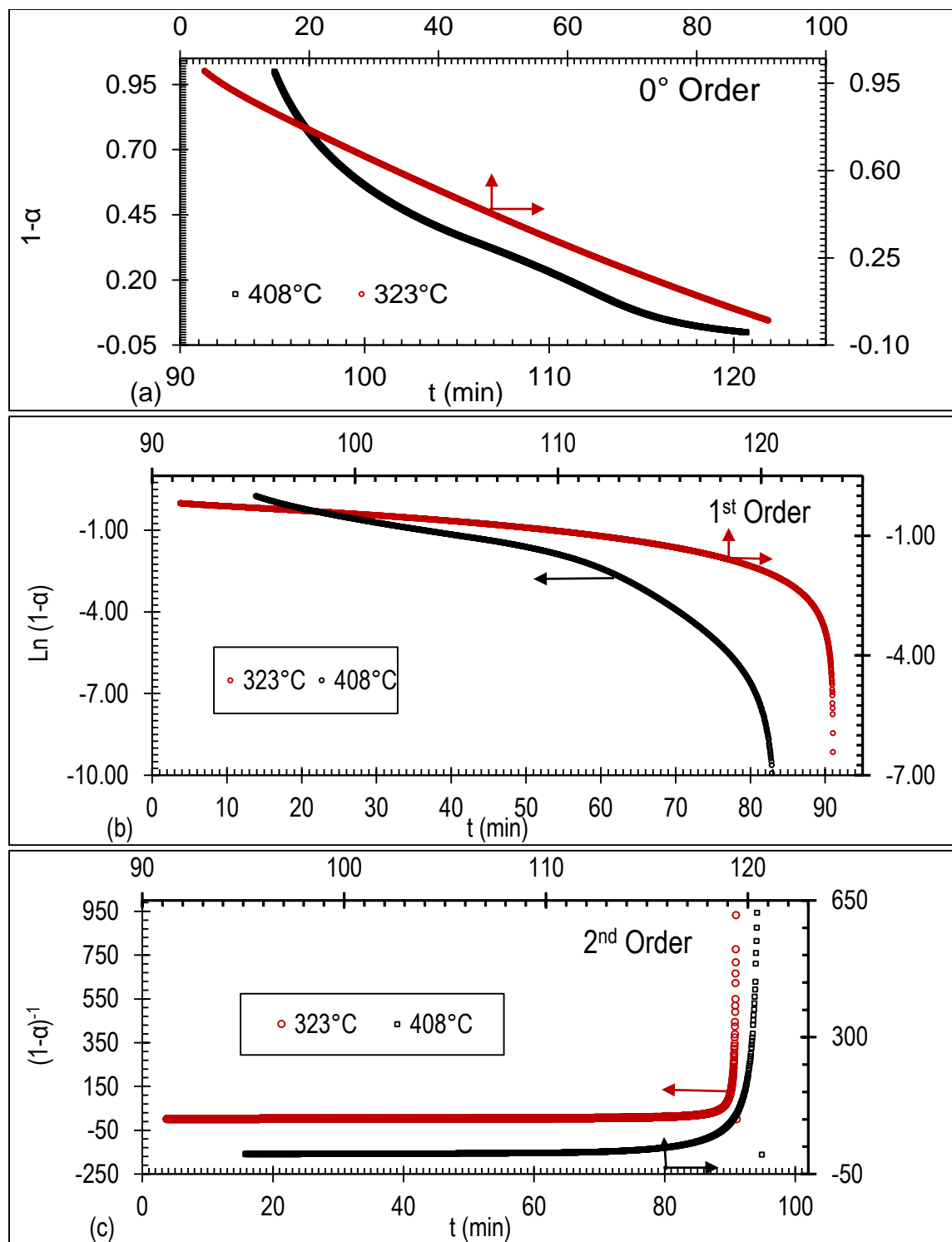


Fig 2. Isothermal curves corresponding to degradation of LG at the indicated temperatures based on Eq(7), Eq(8) and Eq(9) for (a) zeroth, (b) first order, and (c) second order reactions at 323°C and 408°C.

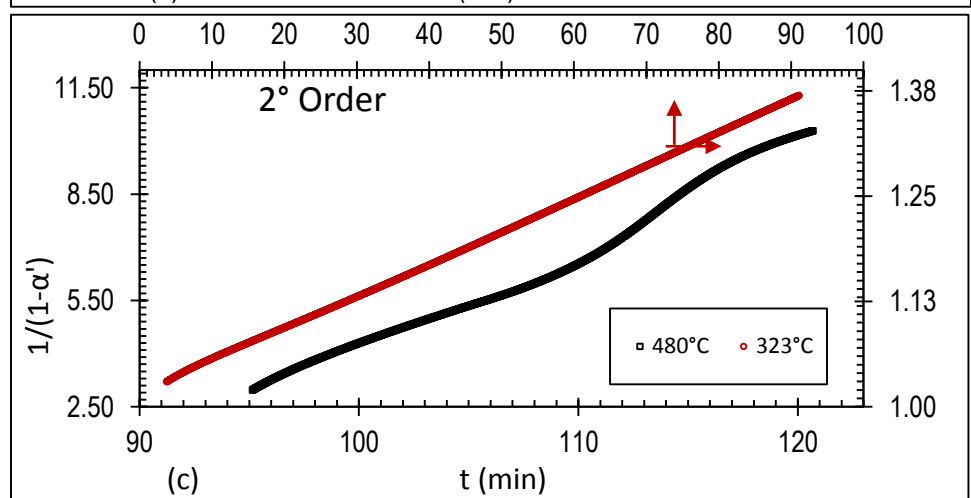
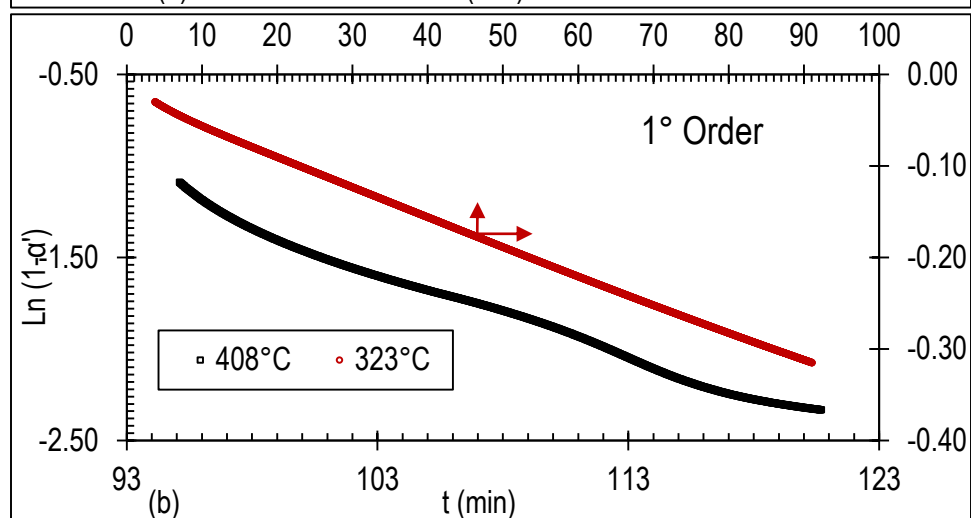
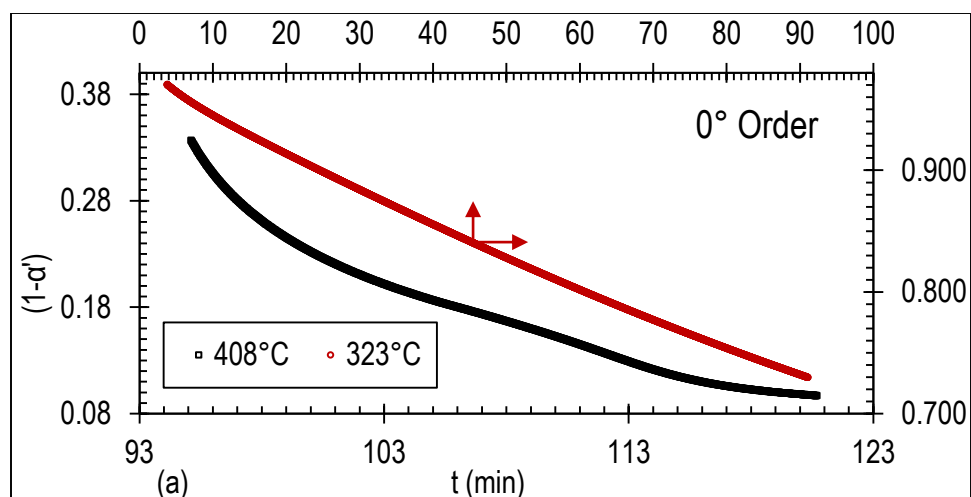


Fig 3. Isothermal curves corresponding to degradation of LG at the indicated temperatures based on Eq(7), Eq(8) and Eq(9) for (a) zeroth, (b) first order, and (c) second order reactions at 323°C and 408°C.

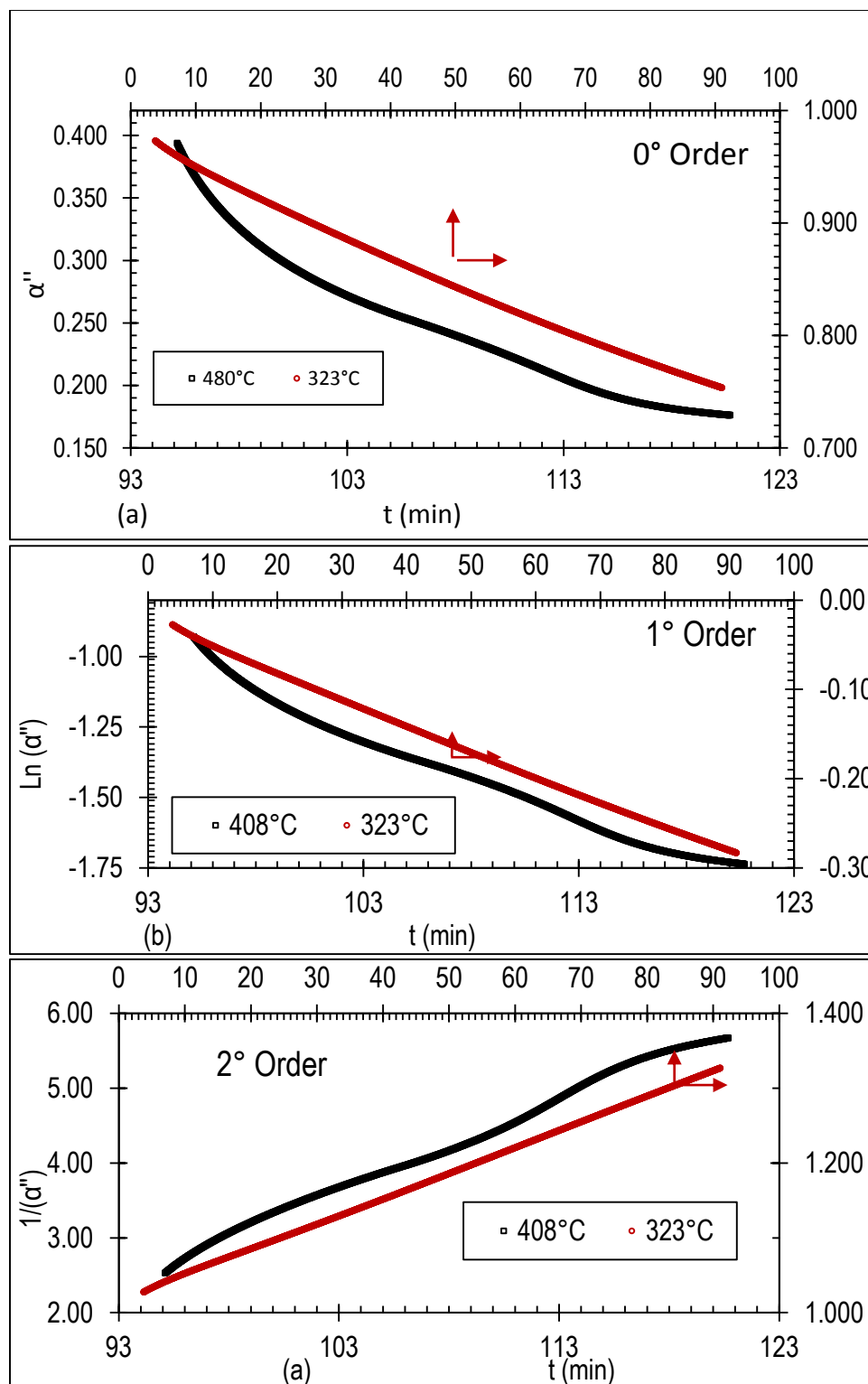


Fig 4. Isothermal curves corresponding to degradation of LG at the indicated temperatures based on Eq(7B), Eq(8B) and Eq(9B) for (a) zeroth, (b) first order, and (c) second order reactions at 323°C and 408°C.

Table 2. The reaction order n, **rate constant** k, and correlation coefficient Rsq of isothermal decomposition of LG at 323°C according to three definition of pyrolysis conversion. The bold face shows the suitable kinetic order and k.

Model	n	323°C		408°C	
		1000k	Rsq	1000k	Rsq
α	0	11.3	0.9966	33.9	0.9505
	1	37.3	0.7795	174	0.8160
	2	704	0.0129	7770	0.0368
α'	0	2.71	0.9966	8.12	0.9505
	1	3.23	0.9995	46.7	0.9933
	2	3.86	0.9997	290	0.9808
α''	0	2.47	0.9966	7.41	0.9505
	1	2.89	0.9993	29.6	0.9851
	2	3.40	0.9999	122	0.9953

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

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:

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

Rearranging Eq (4B) results:

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

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

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

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

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

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

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 (7B) to Eq(9B) relationships. The experimental data at 323°C apparently fits well into zeroth, first and second order, as was the case of α' . But the most suitable fit is for a second order reaction based on the highest value of Rsq (**Table 2**). The experimental data at the isotherm temperature 408°C poorly fits in 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 part 1 for dehydrochlorination of neoprene.

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

3.3 Reaction Order by Reiteration Method.

The value of n in Eq(6) and Eq(6B) 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 (Rsqr or R^2) value of each trial was plotted versus corresponding (1-n) value (eg **Fig 5a**). The n corresponding to the largest Rsqr value represents the best straight line, and the best reaction order. The slope of the plot of $w^{(1-n)}$ versus t (min) (eg **Fig 3b**) represents ak, after it is divided by (n-1). These results are summarized in **Table 3** assuming a = 1.

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 ($^\circ\text{C}$)	Model	1-n	1000Slope	n	1000 k	Rsqr
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

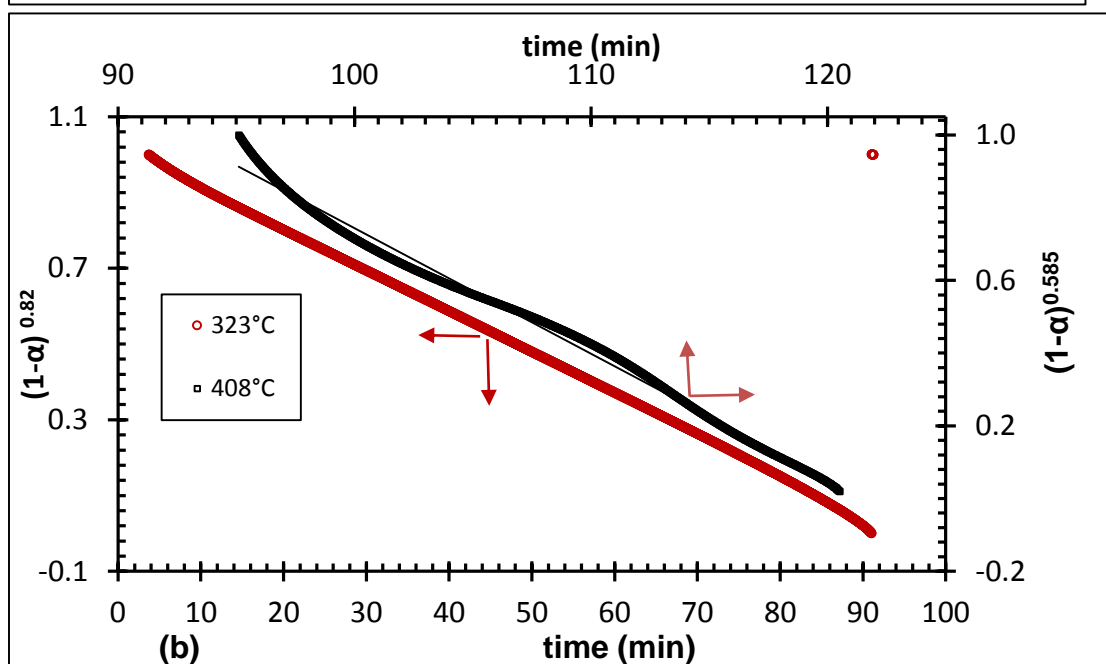
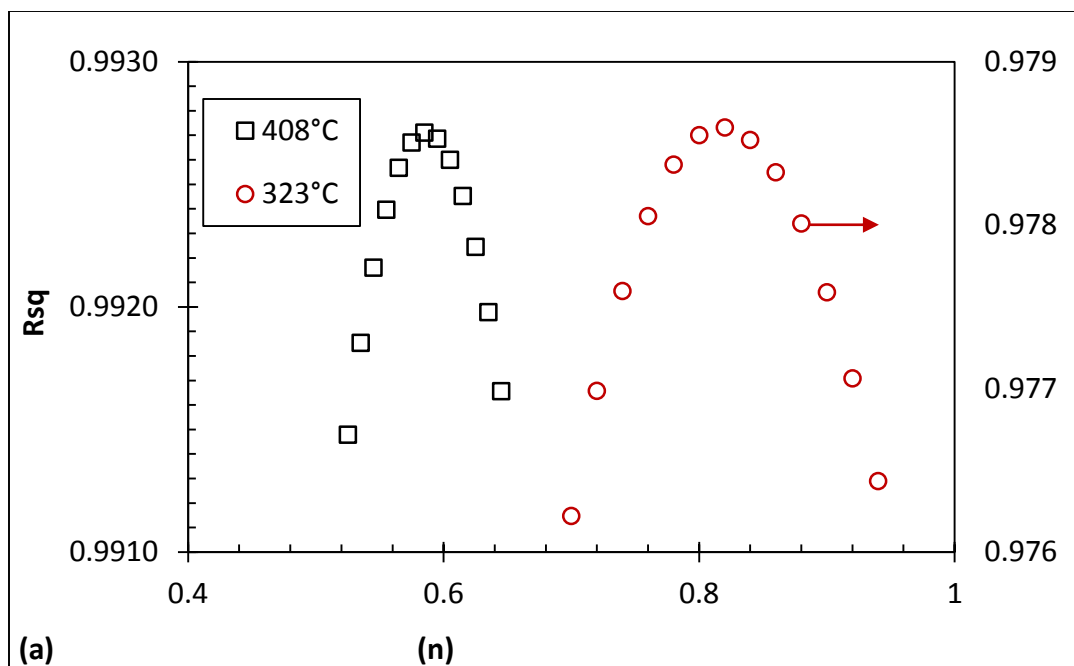


Fig 5. Treatments of the isothermal data at 323 and 408 °C to estimate the kinetics parameters of pyrolysis of LG: (a) the plot of R_{sq} versus reiterated values of $(1-n)$; (b) the plot of $(1-\alpha)^{(1-n)}$ versus t (min) according to Eq (6) for the best n value obtained from max of **Fig 5a**;

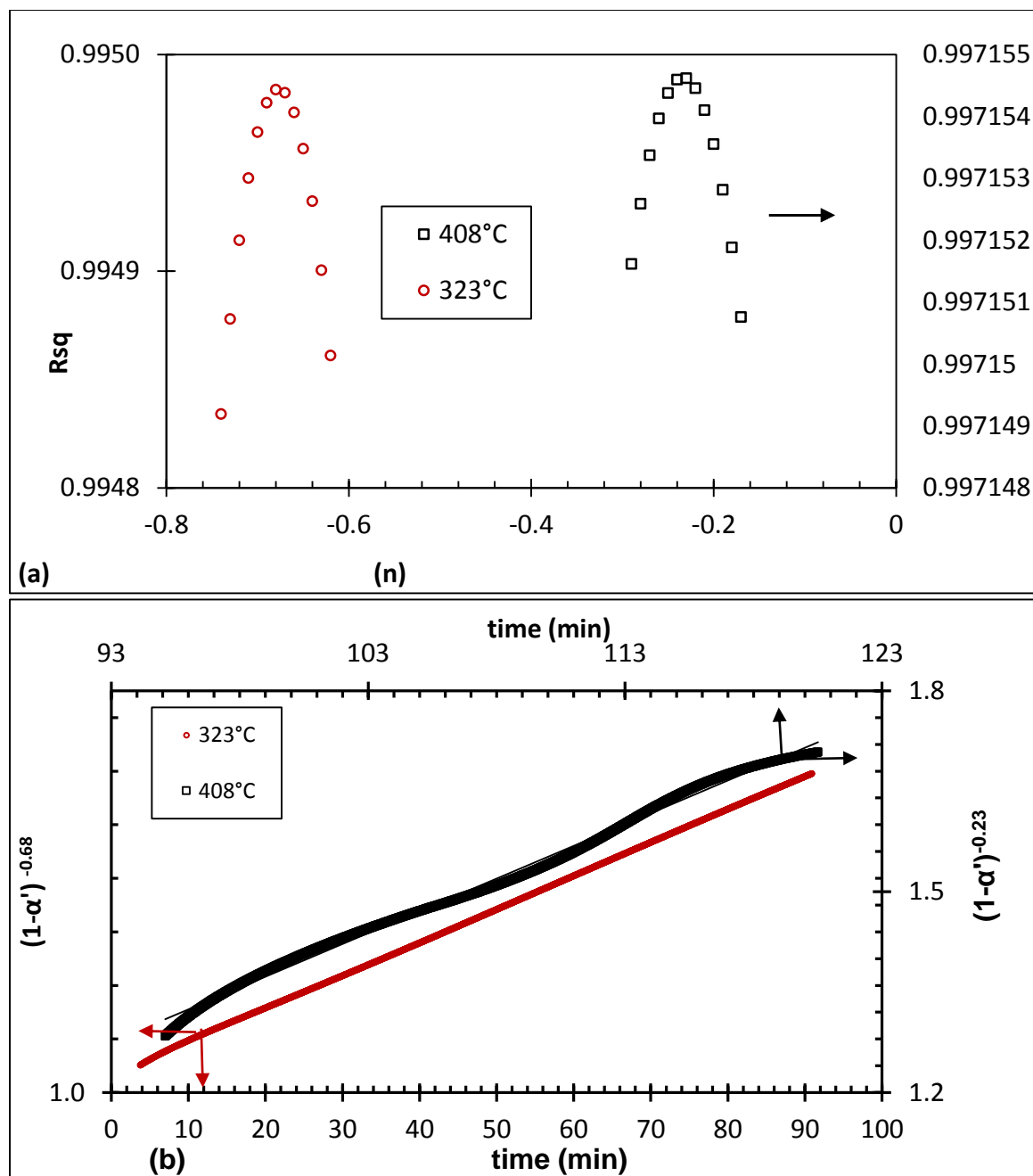


Fig 6. Treatments of the isothermal data at 323 and 408 °C to estimate the kinetics parameters of pyrolysis of LG: (a) the plot of R_{sq} versus reiterated values of $(1-n)$; (b) the plot of $(1-\alpha')^{(1-n)}$ versus t (min) for the best n value obtained from max of Fig 6a;.

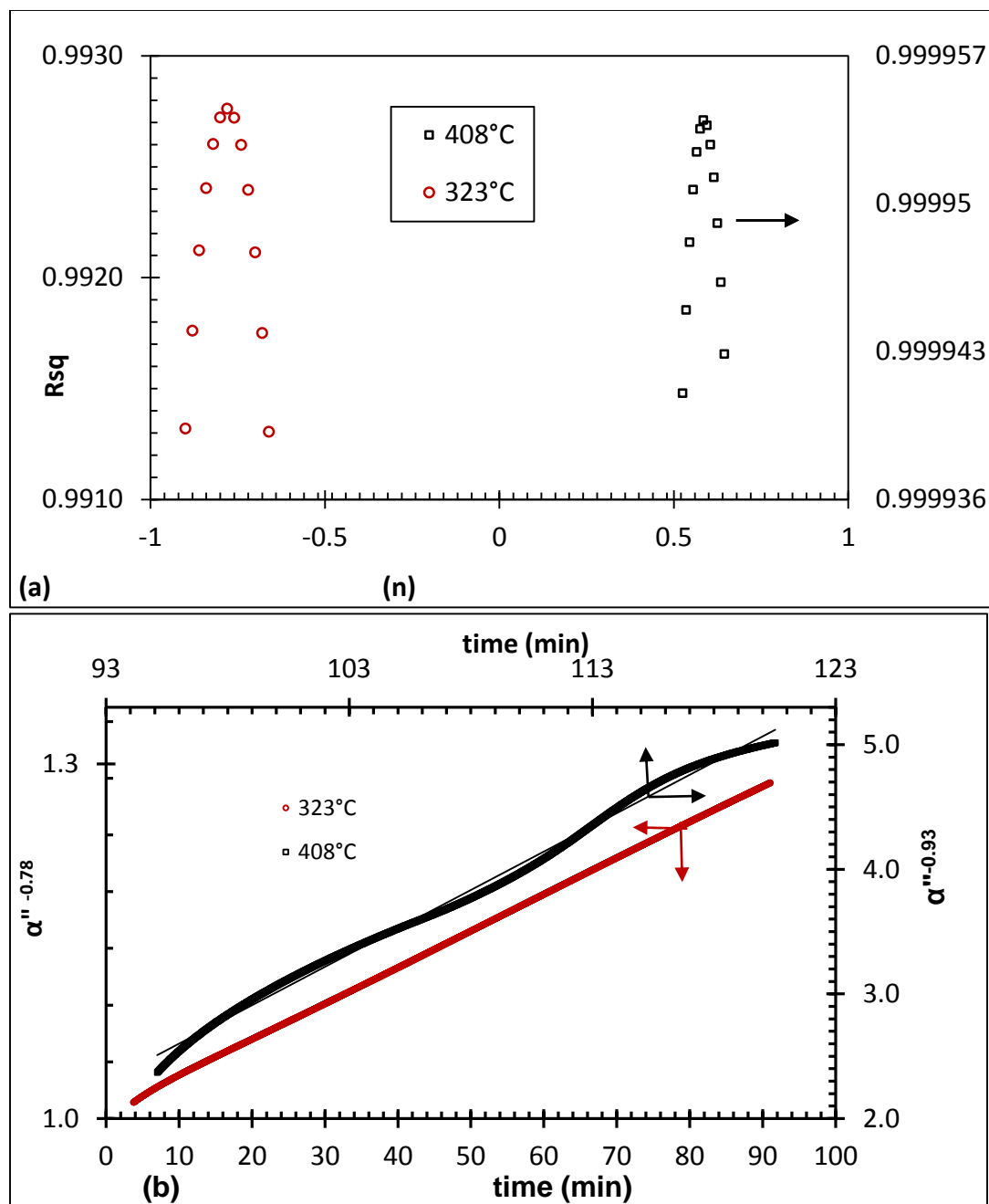


Fig 7. Treatments of the isothermal data at 345 and 405 °C to estimate the kinetics parameters of pyrolysis of LG: (a) the plot of R_{sq} versus reiterated values of $(1-n)$; (b) the plot of $\alpha''^{n(1-n)}$ versus t (min) according to Eq (6B) for the best n value obtained from max of Fig 7a.

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. 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 $6.8 < 1000k \text{ (min}^{-1}\text{)} < 23$ for pyrolysis of lignin with $134 < E_a \text{ (kJ/mol)} < 172$ [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.

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'' :

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

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

For a simple one step reaction the slope of the variation of $\ln r$ versus $\ln(1-\alpha)$, $\ln(1-\alpha')$, $\ln \alpha''$ yields the order of reaction and the intercept is a combination of stoichiometric coefficient of the reactants and rate constant (ak). Fig 8a depicted such a plot 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. The expansion of Fig 8a, indicated that there must be occurrence of many simultaneous zeroth order reactions with their proper k values (intercept). To confirm this, the rate of reaction was calculated again using experimental values of $(1-\alpha)$ at the corresponding time, $\Delta(1-\alpha)/\Delta t$, instead of dw/dt obtained from TGA driving program (Pyris). A plot of the values of rate $= -\Delta(1-\alpha)/\Delta t$, versus $\ln(1-\alpha)$ is illustrated in Fig 8b. In this plot, 5 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 4) were identified. 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].

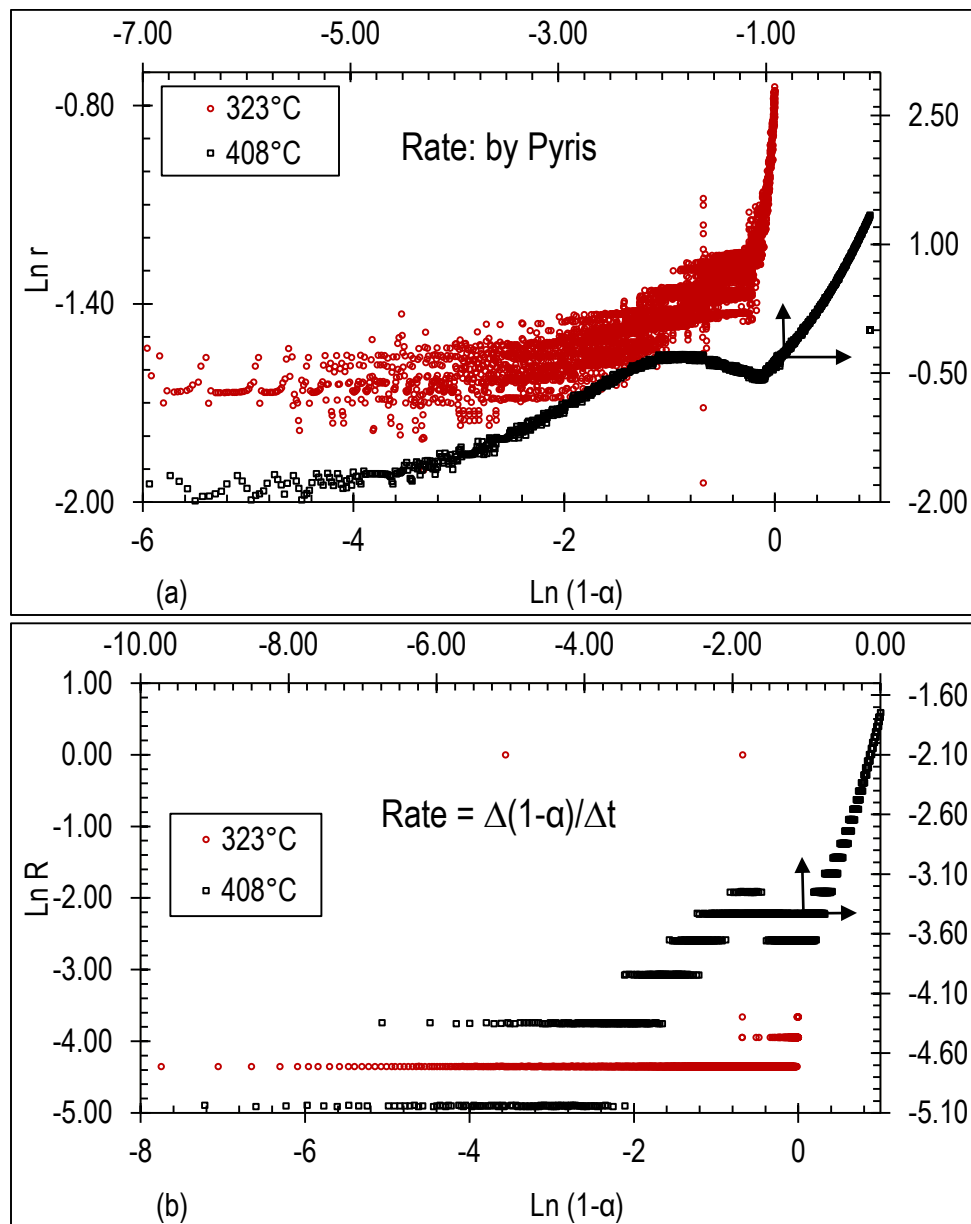


Fig 8 . (a) Double logarithmic variation of rate ($-dw/dt$) obtained by Pyris versus $\ln(1-\alpha)$. (b) Double logarithmic variation of rate ($R = -\Delta(1-\alpha)/\Delta t$) versus $\ln(1-\alpha)$.

277 **Table 4.** The values of $\ln k$ for the zeroth ordered reactions identified in **Fig 8b**

Reaction No.	$\ln k$ at		Reaction No.	$\ln k$ at 408°C
	323°C	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

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 279 Researcher, in order to simulate thermolysis also had assumed many simultaneous chemical reactions at high
 280 temperatures [14,47,48]. For example, Kruse et al [32] presented a detailed mechanism of PS pyrolysis based on
 281 population balance equations and the method of the moments in which up to 93 species and 4500 reactions were
 282 used to describe product distribution and average molecular weight. Similarly, detailed kinetics models of PE,
 283 polypropylene (PP) and PS pyrolysis were presented and discussed by other researchers [7-9]. The reported results
 284 of thermal degradation of plastic blends and their mutual interactions do not completely agree since each research
 285 group depending on their particular interests focused on different effects. The researchers who studied the
 286 decomposing of polymer mixtures discovered that the pyrolysis of a particular polymer in a polymeric mixtures
 287 behaves quite similarly to the pyrolysis of a pure polymer by step-by-step pyrolysis [14-15]. Thus, the additive rule
 288 was applicable to the pyrolysis of a mixture of polymers. Therefore, the pyrolysis of LG, which made of a mixture of
 289 many chemical, will be similar to pyrolysis of each individual ingredient resulting in many simultaneous concurrent
 290 reactions.

291 3.5. Evaluation of E_a from Thermal Scans.

292 Arrhenius relationship (Eq 11) relates the rate constant, k , to the activation energy of reaction E_a , the absolute
 293 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
 294 describe the efficiency of the molecular collisions in a chemical reaction.

$$296 \quad k = ze^{-\frac{E_a}{RT}} \quad (11)$$

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

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

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

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

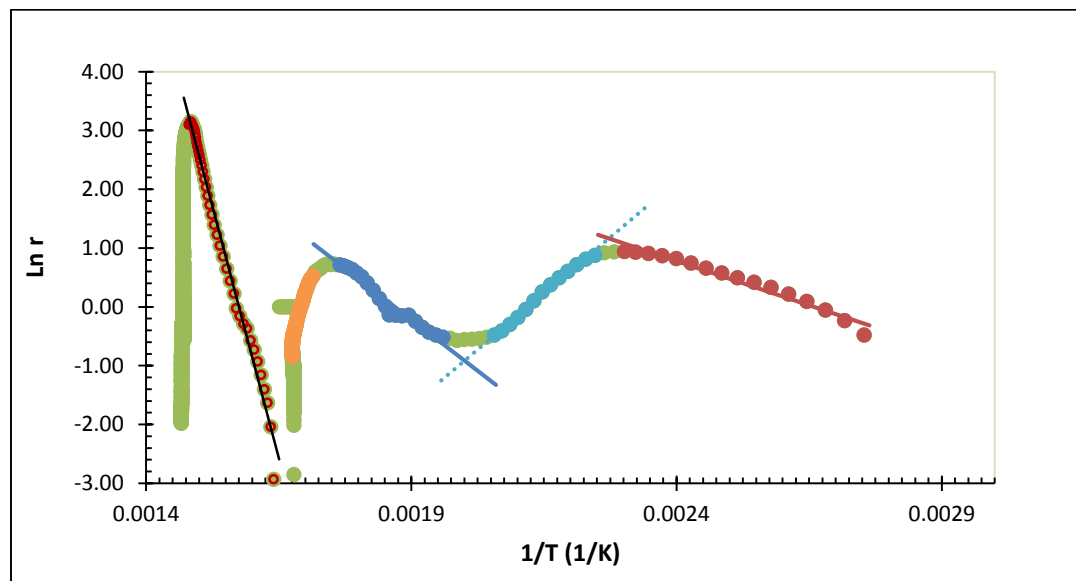


Fig 9 . Variation of logarithm of rate of decomposition of LG versus inverse of temperature.

Table 5. 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)
1	0.62	0.87	0.25	100.36	99.91	0.45	90	161	71	285.1	8.01	25.0
2	0.92	1.12	0.20	99.78	99.51	0.27	172	213	41	205.5	-16.2	-63.5
3	1.23	1.53	0.30	99.44	99.08	0.36	237	293	56	186.7	13.0	58.0
4	1.75	3.72	1.97	98.65	76.12	22.53	310	324	13	6.8	-61.0	-299.4
5	91.62	92.38	0.77	75.30	67.23	8.07	337	402	66	85.8	53.9	284.4
6	92.42	120.68	28.27	66.50	17.63	48.87	403	409	6	0.2	-592	-3350

Fig. 9 represents the application of Eq (13) to the experimental data covering a wide range of temperatures (50 -408 °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 5**). The positive E_a values can be related to the minimum energy required to disassociate a physical bond to release a volatile form a solid such as evaporation of moisture from reactants and to 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 5) 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.

The calculated $E_a = 25.0$ kJ/mol at temperature range of 90-161 °C (Table 5) 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 5) 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 5) 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 5) 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 8b 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 10a). Then, a plot of $\ln k$ versus invers of temperature according to Eq(13) was built (Fig 10b). 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 10b, respectively, which is not in agreement with the one obtained in the previous section. However, a close inspection of Fig 10b 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 6) was calculated from slope and the intercept of the data at higher temperatures (Fig 10b), respectively. This value is in the range with the values of E_a reported for pyrolysis of rubbers in car tires [21], 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.

The $E_a = 2.7$ kJ/mol (Table 6) 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 [42], however, the value of z heavily depends on the kinetic model. Therefore, it will be hard to do any comparison of the z value.

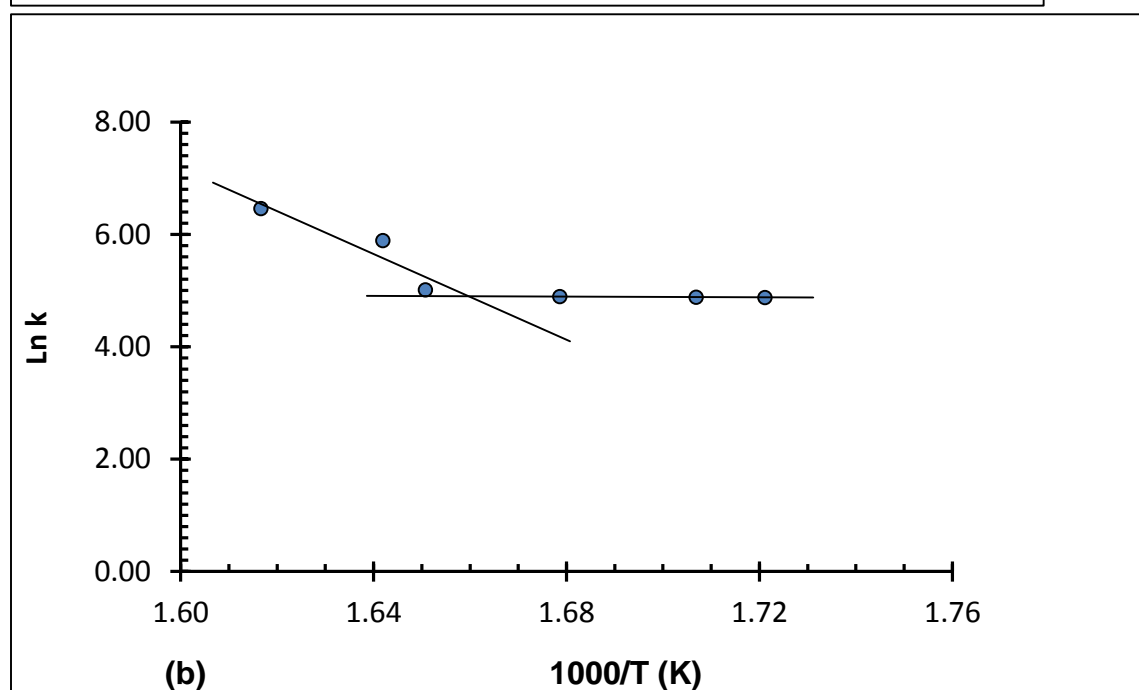
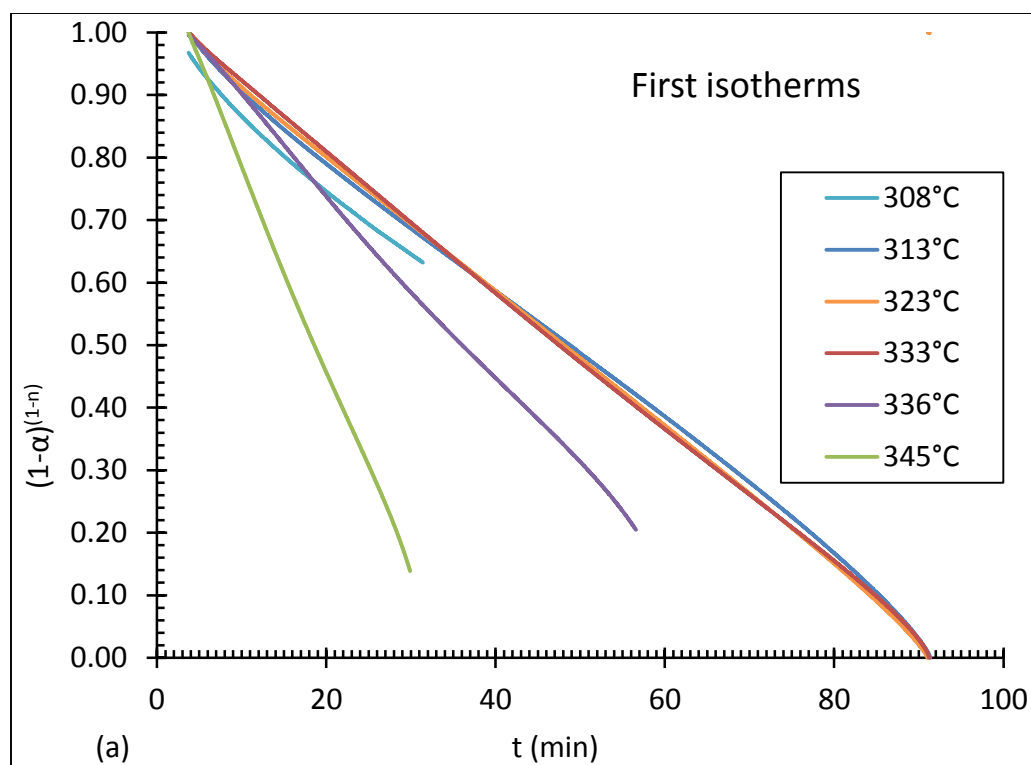


Fig 10. (a) Isothermal cures corresponding to the thermolysis of LG, recorded at 308, 313, 323, 333, 336 and 346 °C. (b) Plot of the values of $\ln k$ obtained from the slope of isotherms of Fig 10a versus corresponding inverse temperature.

Table 6. Arrhenius constant of thermolysis of LG.

	Ea	Z
LG all points	116.8654	3.22E+12
LG Hig T	317.3307	4.36E+29
LG Low T	2.724663	2.31E+02

CONCLUSIONS

The decomposition kinetics of LG at two isotherm 323°C and 408°C was studied by TGA. The obtained results showed that the kinetics parameters depend on the model to choose. Independent of the form of reaction extent function, 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 [52] and PTFE.

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REFERENCES

- 1 Obrecht, W., Lambert, J-P., Happ, M., Oppenheimer-Stix, C., Dunn, J., and Krüger, R. Rubber, 4. Emulsion Rubbers, in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Weinheim (2012).
- 2 Glenn, F. E. Chloroprene polymers, in Encyclopedia of Polymer Science and Technology. Published Online: 14 OCT 2005, doi:10.1002/0471440264.pst053
- 3 Pinto, F., Costa, P., Gulyurtlu, I., & Cabrita, I. (1999). Pyrolysis of plastic wastes. 1. Effect of plastic waste composition on product yield, Journal of Analytical and Applied Pyrolysis, 51(1), 39-55.
- 4 Bockhorn, H, Hornung, A., Hornung, U., Jakobströer, P. (1999). Modelling of isothermal and dynamic pyrolysis of plastics considering non-homogeneous temperature distribution and detailed degradation mechanism. Journal of Analytical and Applied Pyrolysis, Volume 49(1–2), 53-74.
- 5 Halla, W.J., Zakariab, N., and Williams, P.T. (2009). Pyrolysis of latex gloves in the presence of γ -zeolite. Waste Management, 29 (2), 797-803.

-
- 6 Behzadi, S. & Farid, M. **(2006)**. Feedstock recycling and pyrolysis of waste plastics: converting waste plastics into diesel and other fuels. Edited by J. Scheirs and W. Kaminsky, John Wiley & Sons, Ltd ISBN: 0-470-02152-7 P531.
 - 7 Boustier C, Vennande P, Veron J. **(1989)** Evolution of the product yield with temperature and molecular weight in the pyrolysis of polystyrene. *J. Anal. Appl. Pyrolysis*. 15:149. Ranzi, E. Dente, M. Faravelli, T., Bozzano, G. Fabini, S. Nava, R. Cozzani, V., Toguotti, L. **(1997)**. *J. Anal. Appl. Pyrolysis* 40-41, 305
 - 8 Koo, J.K., Kim, S.W., & Seo, Y.H. **(1991)**. Characterization of aromatic hydrocarbon formation from pyrolysis of polyethylene-polystyrene mixtures. *Resources, Conservation & Recycling*, 5(4), 365-382.
 - 9 Westerhout, R.W.J., Waanders, J. Kuipers, I.A.M. van SWaaij, W.P.M, **(1997)**. Kinetics of the low-temperature pyrolysis of polyethene, polypropene, and polystyrene modeling, experimental determination, and comparison with literature models and data. *Ind. Eng. Chem. Res.* 36, 1955-1964.
 - 10 Lehmann, F.A. & Brauer, G.M. **(1961)**. Analysis of pyrolyzates of polystyrene and poly(methyl methacrylate) by gas chromatography. *Analytical Chemistry* 33(6) 679-676.
 - 11 Gargallo, L., Hamidi, N., Radic, D., & Tagles, L.H. **(1989)**. Thermogravimetric Analysis of Poly(dialkylphenyl methacrylate)s. *Thermochemica Acta*, 143, 75-84.
 - 12 Gumula, T, Paluszkiwicz, C., & Blazewicz, S. **(2009)**. Study on Thermal Decomposition Processes of Polysiloxane Polymers—From polymer to Nanosized Silicon Carbide. *Journal of Analytical and Applied Pyrolysis*, 86(2), 375–380.
 - 13 Insura, N., Onwudili, J.A. & Williams, P.T. **(2010)**. Catalytic Pyrolysis of Low-Density Polyethylene over Alumina-Supported Noble Metal Catalysts. *Energy & Fuels*, 24(8), 4231-4240.
 - 14 Koo, J.K., Kim, S.W., & Waste. **(1993)**. Reaction Kinetic Model for Optimal Pyrolysis of Plastic Waste Mixtures. *Management & Research* 11(6), 515-529.
 - 15 Costa, P., Pinto, F., Ramos, A. M., Gulyurtlu, I., Cabrita, I., & Bernardo, M. S. **(2010)**. Study of the Pyrolysis Kinetics of a Mixture of Polyethylene, Polypropylene, and Polystyrene. *Energy & Fuels*. 24(12), 6239-6247.
 - 16 Smolders, K., & Baeyens, J. **(2004)**. Thermal Degradation of PMMA in Fluidized Beds. *Waste Management*, 24(8), 849-857.
 - 17 Straus, S & Madorsky, S. L. **(1953)**. Pyrolysis of Styrene, Acrylate, and Isoprene Polymers in a Vacuum. *Journal of Research of the National Bureau of Standards*, 50(3), 2405.
 - 18 Cooley, J. H. & Williams, R. V. **(2003)**. The Pyrolysis of Polystyrene. *Chem. Educator*, 8, 309-311.
 - 19 Onwudili, J.A., Insura, N., & Williams, P.T. **(2009)**. Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: Effects of temperature and residence time. *Journal of Analytical and Applied Pyrolysis*, 86(2), 293-303.
 - 20 Zakaria, N., Ani F. N., Yunus, M. N. M., and Husain, M .A. S. **(2011)** Oxidative pyrolysis of examination rubber gloves in the integral pyrolysis test plant. *International Journal of Mechanical and Materials Engineering (IJMME)*, Vol.6, No.1, 1-9
 - 21 Mui, E. L. K. , Lee, V. K. C. , Cheung, W. H., and McKay, G. **(2008)** Kinetic Modeling of Waste Tire Carbonization, *Energy & Fuels* 22, 1650–1657
 - 22 Reisman J. I., Lemieux P. M. *Air emissions from scrap tire combustion*, report no. EPA-600/R-97-115, USEPA: Washington, DC, 1997.
 - 23 Sarker, M. Rashid, M. M. Rahman, R. & Molla, M. **(2012)**. Conversion of Low Density Polyethylene (LDPE) and Polypropylene (PP) waste plastics into liquid fuel using thermal cracking process. *British Journal of Environment & Climate Change*, 2(1), 1-11.
 - 24 Williams, E.A., & Williams, P.T. **(1997)**. Analysis of products derived from the fast pyrolysis of plastic waste. *Journal of Analytical and Applied Pyrolysis*, 40-41, 347-363.
 - 25 Williams, P.T., & Williams, E.A. **(1999)**. Fluidised bed pyrolysis of low density polyethylene to produce petrochemical feedstock. *Journal of Analytical and Applied Pyrolysis*, 51(1), 107 – 126.
 - 26 Atal, A.; Yiannis, A.; Levendis, J. C.; Dunayevskiy, Y.; Vourros, P. **(1997)** On the survivability and pyrosynthesis of PAH during combustion of pulverized coal and tire crumb. *Combust. Flame* 110 (4), 462–478.
 - 27 Huggett, C. & Levin, B.C. **(1987)**. Toxicity of the Pyrolysis and Combustion Products of Poly (Vinyl Chlorides): A Literature Assessment. *Fire and Materials*, VOL. II, 131-142.

-
- 28 Miranda, R., Pakdel, H., Roy, C., & Vasile, C. (2001). Vacuum pyrolysis of commingled plastics containing PVC II. Product analysis. *Polymer Degradation and Stability*, 73(1), 47-67.
- 29 Chuantong, Li. Rong, Lui, and Bo, B. Study on Kinetic Properties of Pyrolysis for Hospital Solid Wastes, Proceedings. 3rd ICIPEC, Hangzhou, China, October 2004.
- 30 Achilias, D.S., Roupakias, C., Megalokonomos, P., Lappas, A.A., & Antonakou, E.V. (2007). Chemical recycling of plastic wastes made from polyethylene (LDPE and HDPE) and polypropylene (PP). *Journal of Hazardous Materials*, 149(3), 536-542
- 31 Mastellone, M. L., & Arena, U. (2004). Bed Defluidisation during the Fluidised Bed Pyrolysis of Plastic Waste Mixtures. *Polymer Degradation and Stability*, 85(3), 1051-1058.
- 32 Kruse, T.M., Woo, O.S., Broadbent, L. (2001). Detailed mechanistic modeling of polymer degradation: application to polystyrene. *J. Chem. Eng. Sci.* 56, 971-979.
- 33 Ranzi E, Dente M, Faravelli T, Bozzano G, Fabini S, Nava R, Cozzani V, Tognotti L. (1997). Kinetic modeling of polyethylene and polypropylene thermal degradation J, Anal. Appl. Pyrolysis 40-41: 305.
- 34 Faravelli T, Bozzano G, Seasa C, Perego M, Fabini S, Ranzi E, Dente M, (1999). Gas product distribution from polyethylene pyrolysis J, Anal. Appl. Pyrolysis 52: 87.
- 35 Faravelli E, Pincioli M, Pizno F, Bozzano G, Dente M, Ranzi E. (2001) Thermal degradation of polystyrene. J. Anal. Appl. Pyrolysis 60:103
- 36 Hillier, J., Bezzant, T., and Fletcher, T.H. (2010) Improved Method for the Determination of Kinetic Parameters from Non-isothermal Thermogravimetric Analysis (TGA) Data *Energy Fuels* 24, 2841–2847
- 37 Schmidt, H. & Kaminsky, W. (2001). Pyrolysis of oil sludge in a fluidised bed reactor. *Chemosphere* 45(3), 285-290.
- 38 Zhu H. M., Yan J. H, Jiang X. G, Lai Y. E., Cen K. F. (2008). Study on pyrolysis of typical medical waste materials by using TG-FTIR analysis, *Journal of Hazardous Materials*, 153, 670-676.
- 39 . Hamidi, N., Massoudi, R., Shrestha, S., Lalmansingh, L., Pascoe, T., Oriakhi, C. and Whitesides, L. (2014). Waste Plastics: Pyrolysis of Powdered and Powder-Free Laboratory Examination Waste Gloves. *British Journal of Applied Science & Technology* 4 (6) Pages 967-1019.
- 40 Hamidi, N., Tebyanian, F., Massoudi, R., and Whitesides, L. (2013). Pyrolysis of Household Plastic Wastes. *British Journal of Applied Science & Technology* 3(3): 417-439.
- 41 Faravelli, T., Bozzano, G., Colombo, M., Ranzi, E., & Dente, M. (2003). Kinetic modeling of the thermal degradation of polyethylene and polystyrene mixtures. *Journal of Analytical and Applied Pyrolysis*, 70(2) 761 – 777.
- 42 Sanchez-Jimenez, P.E., Perejon, A., Perez-Maqueda, L.A., and Criado, J M., (2015). New Insights on the Kinetic Analysis of Isothermal Data: The Independence of the Activation Energy from the Assumed Kinetic Model *Energy and Fuel* 29, 392-397
- 43 Jiang, G., Nowakowski, D.J., Bridgwater, A.V. (2010). A systematic study of the kinetics of lignin pyrolysis. *Thermochim. Acta* 498, 61–66.
- 44 Cho, J. Chu, S. Dauenhauer, P. J. and Huber, G. W. (2012). Kinetics and reaction chemistry for slow pyrolysis of enzymatic hydrolysis lignin and organosolv extracted lignin derived from Maplewood. *Green Chemistry Green Chem.*, 14, 428-439.
- 45 Freeman, E.S. and Carroll, B. (1958). The Application of Thermoanalytical Techniques to Reaction Kinetics: The Thermogravimetric Evaluation of the Kinetics of the Decomposition of Calcium Oxalate Monohydrate *J. Phy. Chem* 64(4), 394-397.
- 46 Nasrollah Hamidi (2015) "Kinetics of Powder-Free Laboratory Examination Gloves at 345°C and 405°C by Thermogravimetric Analysis" *Journal of Advances in Research*. (in press)
- 47 Ranzi, E., Dente, M., Faravelli, T., Bozzano, G. Fabini, S. Nava, R. Cozzani, V., Tognotti, L., (1997). Kinetic modeling of polyethylene and polypropylene thermal degradation, J. Anal. Appl. Pyrolysis 40-41, 305-319.
- 48 Faravelli, E. Pincioli, M. Pizno, F. Bozzano, G. Dente, M. Ranzi, E. (2001). Thermal degradation of polystyrene, J. Anal. Appl. Pyrolysis 60, 103-121

-
- 49 Wang, H-H. (2007). Kinetic Analysis of Dehydration of a Bituminous Coal Using the TGA Technique. *Energy & Fuels* 21, 3070–3075.
- 50 Peterson, J.D., Vyazovkin, S., and Wight, C.A. (1999). Kinetic Study of Stabilizing Effect of Oxygen on Thermal Degradation of Poly(methyl methacrylate) J. Phys. Chem. B, 103, 8087-8092 and Grassie, N.; Melville, H. W. Proc. R. Soc., Ser. A 1949, 199, 25.
- 51 Vinu, R. and Broadbelt, L. J. (2012) A mechanistic model of fast pyrolysis of glucose-based carbohydrates to predict bio-oil composition. *Energy & Environmental Science*, 5, 9808-9826.
- 52 Senneca, O.; Salatino, P.; Chirone, R. (1999) A fast heating-rate thermogravimetric study of the pyrolysis of scrap tires. *Fuel*, 78, 1575–1581