Kineticsof Powder-Free Laboratory Examination Gloves at 323°C and 408°Cby Thermogravimetric Analysis

ABSTRACT

At two consecutive temperatures, 323°C and 408°Cas 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 methods were used to evaluate the kinetics parameters related to the decomposition of LG atbothisotherms. The results of the study indicated that the kinetics parmeters depends 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 extend 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 bot temperatures; the best order for the thermolysis found to be 1.78, and 1.93.The activation energy of thermalizes (Ea) was estimated bythermal scans, and isotherms at 308, 313, 323, 333, 336, and 345 °C. The value of Ea for the process at lower temperature was near to Ea corresponding to evaporation of volatiles, and at higher temperaturesEa was below constituents' chemical bond energies but it was in the range of Ea for decomposition of polymethylmethacrylate and it was below of Ea for decomposition of rubber in tires.

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

1. INTRODUCTION

Thedisposalofwaste plasticsisaseriousconcerninthe areaofenvironmentalprotectionandsustainability.Recentprocessingtechniquessuchasenergyrecovery including plastics-derivedfuelhavebeenprovensuccessful[1,2,3,4,5];however,gaseousemission including hydrogen chloride from wastes based on poly(vinyl chloride) (PVC) [6,7] and neoprene[8] resins and polycyclicaromatichydrocarbons (PAHs)evolved from rubber resins[9]inthecombustionprocessremainsabarrierintheapplication. 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 [eg14,15]. Some widely used polymeric materials such as poly(methyl methacrylate) (PMMA), upon heating, decomposed to original monomers [16] likewise PS to styrene [12,17,18,19]. 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 6,7]. Thus the World Health Organization (WHO) is opposed to land filling or incineration of these wastes. A study on kinetics properties of pyrolysis of selected medical wastes such as absorbentcotton, medical respirator, bamboo sticks [21] and cotton gauges, packaging boxes, capsule plates and transfusion tubes [25] were conducted by a number of researchers.

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 [22,23].The researchers were presented several detailed kinetic models describing the polymer degradation [24,25,26,27,28]. 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 [29].

The waste plastics contrary to the other household waste are not consumed by micro-organism in landfill, water, andsurface. Theirincineration in landfills neither contribute to energy gainnor to environmental benefits [30].Therefore, energy recovery by step-by-step thermolysis [31] which converts waste to the valuable petrochemicalsmust be considered [32,33]. To simulate the condition of waste plastics thermolysis, considerable attention was given to the thermal degradation of plastic blends such as polystyrene (PS) mixtures with other materials and their mutual interactions [34,35,36]. The kinetics of decomposition of plastics are of interest from different points of viewincluding evolution of harmful substances during fires or waste incineration, recovering of chemical raw materials from waste plasticsand designing of a practical recycling procedures

The safety protection required in scientific laboratories, technological industries, and health industries has increased demand for the production of latex gloves and consequently natural rubber latex [37]. Neoprene or polychloroprene $(-CH_2-CCl=CH-CH_2-)_n$ is a family of synthetic rubbers that are produced by free-radical polymerization of 2-chlorobutadiene ($CH_2=CCl-CH=CH_2$)[38]. Neoprene exhibits good chemical stability, and maintains flexibility over a wide temperature range. It is used in a wide variety of applications, such as laptop sleeves, orthopedic braces (wrist, knee, etc.), electrical insulation, liquid and sheet applied elastomeric membranes or flashings, and automotive fan belts.[39]

Co-pyrolysis of waste plastic with other natural wastes has been studied. For example, the co-pyrolysis of pine cone with synthetic polymers [40] and characterization of products from the pyrolysis of municipal solid waste [41] and isothermal co-pyrolysis of hazelnut shell and ultra-high molecular weight polyethylene (PE) [42] are indicative of the fact that wastes are also useful materials. To avoid the landfill problem and plastic wastes hazards, various techniques for the treatment of waste plastics have been investigated to complement existing landfill and mechanical recycling technologies. The objectives of these investigations were to convert the waste into valuable products such as fuel, synthetic lubricants, and tar for asphalt pavement before the waste headed to a landfill.

Based on our previous experiments [43,44] 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 [45]. 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 form 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) at this temperature which lead to full degradation of LG. This study reports the results of non-catalytic conversion of examination gloves, a neoprene based materials.

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 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.

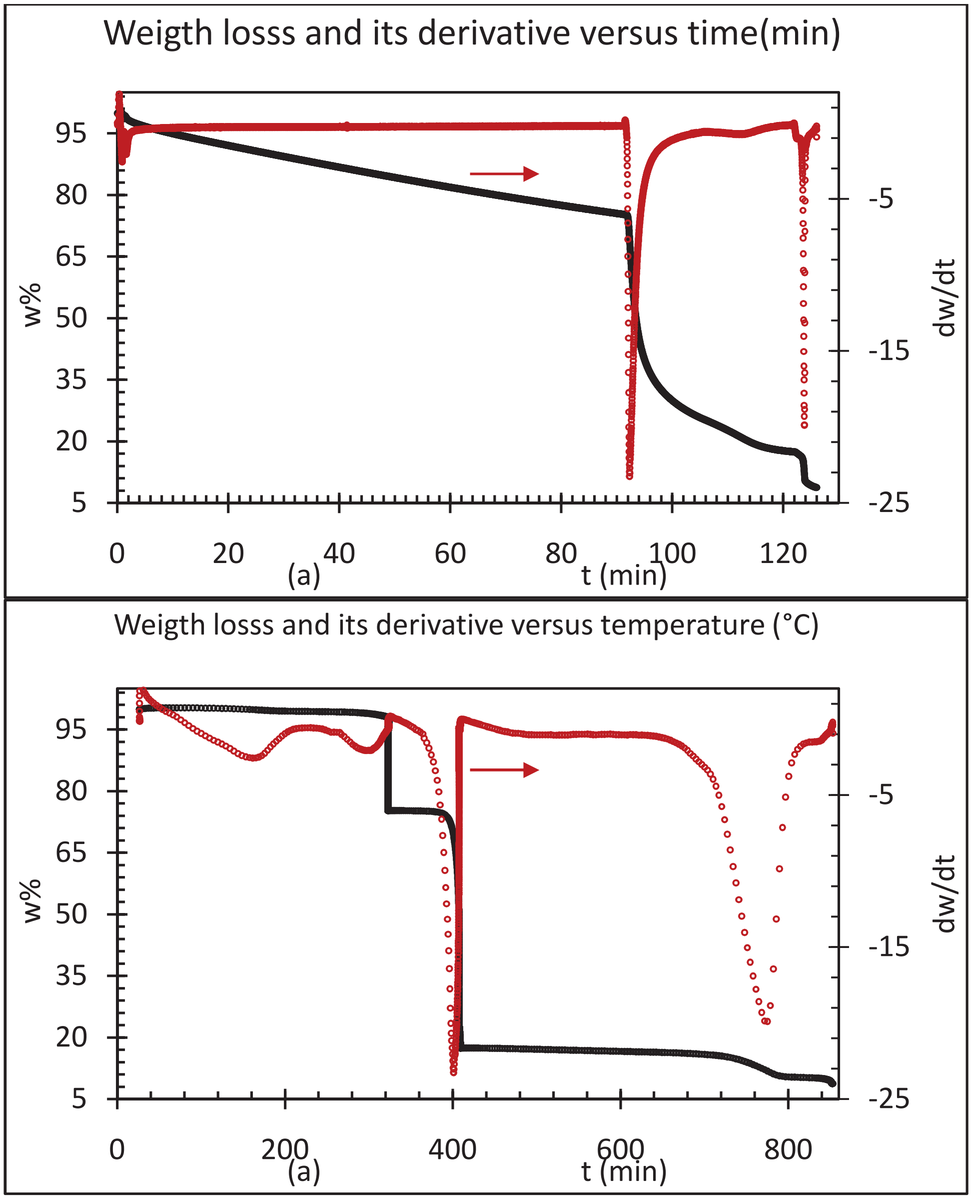


Fig 1. The thermogram of LG sample: (a) weight loss versus time and derivative of weight loss (dw/dt) by time, and (b) weight loss versus temperature and dw/dt at the given temperatures.

The initial sample weight was 6.319 mg; however, in calculations, the weight was normalized to weight percentage of the samples. 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 Excel 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 HClwere 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 30min. 8.86% of material volatized 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).

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%	Δw%	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&6	120.70	126.00	5.30	17.63	8.77	8.86	409	853	444	83.8

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:

$$aA \rightarrow \text{Products} \qquad (1)$$

$$Rate = r = -\frac{dw}{adt} = kw^n \qquad (2)$$

where w is the activity of reactantA 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-gasesare 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 in three ways of evaluation as following:

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

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

The rate of conversion, dα/dt,in relation to reactants, (1-α), can be expressed as:

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

Rearranging Eq (4) results:

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

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

$(1-\alpha)^{1-n} = -(1-n)akt + c$Except for n = 1 (6)

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

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

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

Figs 2 (a,**b,** and**c)** shows 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. However, the experimental data at 323C° fit into azeroth order reaction with R^2= 0.997 (**Fig 2a, Table 2)**.

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.

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

The kinetics equations remain similar as Eq(4) to Eq(9). **Figs 3 (a**, **b,** and **c)** shows 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 fits well into zeroth, first and second order, however the experimental data are more suitable for the second order reaction based on the value of Rsq (**Table** 2). Postolating a second order reaction for the first step radical decomposition of neopren is quate rational based on the following chemical reaction equations:

$(\text{-CH}_2\text{-CCl=CH-CH}_2\text{-})_n \rightarrow (\text{-CH}_2\text{-C.=CH-CH}_2\text{-})_n + \text{Cl.}$ Faster step.

$(\text{-CH}_2\text{-C.=CH-CH}_2\text{-})_n \rightarrow (\text{-.CH-CH=CH-CH}_2\text{-})_n \leftrightarrow (\text{-CH=CH-.CH-CH}_2\text{-})_n$ Faster steps

$(\text{-CH=CH-.CH-CH}_2\text{-})_n + \text{Cl.} \rightarrow (\text{-CH=CH-CH=CH-})_n + \text{HCl.}$ Slowest step.

The rate = k[Cl.][$(\text{-CH=CH-.CH-CH}_2\text{-})_n$], a second order reaction.

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

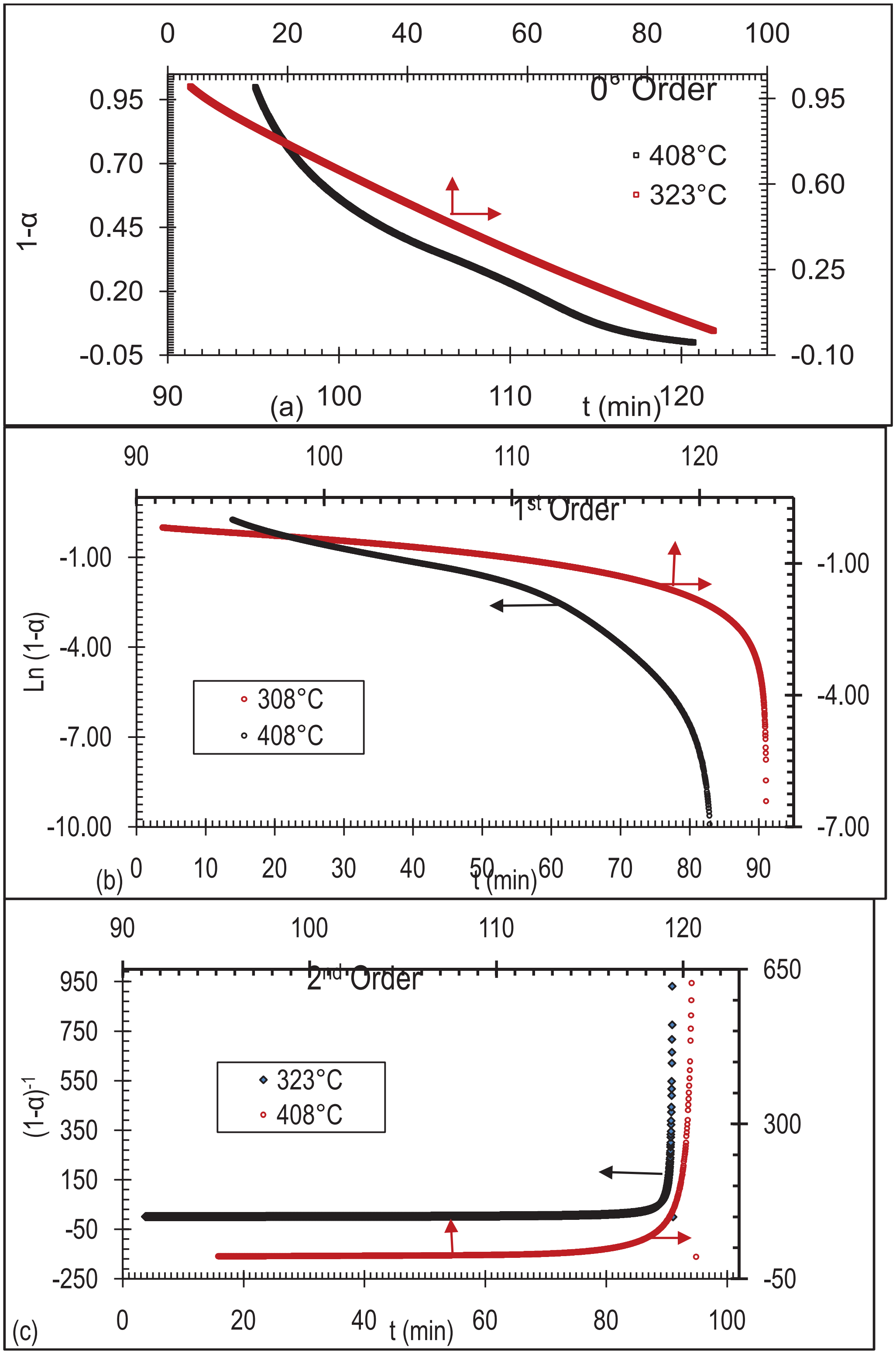


Fig 2. Isothermal curves corrsponding to degradation of LG at the indcated temperaturs based on Eq(7), Eq(8) and Eq(9) for (a) zeroth, (b) first order, and (c) second order reactions at 323°C and 408°C.

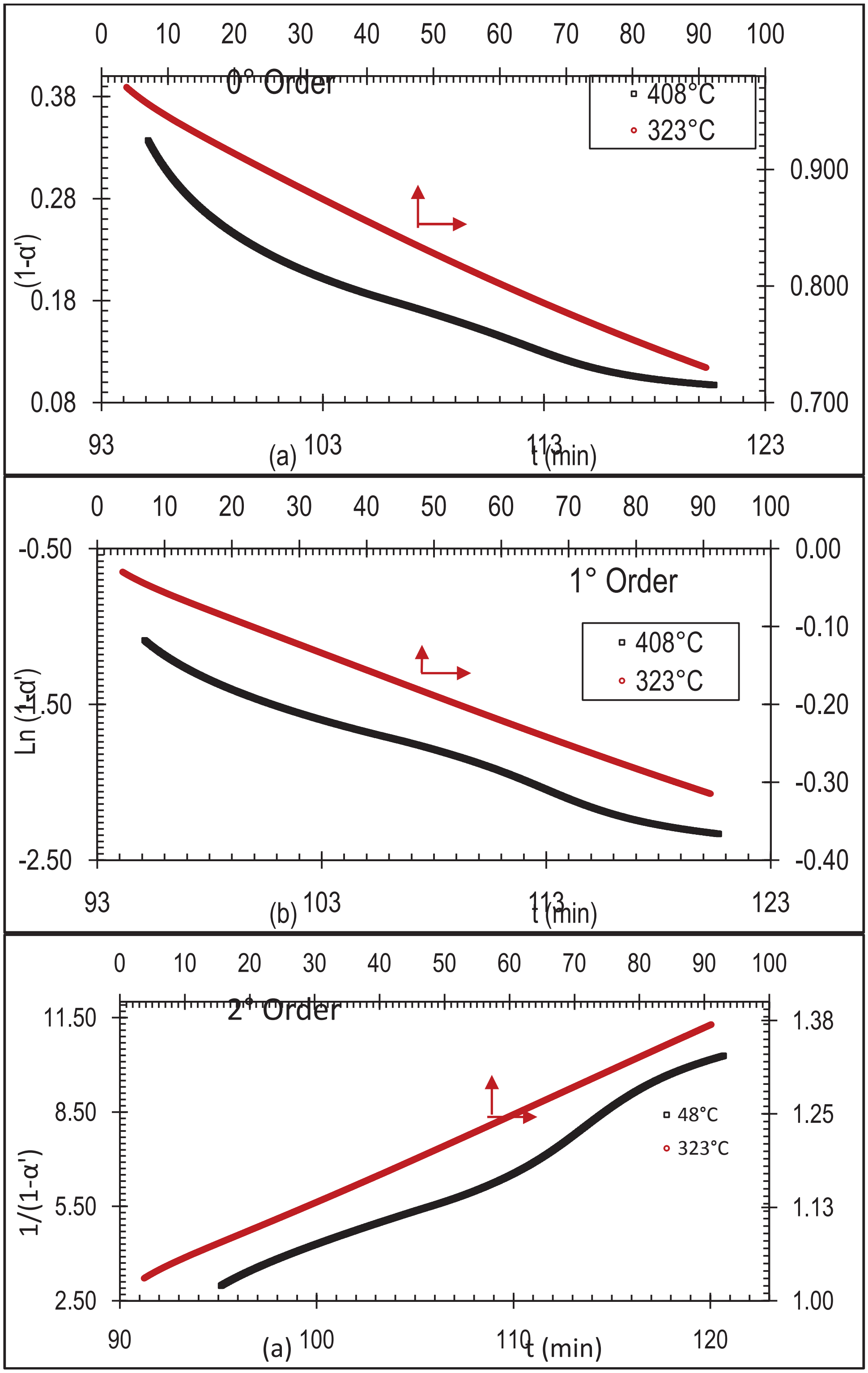


Fig 3. Isothermal curves corrsponding to degradation of LG at the indcated temperaturs based on Eq(7), Eq(8) and Eq(9) for (a) zeroth, (b) first order, and (c) second order reactions at 323°C and 408°C.

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

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

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

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

Rearranging Eq (4B) results:

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

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

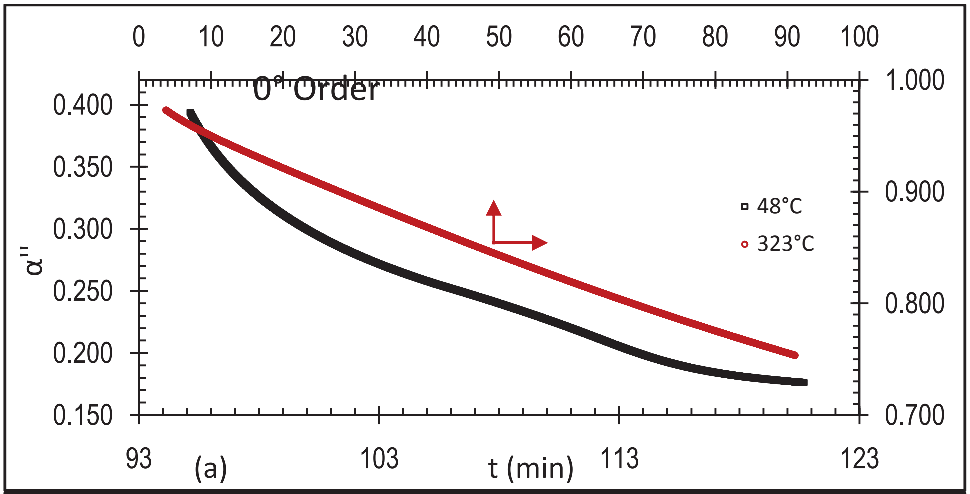
$$\alpha''^{1-n} = -(1-n)akt + c \quad \text{Except for } n = 1 \qquad (6B)$$

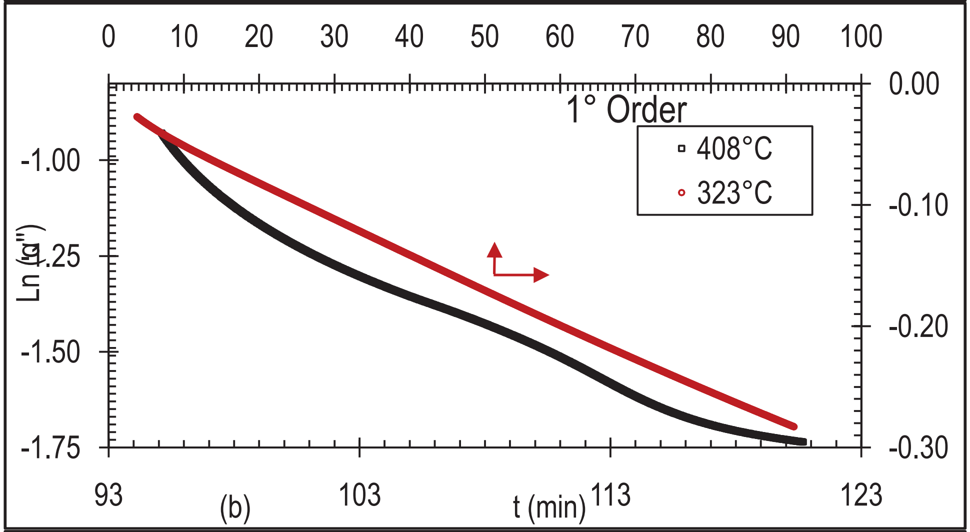
$n = 0$, $\alpha'' = -akt + \alpha''_0$ (7B)

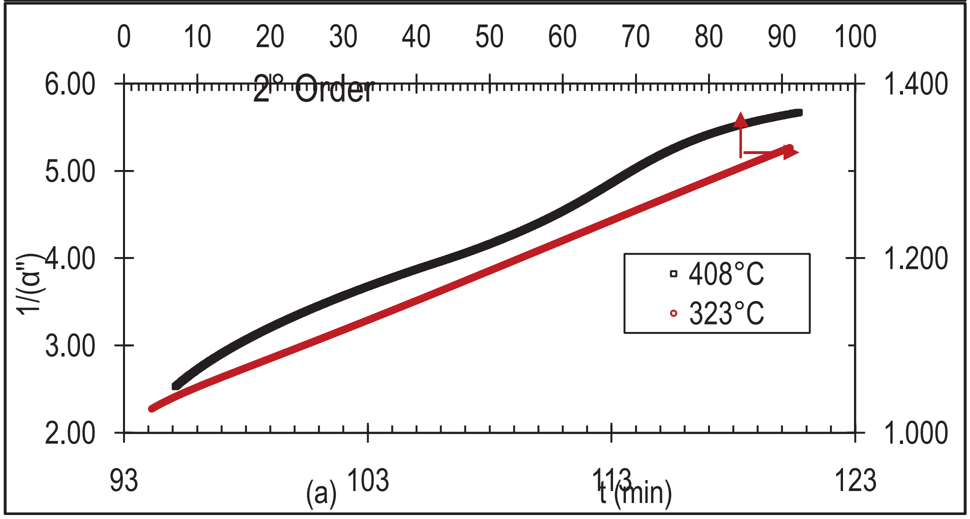
$n = 1$, $\text{Ln}\alpha'' = -akt + \text{Ln}\alpha''_0$ (8B)

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

Figs 4 (a, **b,** and **c)** shows 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). Also, the experimental data at the isotherm temperature 408°C poorly fits in the second order reaction. Postolating a second order reaction for the first step radical decomposition of neopren is quate rational based on the mechanism propues in part 1 for dehydro chlorination of neoprene.


0° Order
0
10
20
30
40
50
60
70
80
90
100
0.400
0.350
0.300
0.250
0.200
0.150
1.000
0.900
0.800
0.700
α''
48°C
323°C
93
103
113
123
(a)
t (min)


1° Order
0
10
20
30
40
50
60
70
80
90
100
-1.00
-1.25
-1.50
-1.75
0.00
-0.10
-0.20
-0.30
Ln (α'')
408°C
323°C
93
103
113
123
(b)
t (min)


2° Order
0
10
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60
70
80
90
100
6.00
5.00
4.00
3.00
2.00
1.400
1.200
1.000
1/(α'')
408°C
323°C
93
103
113
123
(a)
t (min)

Fig *4*. Isothermal curves corrsponding to degradation of LG at the indcated temperaturs 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, k, and correlation coefficient Rsq of isotheral decomposition of LG at 3423°C according to three definition of pyrolysis conversion. The bold face shows the suitable kinetic order and k.

		323	°C	408	°C
Model	n	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 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 of k =0.0047 1/min reported for polytetrafluoroethylene (PTFE) at lowest decomposition temperature, 480°C [[46]].

3.3Reaction 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 eachvalue of n was constructed from experimental data. Then, the correlation coefficient(Rsq or R^2) value of each trial was plotted versus corresponding (1-n) value (eg**Fig 5a**). The n corresponding to the largest Rsq 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.

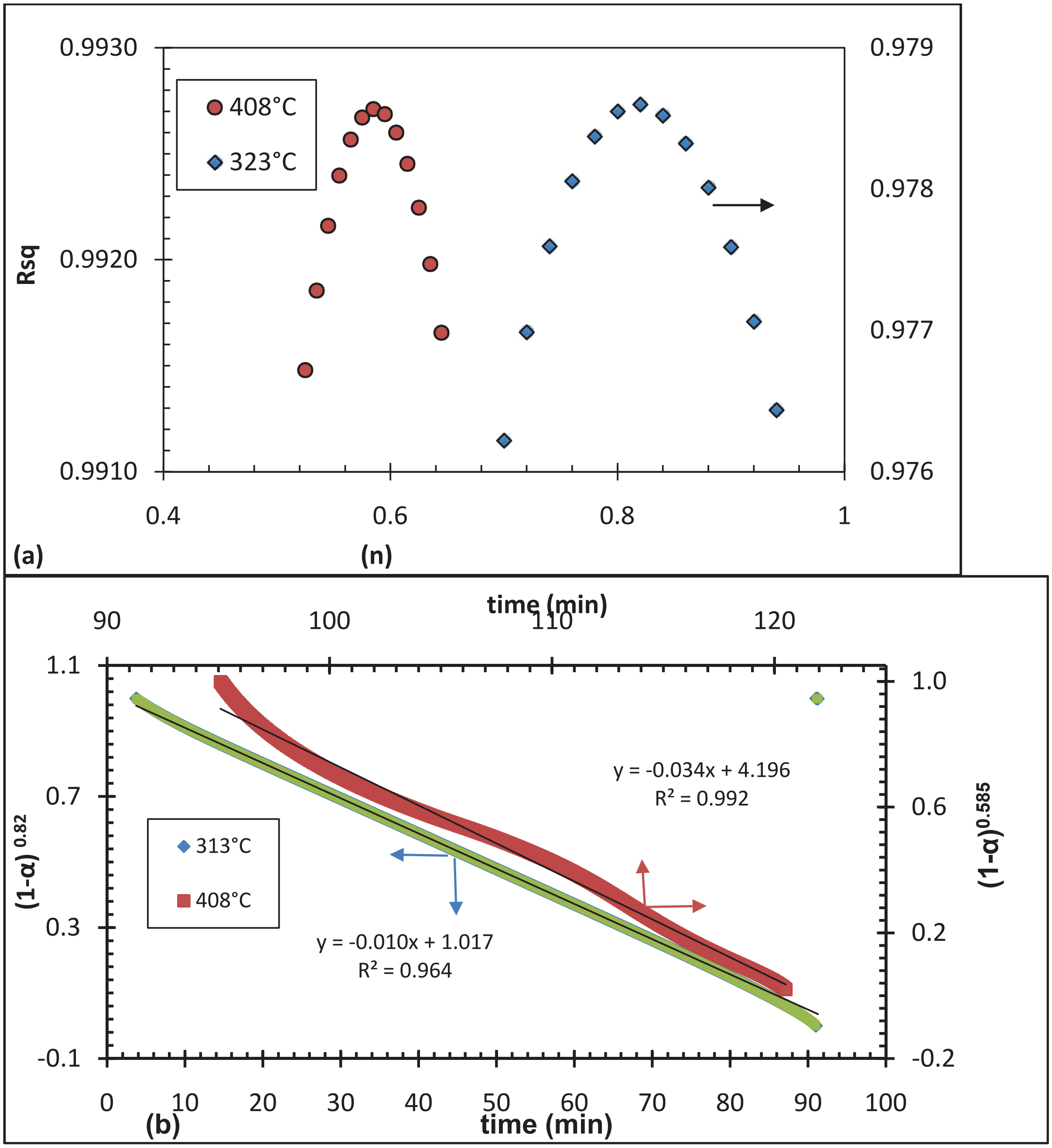

Fig 5. Treatments of the isothermal data at 323 and 408 °C to estimate the kinetics parameters of pyrolysis of LG: (a) the plot of Rsq versus reiterated values of (1-n); (b) the plot of $(1-\alpha)^{(1-n)}$ versus t (min) according to Eq (6) for the best n value obtained from max of **Fig 5a**;.

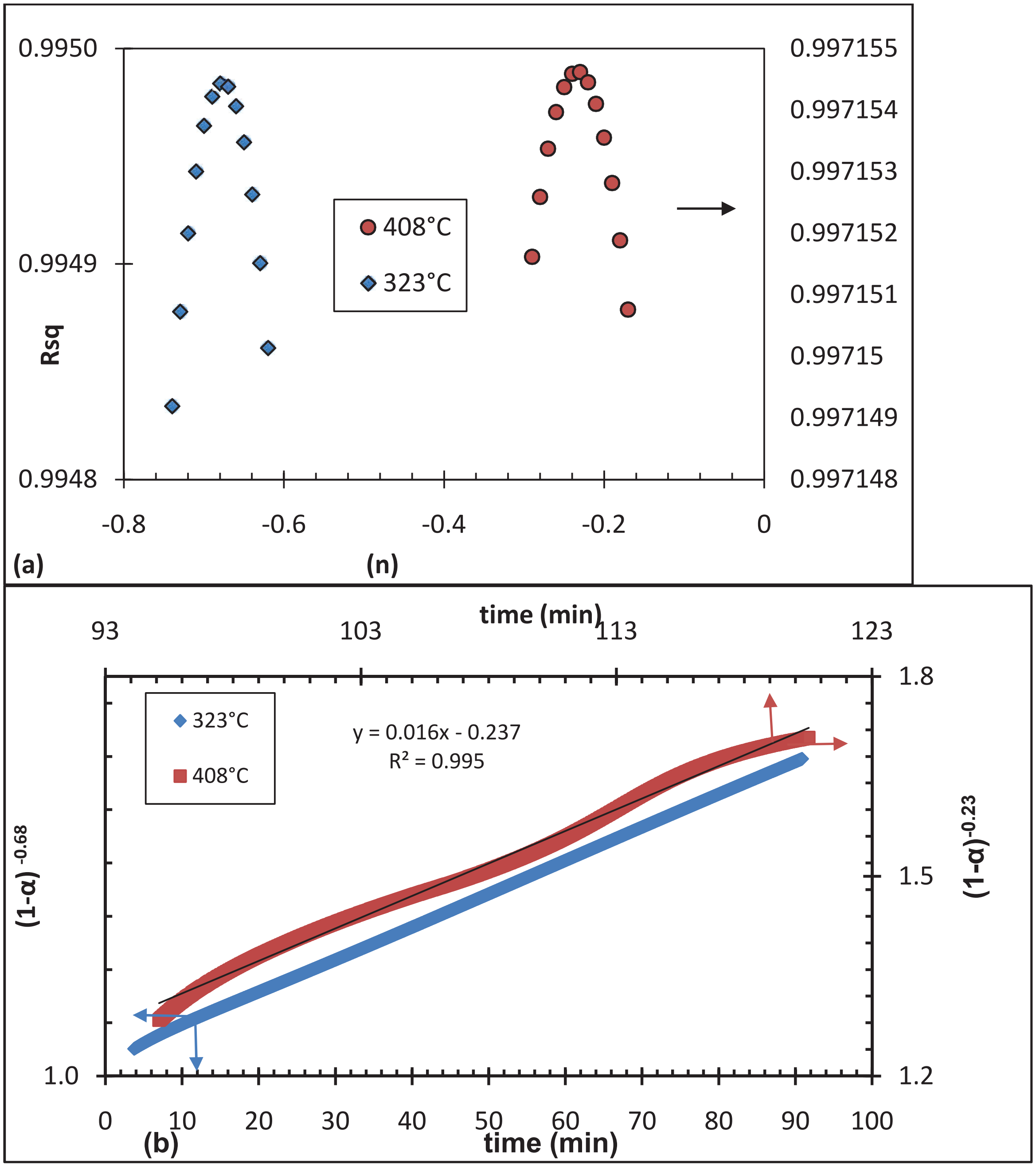

Fig 6. Treatments of the isothermal data at 323 and 408 °C to estimate the kinetics parameters of pyrolysis of LG: (a) the plot of Rsq versus reiterated values of (1-n); (b) the plot of $(1-\alpha')^{(1-n)}$ versus t (min) according to Eq (6) for the best n value obtained from max of **Fig 6a**;.

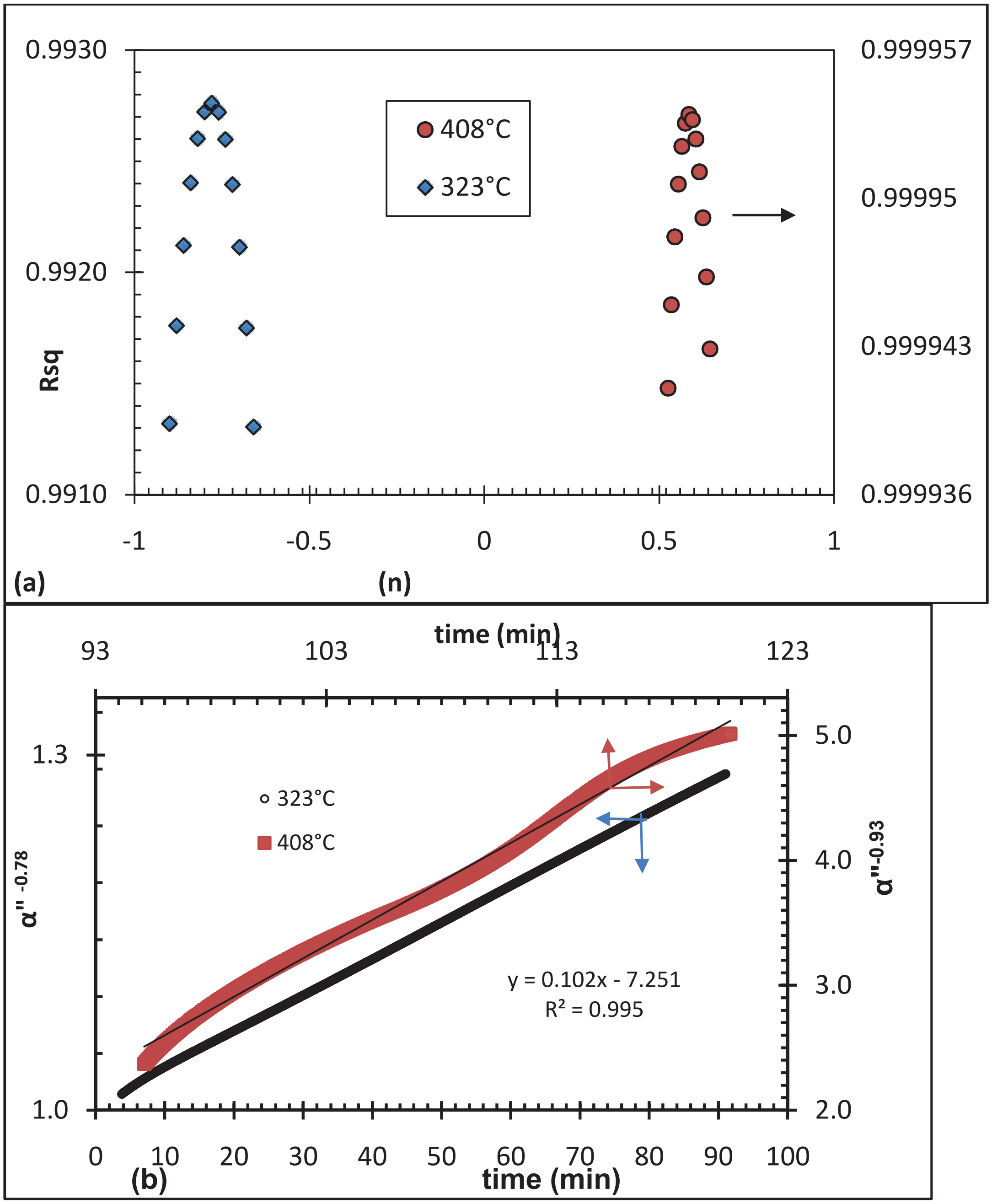

Fig 7. Treatments of the isothermal data at 345 and 405 °C to estimate the kinetics parameters of pyrolysis of LG: (a) the plot of Rsq versus reiterated values of (1-n); (b) the plot of $\alpha''^{(1-n)}$ versus t (min) according to Eq (6B) for the best n value obtained from max of **Fig 6a**;.

Table3. Kinetics parmeters of LG at the isotherms temperatures 323 and 408 °Ccorresponding **Figs 4 - 7.**The PTFE dada are included for comparison [46].

t (°C)	Model	1-n	1000Slope	n	1000 k	Rsq
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

The experimental data fitted well in a straight line with acceptable correlation coefficient for both temperature (**Table 3** 7th column) and three fractions of reactants. The most suitable fit was corresponded to α'' that had highest correlation coefficient at both temperatures. The obtained k values depended on the definition of fraction of reactants, α, α' and α''. The k values of thermolysis at 323°C obtained based on α' and α'' are in the range of k value obtained for pyrolysis of PTFE at lower temperature, 480 °C. Similarly, the values of k obtained from 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 I the **Table 3** are larger than then the reported values for PTFE. The reported Arrhenius k values, 8.32 X 10^{-5} and 2.34 x 10^{-6} for pyrolysis of lignin [47] are considerably lower than the values estimated by above methods for neoprene.Also, the above values are in the same range of $6.8 < 1000k\ (min^{-1}) < 23$ for pyrolysis of lignin with $134 < Ea\ (kJ/mol) < 172$ [48].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.Therefore, the nature of decomposition reactions at the two temperature 323°C and 408°C were different. This is within expectation based on the previous proposed mechanism since neoprene had lost most of chlorine in form of HCl, a lower temperatures.The chlorine free polymer will thermalize with its proper way.

It is instructive to mention that most of researchers assumed a first order reaction rate for thermolysis[e.g.47]. The methods for evaluation of reaction order using thermogravimetric data [e.g.[49]] was worked well for decomposition of inorganic compounds, however it did not worked for LG degradation.

Thermolysis weight loss reactions occurs either in 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 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 ½. Also a result, the 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. These rate laws related to complex reaction for decomposition of LG and are coherent with the nature of reactants. The obtained order by reiteration methods (**Table 3**)$0.18 < n < 1.93$ also depended on the chosen form of the reacted materials, 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, are 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.

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-α):

$$Ln\,r = Lnak + nLn(1-\alpha). \qquad (10A)$$

$$Ln\,r = Lnak + nLn(\alpha''). \qquad (10B)$$

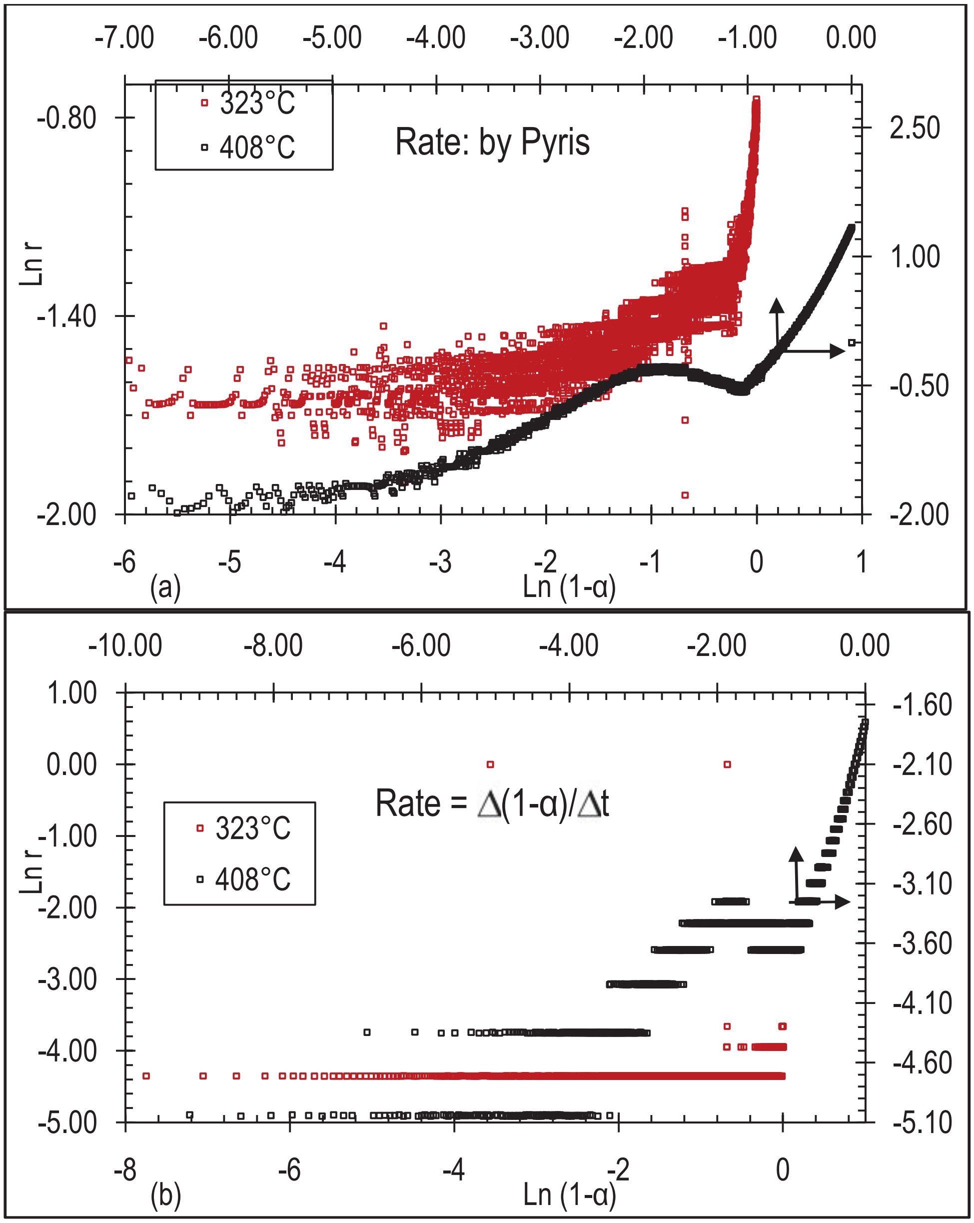

Fig8.(a) Double logarithmic variation of rate (-dw/dt) obtained by Pyris versus Ln(1-α). (b) Double logarithmic variation of rate (r = -Δ(1-α)/Δt)) versus (1-α).

Table 4.**The values of Lnkfor the zeroth ordered reactions identified in **Fig 8b

Reaction	Ln k at	
	323	408
1	0	-1.745
2	-3.958	-1.783
3	-3.945	-1.823
4	-4.35	-1.863
5	-5.043	-1.906

6		-1.95
7		-1.997
8		-2.046
9		-2.097
10		-2.151
11		-2.209
12		-2.269
13		-2.333
14		-2.403
15		-2.476
16		-2.556
17		-2.644
18		-2.739
19		-2.844
20		-2.962
21		-3.098
22		-3.251
23		-3.434
24		-3.657
25		-3.943
26		-4.351

For a simple one step reaction the slope of the variation of Ln r versus Ln of fraction of reactants (Ln(1-α), Ln(1-α'), Lnα") 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 experimental data, at a first view, gave the impression 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-α) 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-α) 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**) 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 [43].

Researcher, in order to simulate thermolysis also had assumed many simultaneous chemical reactionsat high temperatures to explain thermalizes of pure polymeric materials[eg[22,50,51]]. For example, Kruse et al [24] 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 [5], polypropylene (PP) and PS pyrolysis were presented and discussed by other researchers [eg [10]]. The reported results of thermal degradation of plastic blends and their mutual interactions [eg[12,14]] 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 polymerby step-by-step pyrolysis [17]. 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 Eafrom Thermal Scans.

Arrhenius relationship (Eq11) 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 J mol^{-1} K^{-1} and another constant such as z to describe the efficiency of the molecular collisions in a chemical reaction.

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

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

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

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

$$\text{Ln } r = \text{Ln} z(1-\alpha)^n - Ea/RT \qquad (13)$$

Fig. 9represents 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 Eaand three steps with negative vales of Ea (**Table 5**). The positive Ea values can be related to the minimum energy required to decompose a chemical bond, or disassociate a physical bond to release a volatile form a solid such as evaporation of moisture from reactants. 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 Ea value must be more than the bond energy value under same condition.The obtained Ea (**Table 5**) are below the amount of standard bond energies of C-Cl, C-H, and C-C since the reactions occurred at higher temperatures. The negative Ea value are related to the exothermic process including crystallization of melted chemical, and recombination of chemically active liquids results from decomposition reaction.

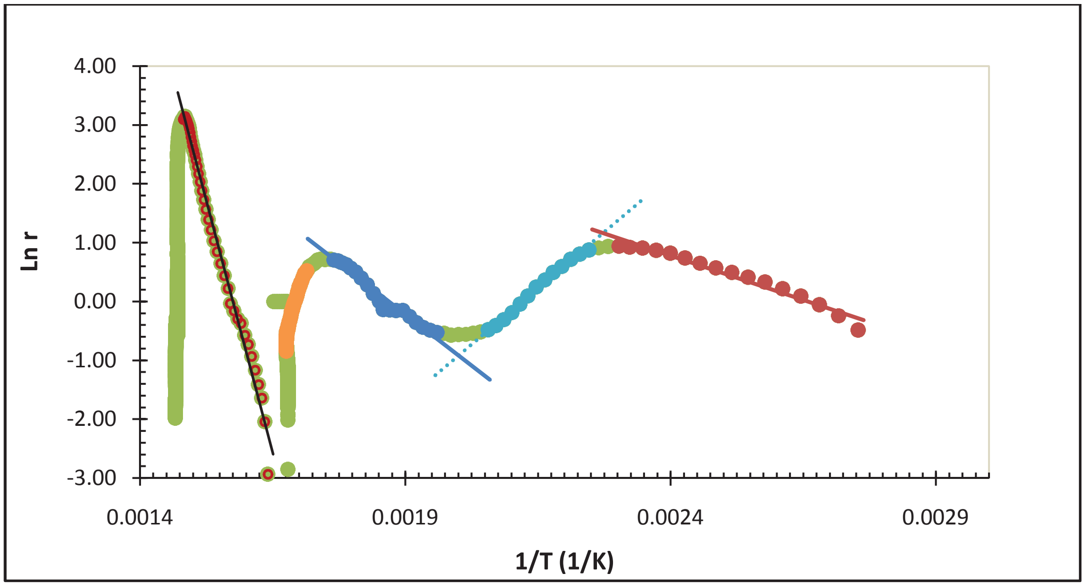

Fig9. Variation of logarithm of rate of decomposition of LG versus inverse of temperature.

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%	Δw%	t_i (°C)	t_f (°C)	ΔT(°C)	ΔT/Δt	Ln Z	Ea (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

The calculated Ea = 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 its structure.This value is in the range of reported 16.2 <Ea (kJ/mol) <27.0 by Wang [52] for dehydration of bituminous coal over a temperature range from 35 – 115°C.The Ea = -63 shows the crystallization of meted materials including combination reaction of melts in the temparture range of 170 – 215 °C. The Ea = 58 kJ/mol at temperature range of 237-293°C is around the Ea related to unzipping of some well know polymers such as polymethylmethacrylate (PMMA). For example, Ea for unzipping PMMA radicals was evaluated to be 60 kJ/mole[53] by radical process. Likewise, the values of 24.6 <Ea (kJ/mol) < 64.0 for various reactions involved in thermolysis of glucose based carbohydrates has been reported [54]. These Eaare considerably lower than involved bond energies which are above 331 kJ/mol. In the temperature range of 310- 324 °C the exothermic recombination reactions in the liquid phase occurred with a very high Ea ≈ 299 kJ/mol. These combination and decomposition reactions continued during the isotherm at 323 °C. The Ea = 284 kJ/mol at temperature range of 337-402°C related to depolymerization of LG. thought, it is smaller than standard bond energies, because of the exothermic reaction of semi-volatile liquids; however, it is in the rage of Ea reported for the thermolysis of other organic resins.

3.6. Evaluation of Ea from isotherms.

Sixisotherms were constructed based on the recorded at temperatures 308, 313, 323, 333, 336 and 346 °C (**Fig 10a**) The plot of $(1-\alpha)^{(1-n)}$ versus reaction time, according to Eq(6) for each reaction was built (**Fig 8b** shows the one was built for temperatures 323 °C and 408°C). The values of k were calculated from the slope of each plot (**Table 3**) at a given isotherm. Then, a plot of Lnk versus invers of temperature according to Eq(13) was built (**Fig 10b)**. Considering the data obtained from six isotherms, the value of Ea = 117 kJ/mol with $z = 3.22 \times 10^{12}$ determined 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 Ea than the isotherm at higher temperatures. In this manner, Ea = 317 kJ/mol with $z = 4.4 \times 10^{29}$ 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 EA reported for pyrolysis of rubbers in car tires [1], and it is closer to the values of the bond energies. It is higherthanEa= 261 kJ/mol for decomposition of PTEE, and the 134<Ea (kJ/mol) <172of lignin at temperature rang 500-800°C.

The Ea = 2.7 kJ/molobtained from isotherms at lower temperatures is not in agreements with the Ea values calculated from previous method; and it is lower thanEa of vaporization of moisture from coal [52]. Therefore, it is related to volatilization of volatile organic compounds from LG structure.The thermolysis Ea according to Sanchez-Jimenez et al is independent of the kinetic model to be used [46], however, the value of z heavily depends on the kinetic model.Therefore, it will be hard to do any comparison of the z value.

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

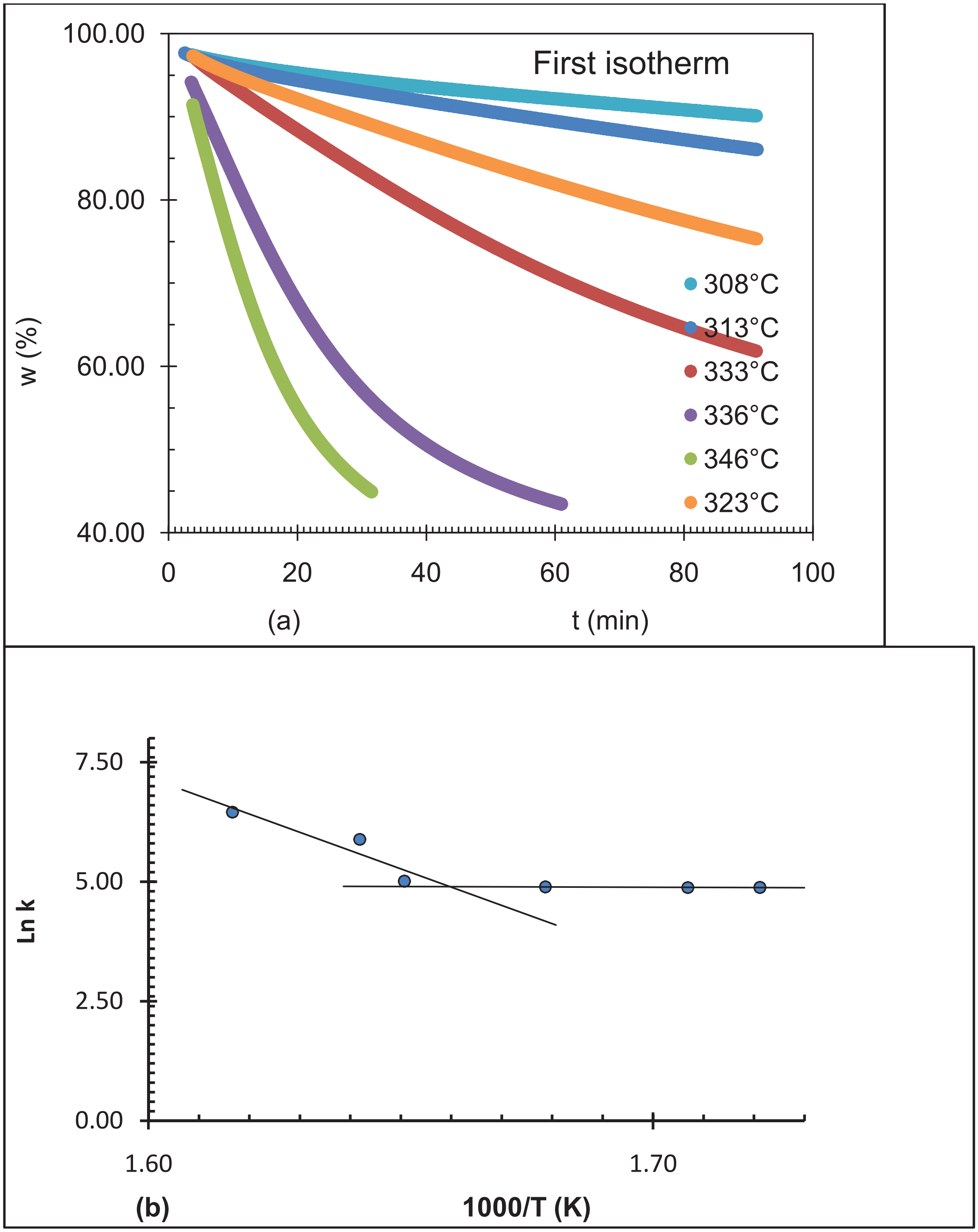

Fig 10.(a) Isothermal cures corresponding to the thermolysis of LG, recorded at 333, 336 and 346 °C. (b) Plot of the values of Ln k versus corresponding invers temperature.

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 depends on the model to choose. Choosing the fraction of reacted reactantswas a challenge for evaluating the kinetics parameters at both isothermal process. Independent of the form of reaction extent function, fractional reaction order for the both isotherm temperature was the best fit to the experimental data. The double logarithmic variation of rate of reaction (Lnr) and unreacted fraction of reactantsshowed 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.

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. The task involves a large number of chemical reactions, and intermediate species. An in-depth discussion on the kinetics models developed by other researchers for the pure polymers can be found elsewhere [e.g. 3-3]. The decomposition of neoprene was not similar to decomposition of rubber in car-tire [55].

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