Kinetics of Powder-Free Laboratory Examination Gloves at 345℃ and 405℃ by Thermogravimetric Analysis

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Author's contribution

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

Original Research Article

ABSTRACT

At two consecutive temperatures, 345℃ and 405℃ as w ell 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 parmeters related to the decomposition of LG at 345℃ and 405℃ isotherms. The results of the study indicated that the kinetics parmeters depends on the model to choose. The reaction at 354℃ based on the models could be second order, fract ional or many zeroth order concurrent reactions. The activation energy of thermalizes (Ea) was estimated by thermal scans, and isotherms at 308, 313, 333, 336, and 345℃. The value of Ea for the process at lower temperature was near to Ea corresponding to evaporation of volatiles, and at higher temperatures Ea was below constituent chemical bond energies as well below of Ea for decomposition of rubber in tires.

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1. INTRODUCTION

The disposal of waste plastics is a serious concern in the area of environmental protection and sustainability. Recent processing techniques such as energy recovery including plastics-derived fuel have been proven successful [1-5]; however, gaseous emission including hydrogen chloride from wastes based on poly(vinyl chloride) (PVC) [6,7] and neoprene [8] resins and polycyclic aromatic hydrocarbons (PAHs) evolved from rubber resins [9] in the combustion process remains a barrier in the application. 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 (eg [14,15]). Some widely used polymeric materials such as poly (methyl methacrylate) (PMMA), upon heating, decomposed to original monomers [16] likewise PS to styrene [12,17-19]. 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 absorbent cotton, medical respirator, bamboo sticks [21] and cotton gauges, packaging boxes, capsule plates and transfusion tubes [21] 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 [24-28]. 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, and surface. Their incineration in landfills neither contribute to energy gain nor to environmental benefits [30]. Therefore, energy recovery by step-by-step

thermolysis [31] which converts waste to the valuable petrochemicals must 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 [34-36]. The kinetics of decomposition of plastics are of interest from different points of view including evolution of harmful substances during fires or waste incineration, recovering of chemical raw materials from waste plastics and 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 (345°C), followed with a 30 min isothermal step at this temperature; sequenced with another linear thermal scan form 345°C to 405°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

The step-by-step pyrolysis of LGs were performed in a Perkin-Elmer (USA) thermogravimetric analyzer (TGA-7). 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 345°C (The calculated average heating rate in this step was 87.2°C/ min.) and then the temperature was kept constant for 30 min at 345°C (Fig. 1).
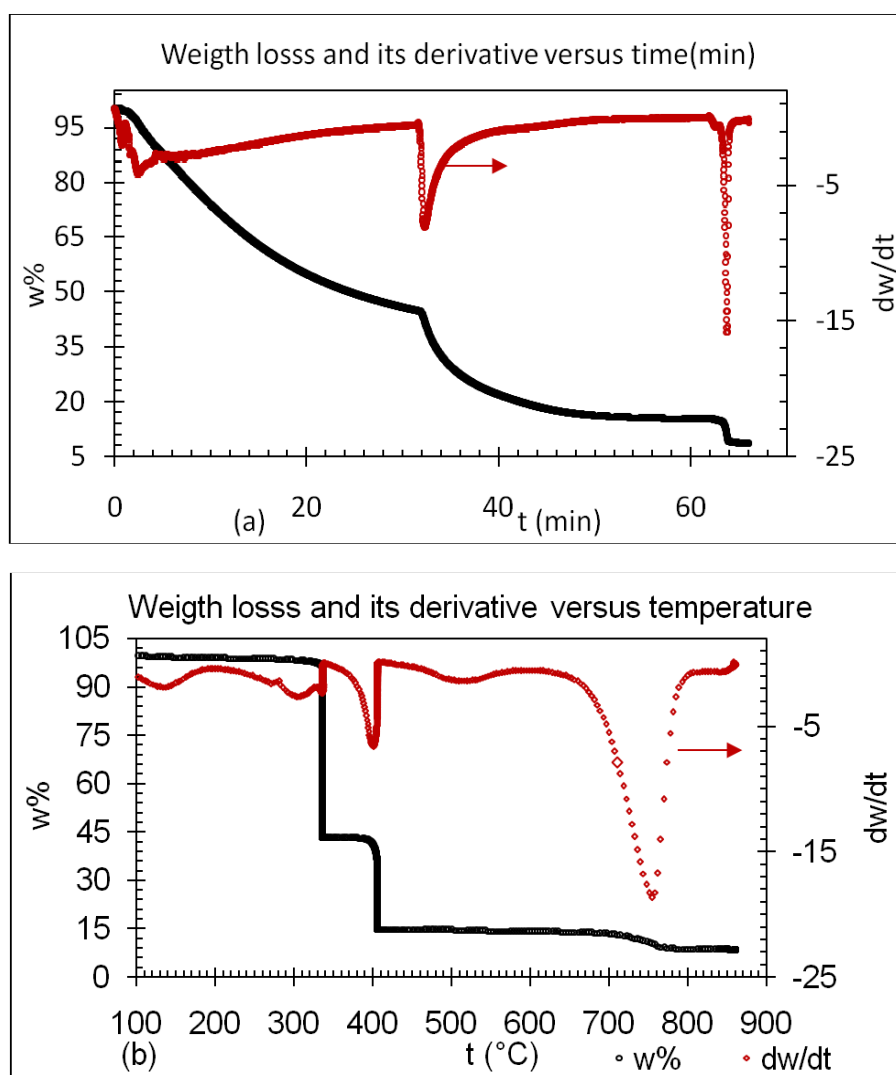

Fig. 1. The thermogram of LG sample: (a) Weight loss versus time (○) and derivative of weight loss (dw/dt) by time (◊), and (b) Weight loss versus temperature (○) and dw/dt at the given temperatures (◊)

In succession, the temperature was rapidly increased (The calculated average heating rate in this step was 35.8°C/ min.) to the second isothermal step (405°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 initial sample weight was 6.166 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 345°C caused about 8.55% of LG weight loss (Fig. 1, Table 1). During 27.80 min at 345°C about 46.60% 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 27.8 min at 345°C isotherm was 44.89% which is 13.90% over the expected weight loss. Therefore, the weight loss composition could be HCl and other volatiles resulted from decomposition of LG.

During the fast heating from 345°C to 405°C (35.8°C/min) about 8.89% of weight loss occurred, and 15.34% of weight loss followed when the sample was held at 405°C for 30 min. 6.74% of material volatized during the scan from 405°C to 846°C and holding there for 2 min where the organic components of the sample was consumed completely. The leftover ashes (about 8.3%) has white color, soluble in hot water, the solution has strongly basic (pH > 10).

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 affects the rate of a reaction, but they may not appear in the overall reaction. For a simple gas-phase reaction:

$$aA \rightarrow \text{Products} \tag{1}$$

$$Rate = r = -\frac{dw}{a dt} = kw^n \tag{2}$$

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, which is defined in terms of the actual, final, and initial mass of sample, w, w_f, and w_i, respectively:

$$\alpha = \frac{w_i - w}{w_i - w_f} \tag{3}$$

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

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

Rearranging Eq (4) results:

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

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

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

$$(1-\alpha) = -akt + (1-\alpha)_0 \qquad \text{for n = 0} \tag{7}$$

$$Ln(1-\alpha) = -akt + Ln(1-\alpha)_0 \text{ for n = 1} \tag{8}$$

$$(1-\alpha)^{-1} = akt + (1-\alpha)_0^{-1} \qquad \text{For n =2} \tag{9}$$

Figs. 2 (a, b, and c) shows the treatment of the experimental data of weight loss over time obtained for LG at 345°C and 406°C according to the above relationships. The experimental data do not fit into zeroth, first, and second order reactions, at both temperatures.
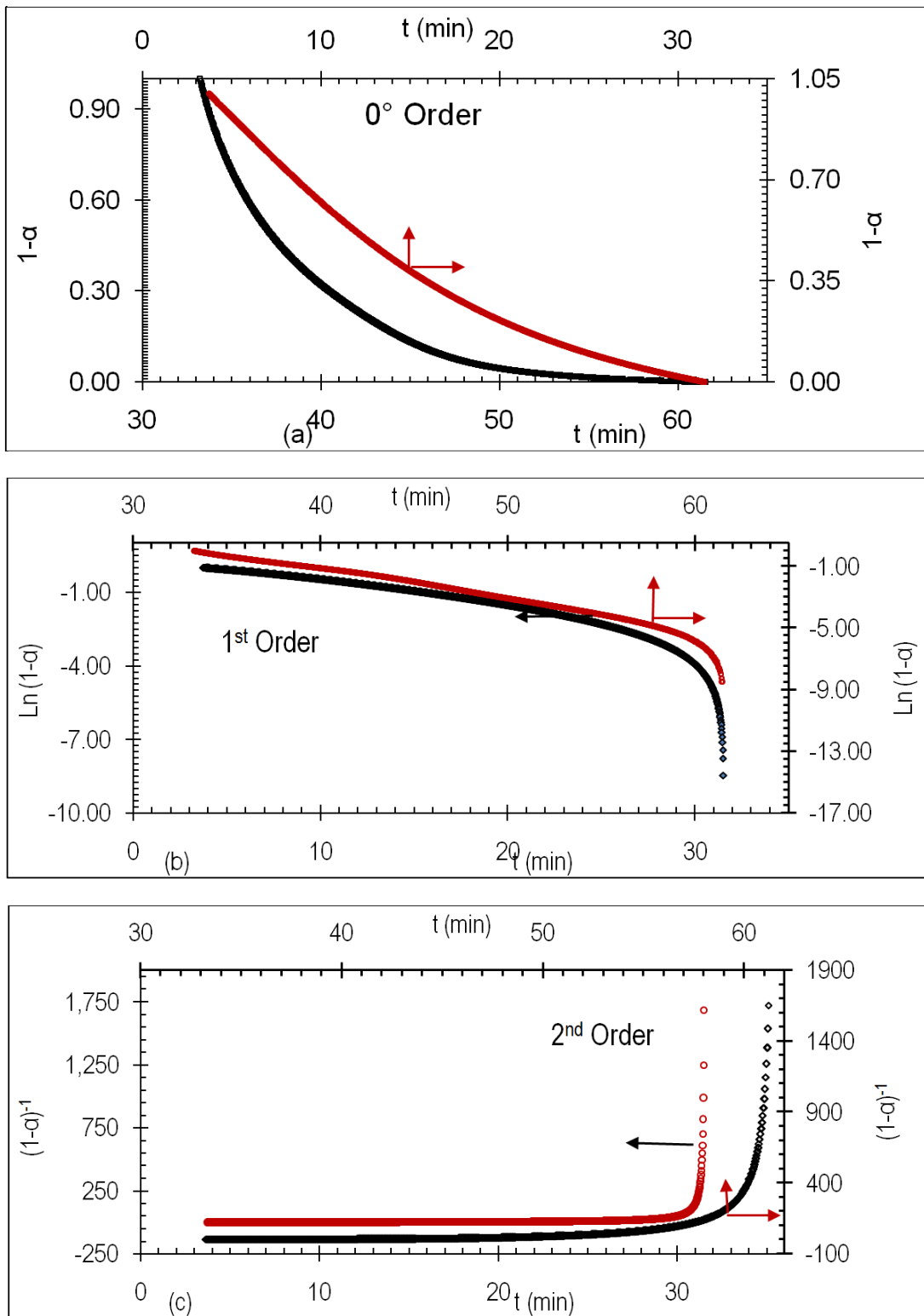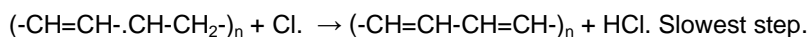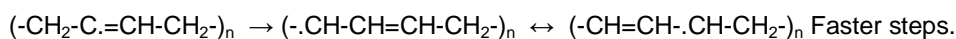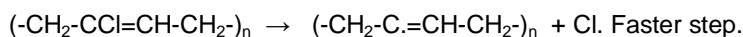
Fig. 2. Isothermal curves corresponding to degradation of LG at the indicated temperatures based on Eq (7), Eq (8) and Eq (9) for (a) Zeroth, (b) First, and (c) second order reactions at 336°C (○ Red), and 406°C (◊ black)

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) ℃

Steps	t_i (min)	t_f (min)	Δt (min)	w_i%	w_f%	Δw w%	t_i (℃)	t_f (℃)	ΔT (℃)
1	0.00	3.70	3.70	100.04	91.49	8.55	24	347	322
2	3.73	31.53	27.80	91.49	44.89	46.60	347	345	-2
3	31.55	33.22	1.67	44.89	36.00	8.89	345	405	60
4	33.23	61.57	28.33	35.92	15.34	20.58	405	405	0
5 & 6	61.58	66.00	4.42	15.34	8.60	6.74	405	846	440

Fig. 3 shows the variation of α' = w/w_i, for the thermolysis at 345℃ according to first a nd second order reaction. Based on the correlation coefficients (Rsq or R^2, Table 2) the experimental data fit into a second order reaction with R^2 = 0.999. Postulating a second order reaction for the first step radical decomposition of neopren is quate rational based on the following chemical reaction equations:

$(-CH_2-CCl=CH-CH_2-)_n \rightarrow (-CH_2-C.=CH-CH_2-)_n + Cl.$ Faster step.

$(-CH_2-C.=CH-CH_2-)_n \rightarrow (-.CH-CH=CH-CH_2-)_n \leftrightarrow (-CH=CH-.CH-CH_2-)_n$ Faster steps.

$(-CH=CH-.CH-CH_2-)_n + Cl. \rightarrow (-CH=CH-CH=CH-)_n + HCl.$ Slowest step.
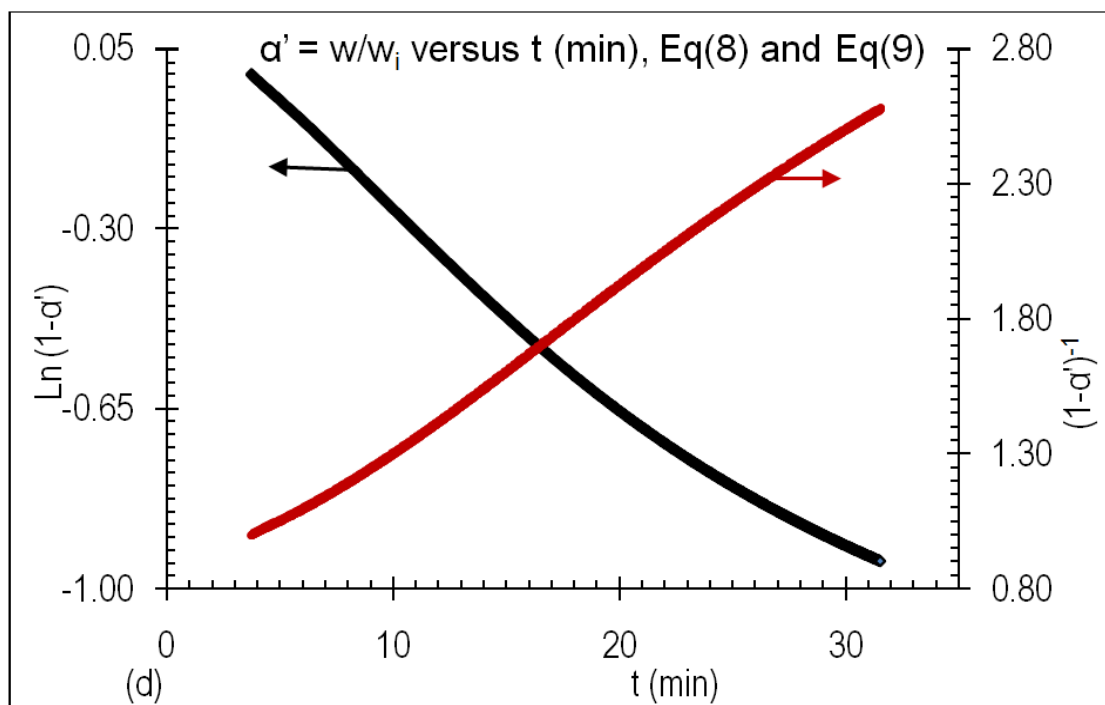
The rate = $k[Cl.] [(-CH=CH-.CH-CH_2-)_n]$, a second order reaction.

Fig. 3. Variation of α' = w/w_i versus time according to Eq (8) first order reaction (◊ black) and Eq (9) second order reaction (○ red)

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 higher than the values of k = 0.0047 1/min reported for polytetrafluoroethylene (PTFE) at 480℃ and lower than k = 0.164 1/min of PTFE at 500℃ [46].

Table 2. The reaction order n, Arrhenius constant k, and correlation coefficient Rsq of isotheral decomposition of LG at 345℃ according to Fig. 3.

t (℃)	n	K	Rsq
345	1	0.0351	0.9879
345	2	0.0596	0.9988

3.3 Reaction Order by Reiteration Method

The value of n in Eq (6) can be determined by reiteration method. In this method, a plot of $(1-\alpha)^{(1-n)}$ versus t (min) for each value 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 (Fig. 4a). 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) (Fig. 4b) represents ak, after it is divided by (n-1). These results are summarized in Table 3 assuming a = 1.
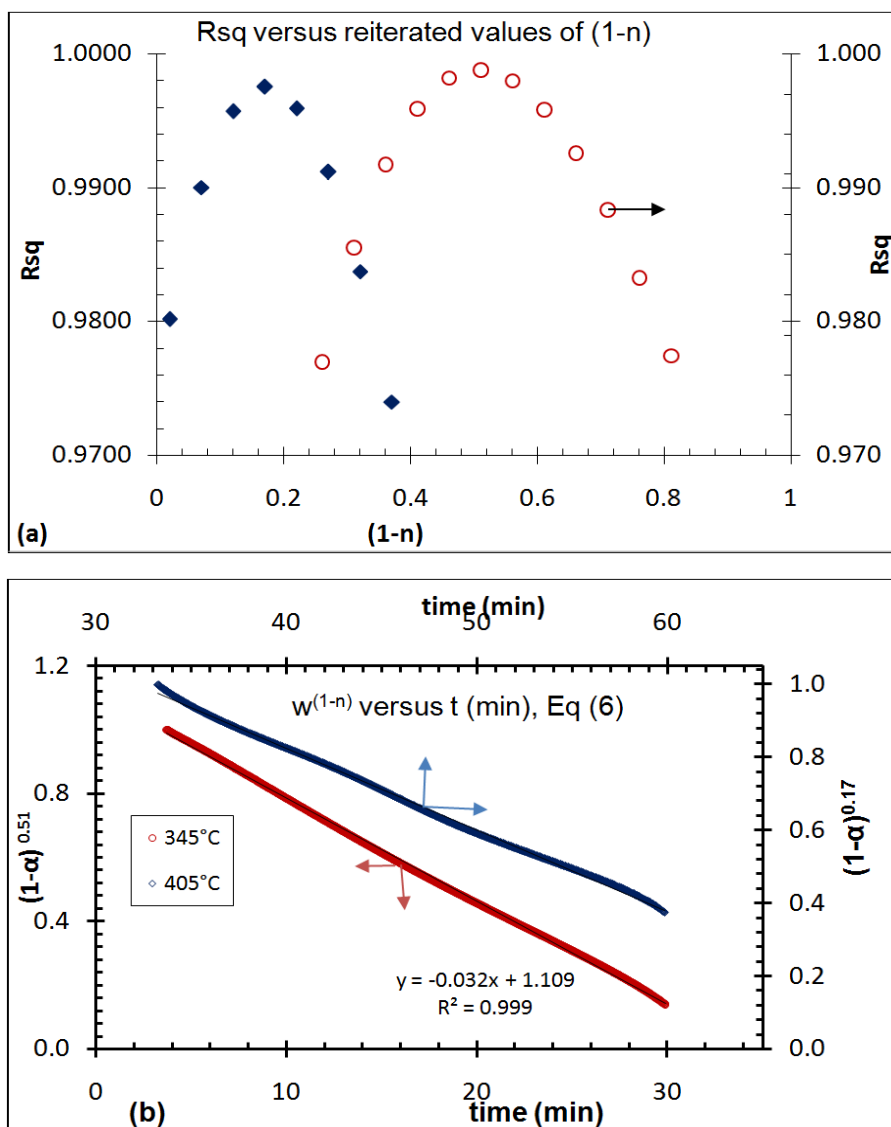

Fig. 4. Treatments of the isothermal data at 345℃ (○ red) and 405 ℃ (♦ blue) to estimate the kinetics parameters of pyrolysis of LG: (a) The plot of Rsq versus reiterated values of (1-n); (b) The plot of $w^{(1-n)}$ versus t (min) according to Eq (6) for the best n value obtained from max of Fig. 4a

Table 3. Kinetics parmeters obtained from isotherms at various temperatures corresponding to LG's pyrolysis from Figs. 4a and b. The PTFE dada are included for comparison [46]

Compound	t (°C)	1-n	10^{-2} Slope	n	10^{-2} k	Rsq
LG 1 isotherm [47]	308	0.75	-0.99	0.25	1.32	0.9969
LG 2 isotherm	407	0.34	-2.45	0.66	7.22	0.9786
LG 1 isotherm	313	0.80	-1.06	0.20	1.32	0.9987
LG2 isotherm	407	0.42	-2.84	0.58	6.77	0.9873
LG 1 isotherm	345	0.51	-3.27	0.49	6.40	0.9988
LG 2 isotherm	405	0.17	-2.25	0.83	13.23	0.9984
PTFE [46]	480			1	0.47	1.000
PTFE [46]	500			1	1.60	0.999

The data fitted well in straight line with acceptable correlation coefficient for both temperature (Table 3 7th column). The obtained k values being very small for a fast decomposition reaction (Table 3) are in order of previous method (Table 2) and they are in the rage of the values reported for other decomposition reactions at higher temperatures. The reported Arrhenius k values, 8.32 X 10^5 and 2.34 x 10^6 for pyrolysis of lignin [48] are considerably lower than the values estimated by above methods for neoprene. As the temperature of pyrolysis was increased the value of k also increased which was within expectations based on Arrhenius relationship, Eq (7), for a given reaction at two temperatures. Therefore, the nature of decomposition reactions at 345°C and 405°C were different. This is within expectation based on the previous proposed mechanism. In the proposed mechanism neoprene had lost all chlorine in form of HCl, the remains chlorine free polymer will have its own ways of decomposition unsimilar to neoprene.

Most of the researchers assumed a first order reaction rate for thermolysis [47]. The proposed method for evaluation of reaction order using thermogravimetric data [49] was worked well for decomposition of inorganic compounds, however it did not worked for LG degradation. The obtained n = 0.83 is near to one (1) but experimental data were not fitted well to order one (1) as Fig. 2b showed but they are fitted well with order n = 0.83 (Fig. 4b).

Thermolysis weight loss reactions occurs either in a 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. As 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.

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):

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

For a simple one step reaction the slope of the variation of Ln r versus Ln(1-α) yields the order of reaction and the intercept is a combination of stoichiometric coefficient of the reactants and rate constant (ak). Fig. 5a depicted such a plot for both isotherms. 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. 5a, 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, R = Δ(1-α)/Δt, instead of dw/dt obtained from TGA driving program (Pyris). A plot of the values of LnR = Ln-Δ(1-α)/Δt, versus Ln(1-α) is illustrated in Fig 5b. In this plot, 36 zeroth order parallel reaction with their proper values of k at 345°C and 53 concurrent zeroth order reactions with proper k values at 405°C (Table 5 Appendix and Fig. 8 Appendix) 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].
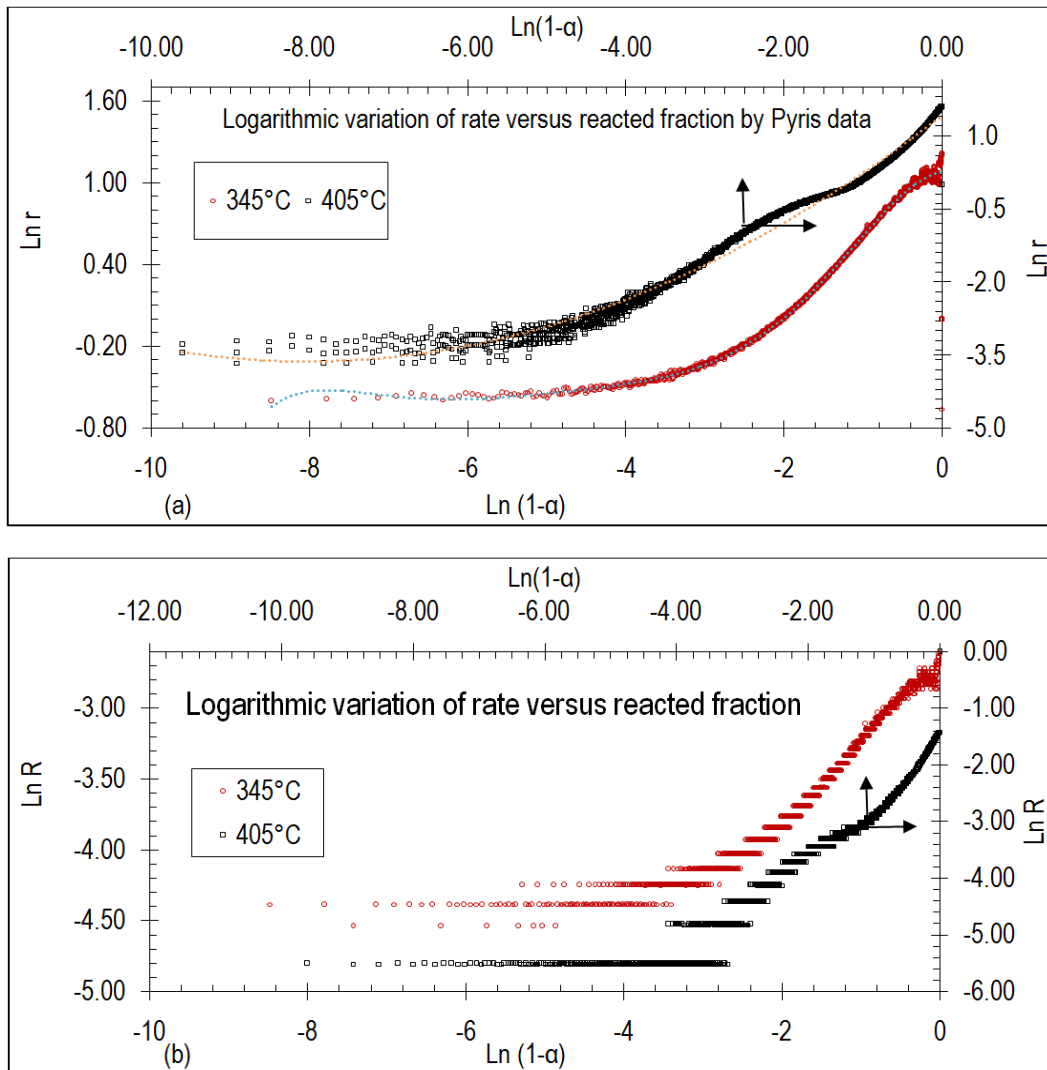
Fig. 5. (a) Double logarithmic variation of rate (-dw/dt) obtained by Pyris versus Ln(1-α) (○ red 345℃ and □ black 405℃). (b) Double logarithmic variation of rate (R = -Δ(1-α)/Δt)) versus (1-α) (○ red 345℃ and □ black 405℃)

Researcher, in order to simulate thermolysis also had assumed many simultaneous chemical reactions at high temperatures to explain thermalizes of pure polymeric materials [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 [10]. The reported results of thermal degradation of plastic blends and their mutual interactions [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 polymer by 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 chemicals, will be similar to pyrolysis of each individual ingredient resulting in many simultaneous concurrent reactions.

3.5 Evaluation of Ea 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 J mol^{-1} K^{-1} and another constant such as z to describe the efficiency of the molecular collisions in a chemical reaction.

$$k = ze^{-\frac{E_a}{RT}} \tag{11}$$

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

$$r = z(1-\alpha)^n e^{-\frac{E_a}{RT}} \tag{12}$$

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

$$Ln\ r = Lnz(1-\alpha)^n - \frac{E_a}{RT} \tag{13}$$

Fig. 6 represents the application of Eq (13) to the experimental data. Three sets of Ea was evaluated from the experimental data each of them corresponded to a given temperature range (Table 4). The 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 equal or more than the bond energy value under same condition. The obtained Ea (Table 4) are below the amount of standard bond energies of C-Cl, C-H, and C-C since the reactions occurred at higher temperatures.
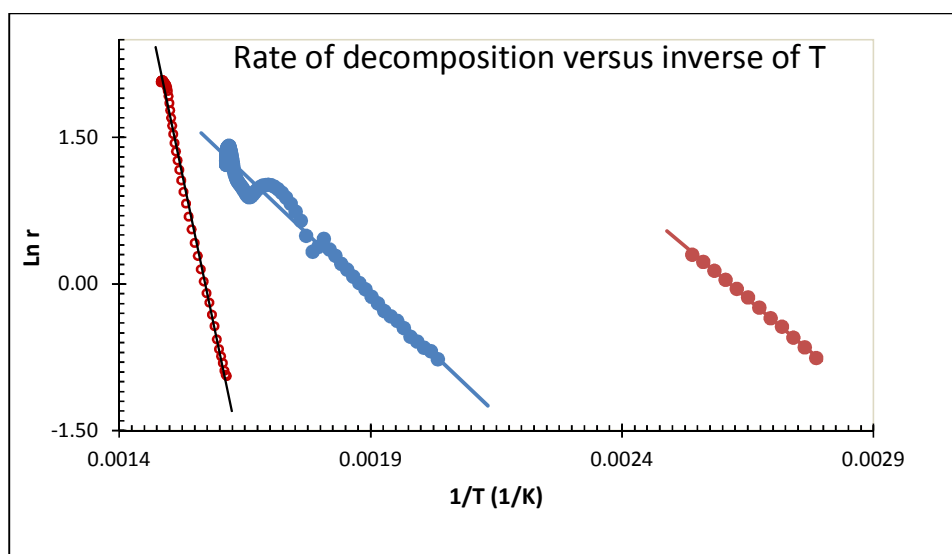

Fig. 6. Variation of logarithm values of rate of decomposition of LG versus inverse of absolute temperatures

Table 4. 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 temperatures (ΔT), average heating rate, and the activation energy

w_i%	w_f%	Δw%	t_i (°C)	t_f (°C)	ΔT(°C)	$\Delta T/\Delta t$	Ea(kJ/mol)
100.	99.86	0.14	86	121	35	190.1	36.7
99.34	92.05	7.29	219	347	128	53.1	39.7
44.87	40.72	4.15	346	402	56	63.4	202.5

The calculated Ea = 36.7 kJ/mol at temperature range of 85-121℃ (Table 4) could be related to vaporization of volatile and moisture within LG plus some fundamental changes in its structure. This value is higher than reported 16.2 < Ea (kJ/mol) <27.0 by Wang [52] for dehydration of bituminous coal over a temperature range from 35 – 115℃. The Ea = 39.7 kJ/mol at temperature range of 219-347℃ could be related to slow decomposition of LG materials, though, this values is far smaller than the bond energy for decomposing of Cl-C bonds (331 kJ/mol at 25℃) and C-C single bond (346 kJ/mol at 25℃) by radical mechanism under standard conditions. However, the Ea values lower than bond energy also has been reported for decomposition of other polymers; for example, Ea for unzipping polymethylmethacrylate radicals was evaluated to be 60 kJ/mole [53] by radical unzipping 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] which are considerably lower than involved bond energies.

The Ea = 202.5 kJ/mol at temperature range of 346-402℃ also is smaller than standard bond energies, however, it is in the rage of Ea reported for other organic resins.

3.6 Evaluation of Ea from Isotherms

Five isotherms were constructed based on the recorded at temperatures 308, 313, 333, 336 and 346℃. Fig 7a shows three isotherm curves corresponding to thermolysis of LG recorded at temperatures of 333, 336 and 346℃. The plot of $(1-\alpha)^{(1-n)}$ versus reaction time, according to Eq(6) for each reaction was built (Fig 5b shows the one was built for temperatures 345℃ and 405℃). 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. 7b).
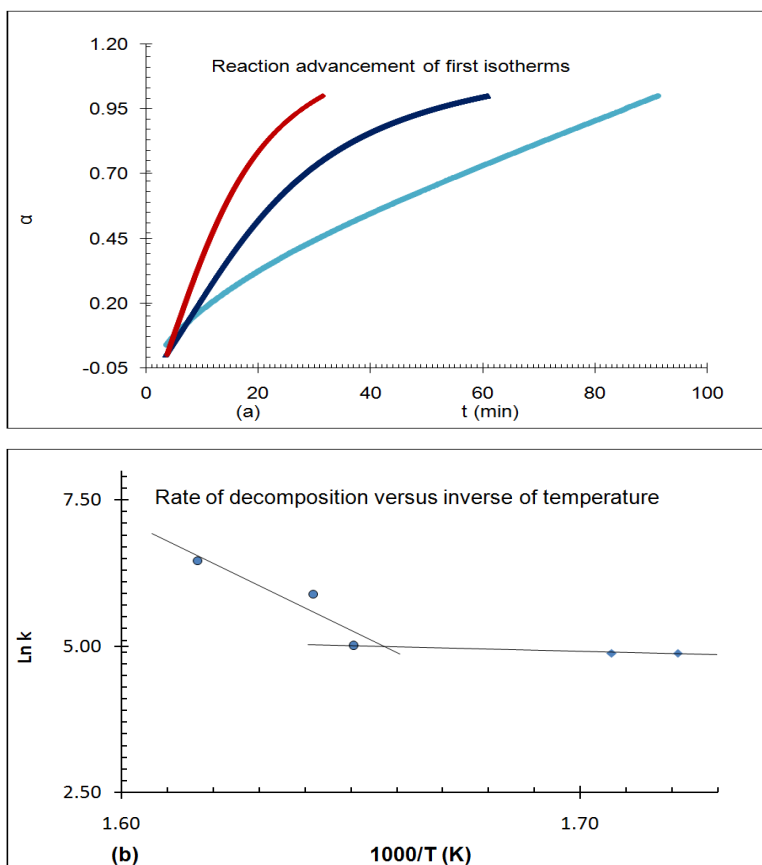

Fig. 7. (a) Isothermal cures corresponding to the thermolysis of LG, recorded at 333℃ (• magenta), 336 ℃ (Δ blue) and 346 ℃ (◊ red). (b) Plot of the values of logarithm values of rate of decomposition of LG versus inverse of temperatures; lower isothermal temperatures 308, 313 and 333℃ (♦) and higher isothermal temperatures (•)333, 336, and 346°C

Considering the data obtained from all five isotherms, the value of Ea = 113 kJ/mol with Z = 1.6 X 1012 determined from slope and the intercept of Fig. 7b, respectively, which is not in agreement with the one obtained in the previous section.

However, a close inspection of Fig. 7b indicated that the first three isotherms may have a different Ea than the others one. In this manner, Ea = 317 kJ/mol with Z = 4.4 X 10^{29} was calculated from slope and the intercept of the data at higher temperatures (Fig. 7b), respectively. This value is higher than the Ea obtain in the previous method. Also, this value of Ea is higher than Ea = 261 kJ/mol for decomposition of PTEE, and it is in the range with the values of EA reported for rubbers in car tires [1], and it is closer to the values of the bond energies.

The Ea = 16.5 kJ/mol obtained from isotherms at lower temperatures is not in agreements with the Ea values calculated from previous method,, However, it is in the rage of Ea of vaporization of moisture from coal [52]. Therefore, it is related to volatilization of moisture and volatile organic compounds from LG structure. The thermolysis Ea according to Sanchez-Jimenez et al. [46] is independent of the kinetic model to be used, however, the value of z heavily depends on the kinetic model. Therefore, it will be hard to do any comparison of the z value.

4. CONCLUSIONS

The decomposition kinetics of LG at two isotherm 345℃ and 405℃ was studied by TGA. The obtained results showed that the kinetics parameters depends on the model to choose. Choosing the fraction of reacted reactants as w/w$_i$, the decomposition of LC at 345℃ could be explain as a second order reaction where the slowest step be the abstraction of a hydrogen by chlorine radical from the substrate. However, when, the reacted fraction was calculated by Eq (3), the reaction order at temperatures 345 and 405℃ were fractional values which relates to a complex multi-steps decomposition reactions. The double logarithmic variation of rate of reaction (Ln r) and unreacted fraction of reactants (1-α) showed that the order of thermolysis reaction was zero at any isotherm, and many parallel concurrent reactions were occurred simultaneously with proper k values. The small values of Ea at the first stage of pyrolysis was related to easy evaporation of the volatile material. For the thermolysis at the higher

temperatures Ea was higher which was related to thermolysis of LG.

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 investigators for the pure polymers can be found elsewhere [10-19]. The decomposition of neoprene was not similar to decomposition of rubber in car-tire. It must be mentioned that the tire rubber pyrolysis is consist of two different stages such as main-chain scission and depolymerisation at lower temperature (primary pyrolysis), followed by cyclization and degradation of cyclized products at higher temperatures (secondary pyrolysis) [55].

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COMPETING INTERESTS

Author has declared that no competing interests exist.

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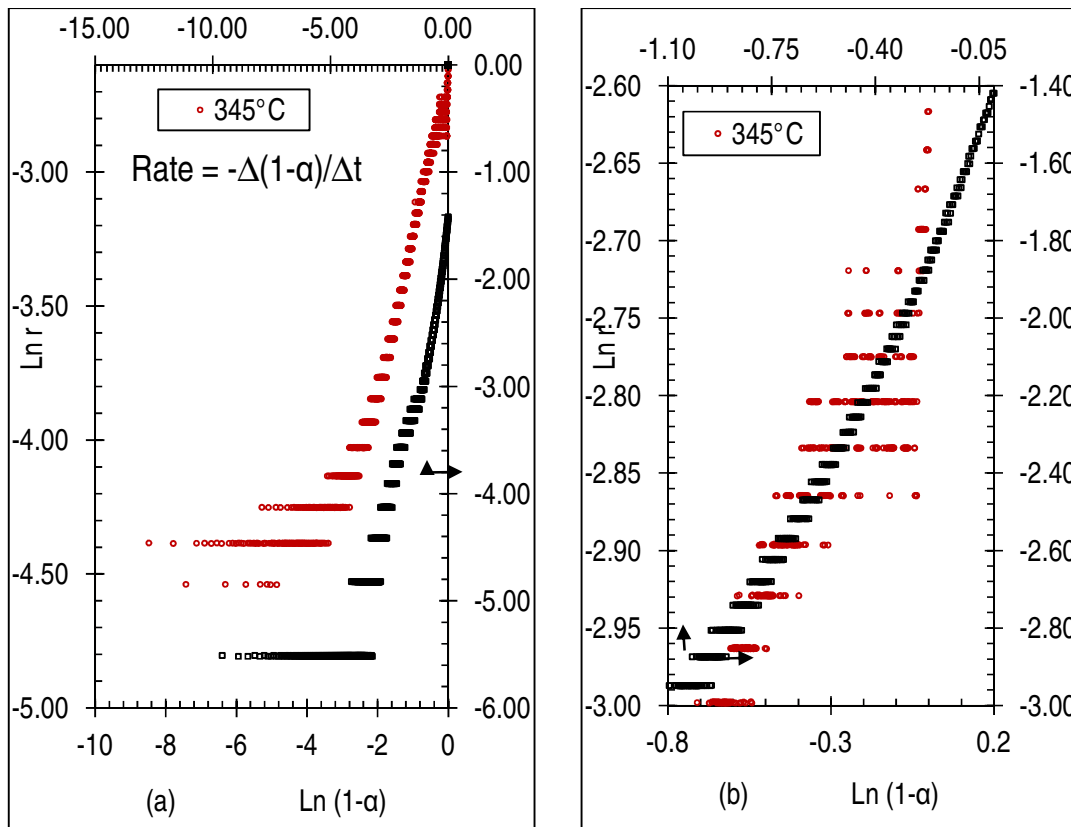
APPENDIX

Fig. 8. (a) Illustrations of many zeroth order simultaneous reactions rusted from decomposition of LG at 345 and 405°C according to t he double logarithmic variation of rate (r = -Δ(1-α)/Δt)) versus (1-α). (b) Expansion of upper part of Fig. a to view better the reactions

Table 5. Values of Ln k for many zero order reactions identified from intercept of Lnr versus ln(1-α)

Reaction	Lnk at	
	345°C	**405248C**
1	-2.616	-1.436
2	-2.641	-1.452
3	-2.666	-1.47
4	-2.6926	-1.487
5	-2.716	-1.506
6	-2.7467	-1.524
7	-2.775	-1.542
8	-2.804	-1.561
9	-2.834	-1.581
10	-2.865	-1.601
11	-2.896	-1.641
12	-2.929	-1.663
13	-2.963	-1.684
14	-2.997	-1.707
15	-3.035	-1.729

Reaction	Lnk at	
	345℃	405248C
16	-3.072	-1.752
17	-3.11	-1.776
18	-3.152	-1.7997
19	-3.195	-1.824
20	-3.239	-1.85
21	-3.286	-1.876
22	-3.335	-1.902
23	-3.386	-1.93
24	-3.44	-1.957
25	-3.497	-1.987
26	-3.558	-2.017
27	-3.623	-2.047
28	-3.691	-2.079
29	-3.766	-2.112
30	-3.875	-2.217
31	-3.932	-2.254
32	-4.028	-2.378
33	-4.133	-2.422
34	-4.251	-2.517
35	-4.385	-2.569
36	-4.539	-2.623
37		-2.6795
38		-2.741
39		-2.805
40		-2.874
41		-2.948
42		-3.027
43		-3.115
44		-3.211
45		-3.316
46		-3.434
47		-3.568
48		-3.721
49		-3.903
50		-4.128
51		-4.412
52		-4.819
53		-5.509