



## Kinetics and Thermal Degradation of Powder-free Laboratory Examination Gloves by Thermogravimetric Analysis at 333°C and 422°C

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### Author's contribution

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

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### ABSTRACT

The kinetics of thermolysis of laboratory safety gloves (LG), was studied by thermogravimetric analysis (TGA) at two consecutive isotherm temperatures: 333°C, and 422°C as well as two thermal scan between these two temperatures. Three methods were used to evaluate the kinetics parameters related to the decomposition of LG at 333°C and 422°C isotherms. The results of the study indicate that many zeroth order reactions were occurred, simultaneously. The thermolysis at 333°C fitted better in a second order reaction, while the data at 422°C were not fit to a given order directly. The TGA data at 422°C also fit in a surface decomposition model since the initial reaction order was one and as the reaction progressed the order reached near to zero. The TGA data at 333°C were not fit to this model directly since the surface was saturate before reaching to the isotherm temperature. The activation energy of thermalizes ( $E_a$ ) from thermal scan was estimated; it was below the amount of C-Cl standard bond energy.

**Keywords:** Kinetics; thermogravimetric analysis of powder free examination gloves; examination gloves; latex gloves; pyrolysis of gloves; neoprene; thermalizes.

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## 1. INTRODUCTION

The common practice to disposing wastes includes landfilling, incineration, and recycling. The waste plastics (WPs) contrary to the other household waste do not undergo decomposition in landfill, water, and surface. The incineration of WPs in landfills neither contribute to energy gain nor to environmental benefits. Therefore, new practices must replace the existing methods. One of the promising method is step-by-step thermolysis [1] which converts waste to the valuable original petrochemicals or new fine chemicals. Thermolysis and gasification of WPs are recognized as promising routes for the upgrading of WPs to more valuable and energy-dense materials, such as fuel (gas and oil), lubricants, or to high value feedstock useful to the chemical industry [2,3]. 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 WPs and designing of a practical recycling procedures. Based on our previous experiments [4,5] and the results reported by other researchers, one possible process for recovering valuable chemical and petrochemical products from chlorine-resin based WPs is the stepwise thermal degradation of recovered WPs. In theory, this process allows step-by-step separation of the different product fractions generated by degradation of the WPs blend [6]. In this paper we report the effect of temperature on kinetics of thermolysis of WPs particularly powder-free latex gloves (LG), the ones made of chloroprene as rubber ingredient. Ten (10) samples of LG was thermalized in six consecutive steps at 10 initial isotherms from 308°C to 400°C, then at a second isotherm above 410°C, since the highest decomposition rates of pyrolysis was at 410°C. This reports the results of one of those ten studies in order to keep the manuscript simple and short. The six consecutive steps of this study consisted of: a fast increase of temperature to initial decomposition temperature (333°C), followed with a 90 min isothermal step at this temperature; sequenced with another linear thermal scan from 333°C to 422°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.

The researchers were presented several detailed kinetic models describing the polymer

degradation [7,8,9,10]. These kinetics models can be useful in the study and analysis of the role of mixing in the thermal degradation of polymer blends. Considerable attention was given to the thermal degradation of plastic blends such as polystyrene (PS) mixtures with other materials and their mutual interactions [11,12,13].

The decomposition of pure, freshly prepared polymeric materials, has been of interests to scientists since the applied knowledge of polymeric materials gained relevance [14,15,16]. The decomposition kinetics of polymeric materials [17,5] and the mechanism of decomposition have been studied by many researchers [eg18,19]. Researchers have discovered that some widely used polymeric materials such as poly(methyl methacrylate) (PMMA), upon heating, decomposed to original monomers [20] likewise PS to styrene [12,21,22,23]. However, poly(vinyl chloride) (PVC), [24,25] and neoprene resins [26] thermolysis took a different route than the above mentioned polymers. These polymers decomposed to hydrogen chloride and other fragments upon heating. 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 [27,28]. Therefore, the knowledge of decomposition of WPs provided by this research gains relevance.

The pyrolysis of LGs has attracted the attention of the engineers for designing pilot plants [29]. The wide use of LGs resulted in the accumulations of untraditional wastes not native to the mother earth life cycle. The disposal of LGs in medical wastes presents several problems as they are hazardous biologically, non-biodegradable, and do generate HCl and chlorinated organic compounds upon incineration. Thus the World Health Organization (WHO) is opposed to land filling or incineration of these wastes. Therefore, a new technology that is both environmentally friendly and biologically safe would be required to process these wastes. There is still a lack of data concerning the characteristics and the kind of product produced at various temperatures to better understand the LG thermalizes process. A study on kinetic properties of pyrolysis of selected medical wastes such as absorbent cotton, medical respirator, bamboo sticks [30] and cotton gauges, packaging boxes, capsule plates and

transfusion tubes [25] were conducted by a number of researchers.

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 [31]. Neoprene or polychloroprene ( $-\text{CH}_2-\text{CCl}=\text{CH}-\text{CH}_2-$ )<sub>n</sub> is a family of synthetic rubbers that are produced by free-radical polymerization of 2-chlorobutadiene ( $\text{CH}_2=\text{CCl}-\text{CH}=\text{CH}_2$ ) [32]. 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 [33].

The increase of petroleum and petrochemical prices has opened the way for industries to invest in recycling of plastic wastes to petrochemicals [34,35,36]. Nowadays, plastic landfills are as valuable as petroleum mines. Models for reaction's kinetics for optimal pyrolysis conditions of plastic waste mixtures have been proposed by researchers. Literature abounds on the recycling of these non-traditional wastes to petrochemicals [37,38,39]. As a result many industries are emerging to recycle WPs. From a scientific-engineering point of view, non-degradability of plastics is no longer an environmental issue in landfills since the plastics can be recycled [40]. However, run-away plastic wastes are continuing to be a huge hazard on the surface and in surface water such as waterways, seas and oceans, endangering safe life for both animals and humans [41].

Co-pyrolysis of waste plastic with other natural wastes has been studied. For example, the co-pyrolysis of pine cone with synthetic polymers [42] and characterization of products from the pyrolysis of municipal solid waste [43] and isothermal co-pyrolysis of hazelnut shell and ultra-high molecular weight polyethylene (PE) [44] 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.

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<sup>-1</sup>). The heating rate in all dynamic experiments was kept at the maximum capacity of the TGA instrument, 200°C min<sup>-1</sup>. The LG was thermolysis in six steps: first, the sample was rapidly heated up to 333°C (The calculated average heating rate in this step was 74°C/ min.) and then the temperature was kept constant for 90 min at 333°C (Fig. 1). In succession, the temperature was rapidly increased (The calculated average heating rate in this step was 60°C/ min.) to the second isothermal step (422°C) and maintained there for 30 min; successively, the temperature was rapidly increased to 860°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 8 mg; however, in calculations, the weight was normalized to weight percentage of the samples.

## 3. RESULTS AND DISCUSSION

### 3.1 Thermograms Analysis

Table 1 summarizes the main points of thermolysis of the LG. Less than 2% of LG mass (Fig. 1) was lost during the scan from room temperature to 333°C. During 90 min at 333°C about 36% of the LG was volatilized. However, the effects of high temperature on the structure of materials was not limited to the weight losses. A pure sample of neoprene, ( $-\text{CH}_2-\text{CCl}=\text{CH}-\text{CH}_2-$ )<sub>n</sub>, contains 40.08% Cl and 41.21% HCl. In a case of step-by-step decomposition, all primary volatiles will be HCl, then a weight loss of 58.79% will be expected. The actual weight loss at the end of 90 min at 333°C isotherm was 61.79% which is 3% less than expected weight loss.

During the fast heating from 333°C to 422°C about 17% of weight loss took place and 30% of weight loss occurred when the sample was held at 422°C for 30 min. 7% of material volatilized

during the scan from 422°C to 863°C and holding there for 2 min where the organic components of the sample was consumed completely. The leftover ashes (about 8%) has white color, soluble in hot water, the solution has strong basic property (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 effects the rate of a reaction, but they may not appear in

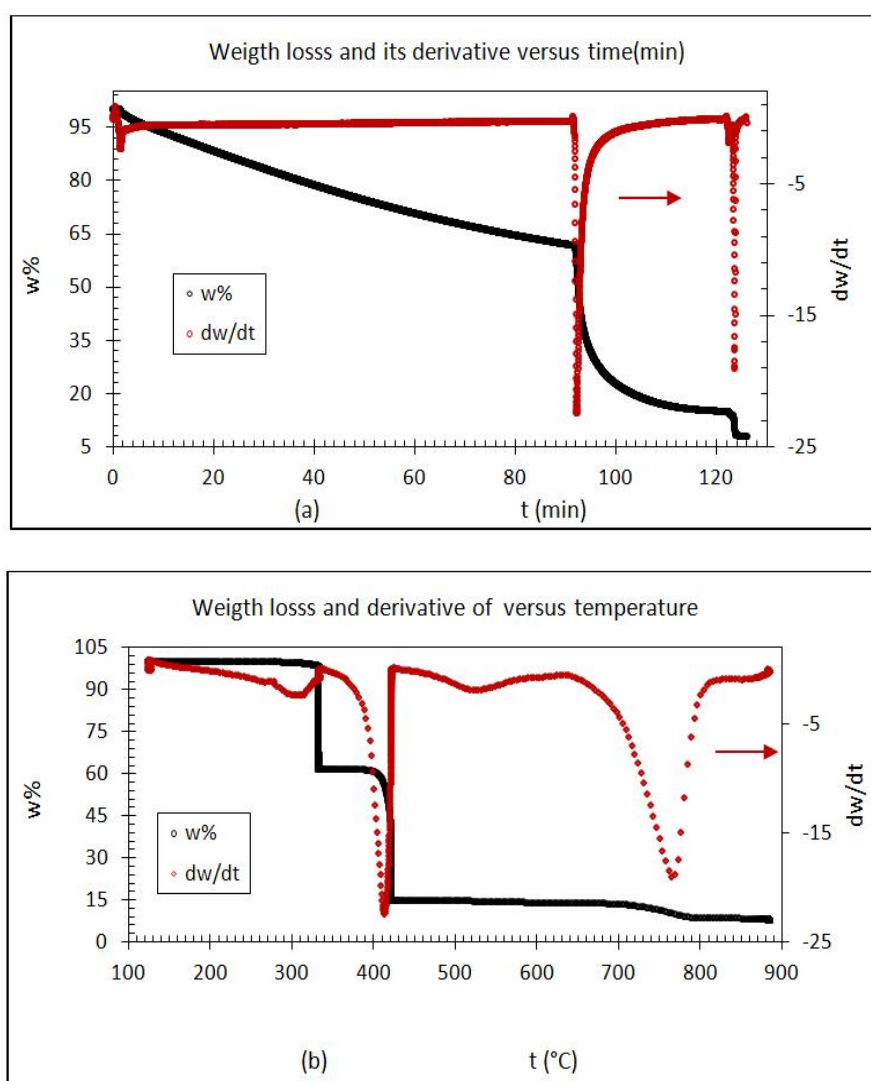
the overall reaction. For a simple pyrolysis reaction of  $w$ :



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

where  $w$  is the mass of unreacted material at time  $t$ ;  $n$  is the order of reaction at the slowest step, and  $k$  is the rate constant of the reaction. Rearranging Eq (2) results:

$$w^{-n}dw = -kdt \quad (3)$$



**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**

Integration of Eq (3) for values of  $n = 0, 1,$  and  $2$  results:

$$n = 0, w = -kt + c_0 \quad (4)$$

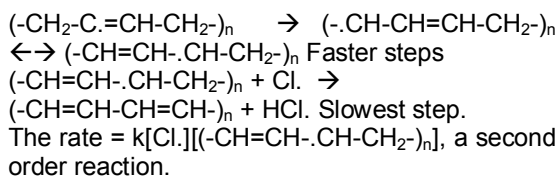
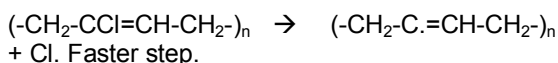
$$n = 1, \ln w = -kt + c_1 \quad (5)$$

$$n = 2, w^{-1} = kt + c_2 \quad (6)$$

Figs. 2a, 2b and 2c show the treatment of the experimental data of weight loss over time obtained for LG at 333°C and 422°C treated according to the above relationships. The experimental data at 422°C does not fit into zeroth, first, and second order reactions.

However, a large number of data at the initial time and the end time fitted well into the above orders. The kinetics parameters obtained from initial time of process (i) and end of process (f) according to the respective orders for both isotherms are tabulated in the Table 2.

However, the experimental data at 333°C fit better in a second order reaction (Fig. 2c). Considering a second order reaction for the first step decomposition requires:



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 advantage of a detailed pyrolysis kinetic model is to allow the prediction of the full detail of the product distribution which is a significant step forward in the possibility of upgrading of solid wastes to useful chemicals.

### 3.3 Activation Energy of Pyrolysis

The  $E_a$  for a simple pyrolysis reaction may be estimated by Eq (7) assuming the reactants are the same materials at both temperatures, and the  $E_a$  is independent of temperature.

$$\ln \frac{K_2}{K_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (7)$$

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

Steps	$t_i$ (min)	$t_f$ (min)	$\Delta t$ (min)	$w_i\%$	$w_f\%$	$\Delta w\%$	$t_i$ (°C)	$t_f$ (°C)	$\Delta T$ (°C)
1	0.02	2.78	2.77	99.98	98.11	1.87	128	333	205
2	2.80	91.40	88.60	98.11	61.79	36.32	334	333	-1
3	91.42	92.87	1.45	61.79	44.74	17.05	333	420	87
4	92.88	121.83	28.95	44.53	14.94	29.59	421	422	2
5&6	121.88	125.95	4.07	14.94	7.88	7.06	422	883	461

**Table 2. The kinetics parameters, including reaction's order,  $k$ , and  $E_a$  of LG pyrolysis based on Eqs (4), (5) and (6). Subscript i indicates the value of parameter at initial time and f indicates the same value the end of trace**

n	$k_i$	$k_f$	t (°C)	$E_{a_i}$ (kJ/mol)	$E_{a_f}$ (kJ/mol)
0	8.47E-01	2.29E-01	333	30.0	-14.0
0	8.34E+00	7.87E-02	422		
1	8.63E-03	3.70E-03	333	37.8	4.6
1	1.54E-01	5.26E-03	422		
2	8.80E-05	5.97E-05	333	50.6	23.3
2	4.17E-03	3.51E-04	422		

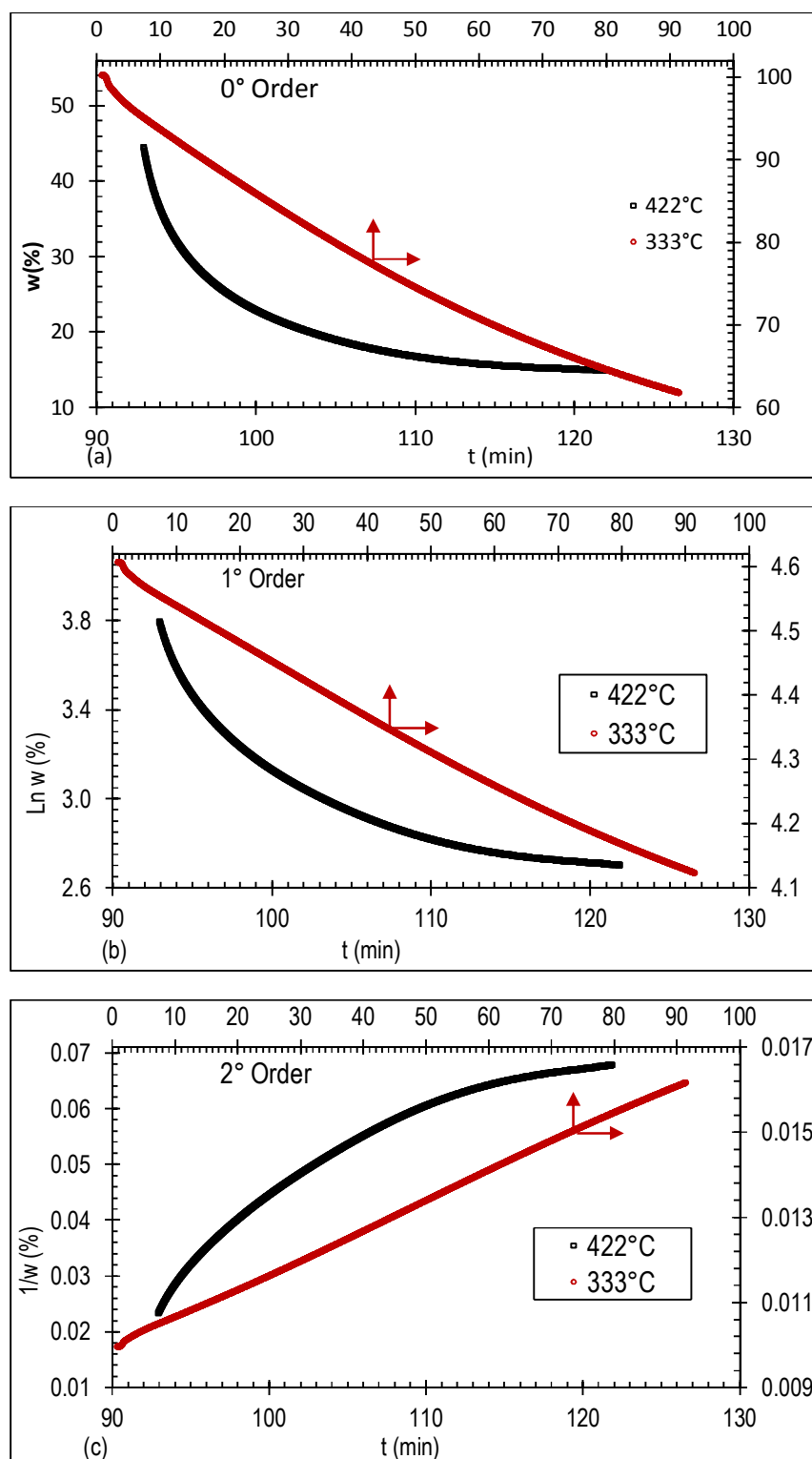


Fig. 2. Treatments of the variation of weight loss over time based on: (a) zeroth order, Eq (4); (b) first order, Eq (5); and (c) second order reactions, Eq (6)

The obtained  $E_a$  values also were tabulated in the Table 2 (columns 5 and 6) for each reaction order. For all reaction order the  $E_a$  related to initial time of reaction was larger than the  $E_a$  for the end of the process. This indicates that there were chemical changes in the nature of reactants. The  $E_a$  values can be related to the minimum energy required to decompose a chemical bond. 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. These values of  $E_a$  (Table 2) are below the amount of standard bond energies of C-Cl, C-H, and C-C. The  $E_a$  values lower than bond energy also has been reported for decomposition of other polymers; for example,  $E_a$  for unzipping polymethylmethacrylate radicals was evaluated to be 60 kJ/mole [45]. Likewise, the values of  $24.6 < E_a$  (kJ/mol)  $< 64.0$  for various reactions involved in thermolysis of glucose based carbohydrates has been reported [46] which are considerably lower than involved bond energies.

### 3.4 General solution for Eq (3)

Integrating Eq (3) for all values of  $n$ , except  $n = 1$ , results in Eq (8)

$$w^{1-n} = -(1-n)kt + C \text{ for all values of } n \neq 1 \quad (8)$$

Reiteration method was used to estimate the order of reaction by plotting  $w^{(1-n)}$  versus  $t$  (min) for a numbers of  $n$  values. Then, the  $R_{sq}$  values of each trial was plotted versus corresponding  $(1-n)$  value (Fig. 3a). The  $n$  corresponding to the largest  $R_{sq}$  value represents the best reaction order. Using the best  $n$  value into Eq (8), the slope of a plot of  $w^{(1-n)}$  versus  $t$  (min) (Fig. 3b) represents  $k$  when it is divided by  $(n-1)$ . These results are summarized in Table 3.

Thermolysis reactions occurs either in in solid or liquid state where a typical reaction order of zero or one is expected. Therefore, the second order reaction at 333°C will be acceptable base on the proposed radical mechanism as was describe in previous section. The reaction order above 2 is rare in the solid and liquid state where the predominant reactions are decomposition reactions. Although, methods for evaluation of

reaction order using thermogravimetric data are available [e.g. 47], however assuming first order for the thermolysis reaction is common [e.g. 48]. The obtained  $k$  values being very small for a fast decomposition reaction (Table 3) are in order of previous method (Table 2). The reported Arrhenius  $k$  values,  $8.32 \times 10^5$  and  $2.34 \times 10^6$  for pyrolysis of lignin are well considerably higher than the values estimated by above methods for neoprene. On the other hand, as the temperature of pyrolysis was increased the value of  $k$  decreased which was not within expectations based on Arrhenius relationship, Eq (7) for a given reaction at two temperatures. Therefore, the nature of decomposition reactions at 333°C and 422°C were different. This is within expectation based on the previous proposed mechanism.

### 3.5 Reaction Order from Rate of Pyrolysis

The logarithmic plot of  $r$  by  $w$  for a simple reaction must be linear with the slope and intercept being the order and  $\ln k$  of a given reaction according to:

$$\ln(r) = n\ln(w) + \ln(k) \quad (9)$$

The experimental data at 333°C has an interesting trends, at a first view they give an impression that a straight line can be fitted in the initial data point with an  $n = 14$ . Knowing that the order above 2 for these kind of reaction in solid or liquid state are rare; and an order near to zeroth, is more acceptable for decomposition at higher temperatures. The expansion of Fig 4a, confirms this idea (Fig. 4b). Magnifying the experimental data (Fig. 4b) showed the occurrence of many simultaneous zeroth order reactions with their proper  $k$  values (intercept). In this manner, over 130 hypothetical parallel reactions, were identified. The existence of many parallel chemical reactions 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 [3,5].

The experimental data at 422°C were scattered and did not fall in a straight line as was expected (Fig. 4a). However, the major section of experimental data at 422°C followed a straight line (Fig. 4a),

$$\ln(r) = 3.372 \ln(w) - 10.485, \quad (R^2 = 0.999) \\ 2.89 < \ln(w) < 3.66 \quad (10)$$

The slope  $n = 3.37$  is near to the order of reaction that was obtained from previous method ( $n = 3.4$ ) and the obtained value of  $k = 2.79 \times 10^{-5}$  is near to the  $k$  value obtained in the previous method (Table 2). Also, a polynomial regression can be fitted to all data (Eq (10A)). In this case, the order of reaction vary by weight loss as estimated by Eq (10B) which for most  $\ln w$  was  $0.53 < n < 1.34$   $w$  which is within expectation.

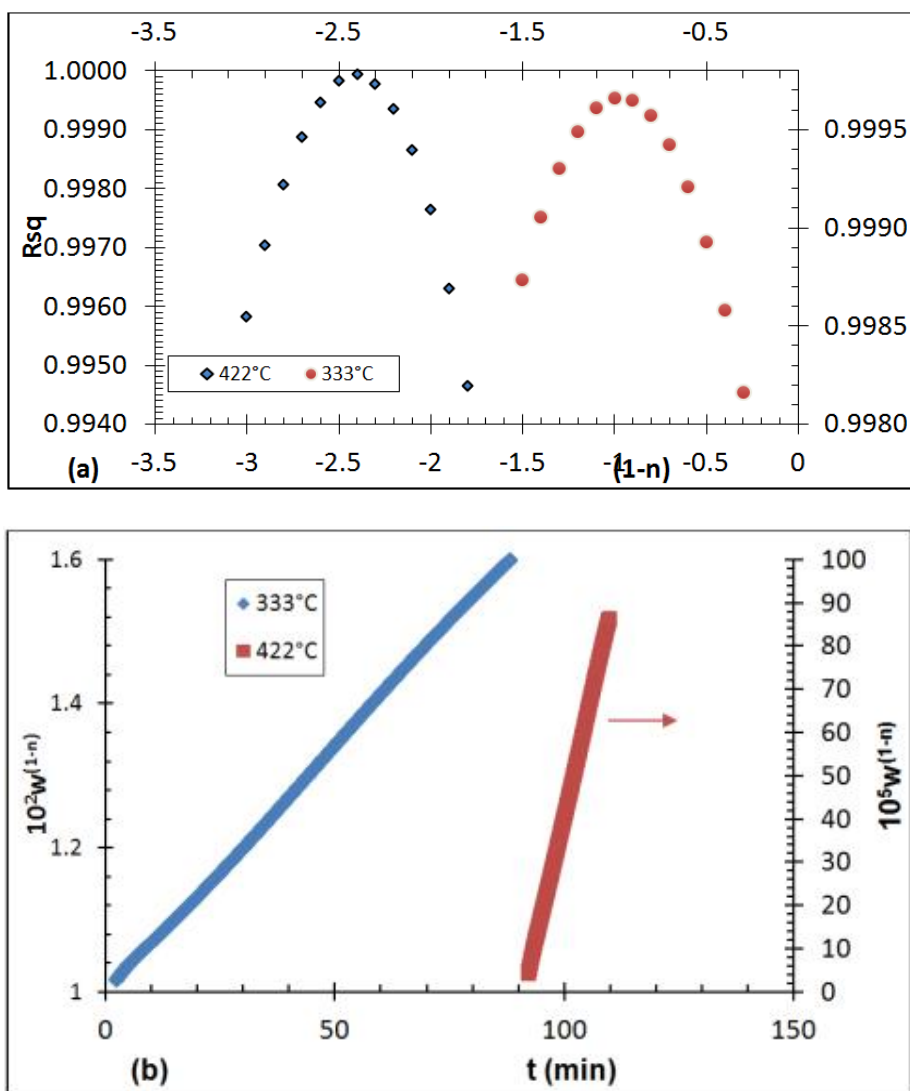
$$\ln r = 67.167\ln w^5 - 1087.6\ln w^4 + 7033\ln w^3 - 22703\ln w^2 + 36586\ln w - 23551, \quad (10A)$$

Rsq=0.988

$$n = (\ln r)' = 335.835 \ln w^4 - 4350.4 \ln w^3 + 210099\ln w^2 - 45406 \ln w + 36586$$

$$2.70 < \ln w < 3.60 \quad (10B)$$

The advantage of a polynomial regression was that at any value of  $w$  a value for order of reaction was obtained (Table 4). The value of reaction's orders  $0.53 < n < 1.34$  are better describing the thermalize reaction order than the slope of single line passing through experimental data. At the end of reaction, the data were very scatter, therefore the order of reaction such as 4 and above are not within expectations.



**Fig. 3. Estimation of kinetics parameters of pyrolysis of LG: (a) plot of Rsq versus reiterated values of  $(1-n)$ ; (b) plots of  $w^{(1-n)}$  versus  $t$  (min) (Eq (8)) for the best  $n$  value obtained from max of Fig. 3a**



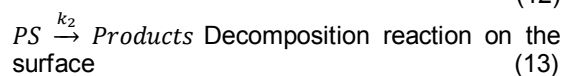
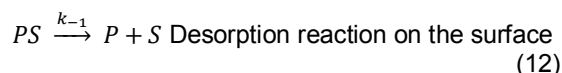
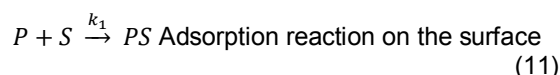
**Table 3. Pyrolysis parameters obtained from Figs. 3a and b**

t (°C)	n	k
333	2.0	6.90E-05
422	3.4	2.56E-05

Other researchers [e.g. 7,49,50] also had assumed many simultaneous chemical reactions at high temperatures to explain thermalizes of pure polymeric materials. For example, Kruse et al. [7] presented a detailed mechanism of PS pyrolysis based on population balance equations and the method of the moments in which up to 93 species and 4500 reactions were used to describe product distribution and average molecular weight. Similarly, detailed kinetics models of PE, polypropylene (PP) and PS pyrolysis were presented and discussed by other researchers [eg 5,10]. The reported results of thermal degradation of plastic blends and their mutual interactions [e.g. 11,12] 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 [13]. 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.

### 3.6 Reaction on the Surface

The shape of the curves related to decomposition rate of LG,  $r$  versus  $w$  at 333°C and 422°C (Fig. 5) are similar to the decomposition of IH on gold or NH<sub>3</sub> on molybdenum surface in the sense that the initial reaction apparently was first order and after certain time the reaction order reached to zero. In this case, a polymer molecule has to absorb energy from the surface of the TGA pan prior to undergo any reaction. Therefore, it could be considered that the molecules of LG are decomposing on the surface after receiving appropriate activation energy. In the case of simple decomposition of a LG molecule (P) on a vacant site on the surface of TGA pan (S), the P has two options: it may desorb unchanged or may decompose to products as:



The rate of reaction (R) per square meter of surface at the concentration (mol/m<sup>2</sup>) of LG (C<sub>PS</sub>) is expressed as:

$$R = k_2 C_{PS} \quad (14)$$

Let C<sub>p</sub> be the total concentration of surface sites per square meter and let q be the fraction of these sites that are covered by P. Then, the rate of reaction related to the concentration of vacant sites on the surface: C<sub>PS</sub> = C<sub>p</sub>q, can be written:

$$R = k_2 C_p q \quad (15A)$$

The value of q is obtained by applying the study-state concentration to the rate of formation of PS when C<sub>p</sub> be the concentration of P but not on the surface:

$$\begin{aligned} dC_{AP}/dt = 0 &= k_1 C_p C_s - k_{-1} C_{PS} - k_2 C_{PS} \\ &= k_1 C_p C_s (1-q) - k_{-1} C_p q - k_2 C_p q \end{aligned} \quad (15B)$$

$$q = k_1 C_p / (k_1 C_p + k_{-1} - k_2) \quad (16)$$

Replacing this value of q in the rate law equation yields:

$$R = k_1 k_2 C_p C_s / (k_1 C_p + k_{-1} + k_2) \quad (17)$$

When the rate of decomposition is very small compared with the rate of adsorption and desorption, q become the Langmuir adsorption isotherm. In this case, the occurrence of the decomposition does not affect the adsorption equilibrium at all. In this case both q and R depend on C<sub>p</sub>:

$$\begin{aligned} R &= k_1 k_2 C_p C_s / (k_1 C_p + k_{-1}) \\ &= (k_1/k_{-1}) k_2 C_p C_s / ((k_1/k_{-1}) C_p + 1) \end{aligned} \quad (18)$$

At lower concentrations, where (k<sub>1</sub>/k<sub>-1</sub>)C<sub>p</sub> << 1 and q = (k<sub>1</sub>/k<sub>-1</sub>)C<sub>p</sub>; the coverage is small. Then the reaction is first order in concentration of P (Fig. 5) as it is the case of LG initial rate.

$$\begin{aligned} R &= (k_1/k_{-1}) k_2 C_p C_s = 1.012w - 32.999, \\ R^2 &= 0.9994, 42.68 < w\% < 44.53 \text{ at } 422^\circ\text{C} \end{aligned} \quad (19A)$$

The value of slope decreased gradually, at the end of reaction reach near to zero (0.11).

$$R = (k_1/k_{-1})k_2C_pC_s = 0.113w - 1.633,$$

$$R^2 = 0.766, 14.96 < w\% < 17.39 \text{ at } 422^\circ\text{C}$$

(19B)

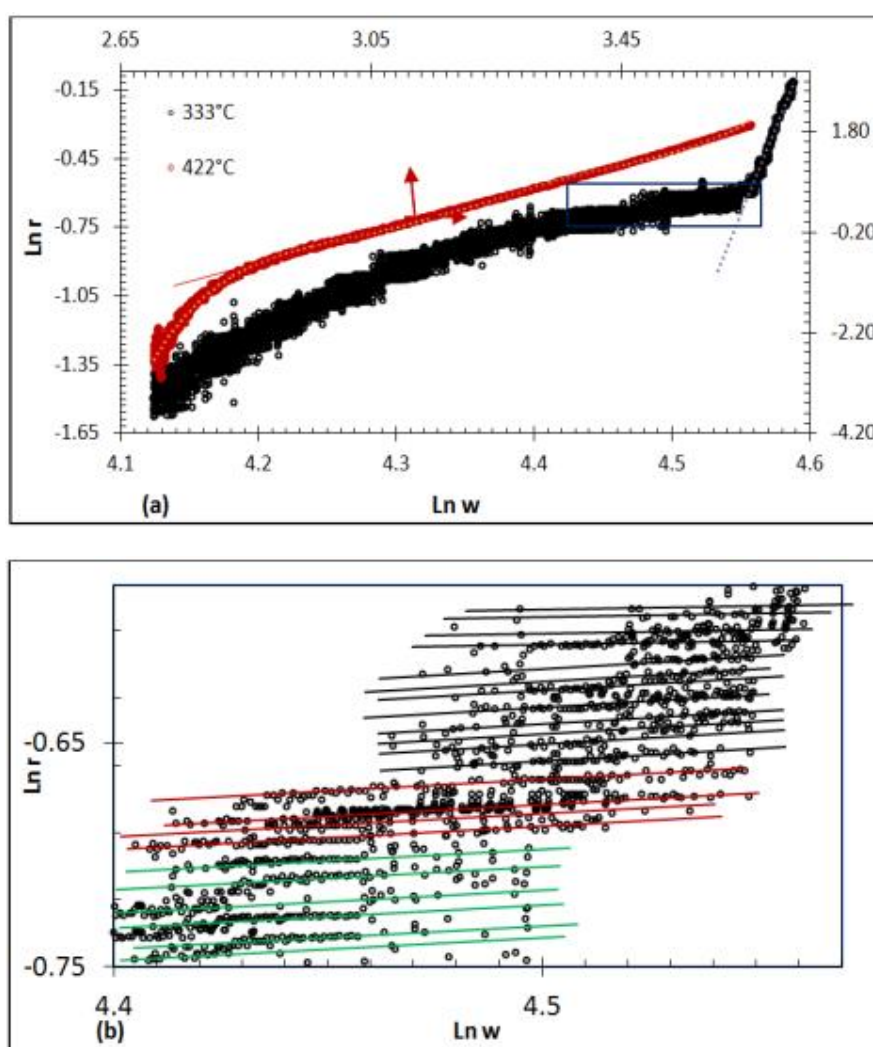
At high concentration of  $w$ , where  $(k_1/k_{-1})C_p \gg 1$  and  $q \approx 1$ ; then the reaction is zero order with respect to  $w$  (Fig. 5) since surface is saturated with LG which needs absorb energy to

decompose. In other words the thermolysis became independent of the amount of reactants (zero order) and solely depends on the amount of energy that can absorb from surface. Eq (18) became as simple as Eq (20), a zero order reaction with respect to LG.

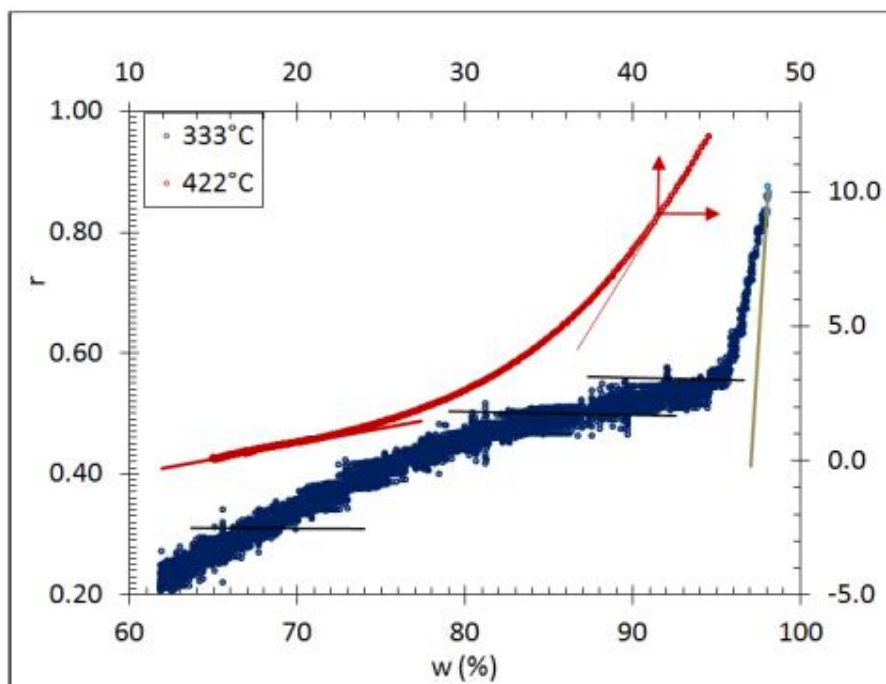
$$R = k_2C_s \quad (20)$$

**Table 4. Order of pyrolysis reaction obtained from Eq (10B) at the indicated  $\text{Ln}w$**

$\text{Ln}w$	3.55	3.45	3.35	3.25	3.15	3.05	2.95	2.85
$n$	1.17	0.53	1.08	1.52	1.34	0.87	1.21	4.29



**Fig. 4. (a) Double logarithmic variation of rate of weight loss ( $r$ ) versus the mass of reactant  $w\%$ . (b) Expansion of the marked section of the plot of Fig. 4a where each adjusted line passed through the experimental points indicated a reaction with near to zero order**



**Fig. 5. Variation of rate of weight loss( $r$ ) versus the amount of reactants ( $w\%$ ) for the isothermal process at  $333^{\circ}\text{C}$  and  $422^{\circ}\text{C}$ . The initial slope of the experimental data are indicated in the graph. After a certain time a plateau of experimental data were observed. Many reactions with Zeroth order could be identified in the plot (blue lines are some examples)**

The initial thermalizes reaction at  $333^{\circ}\text{C}$  was not a first order reaction with respect of reactants  $w\%$  (Fig. 5). As the reaction moves forward, it became evident that many simultaneous reactions with zero order were presented as it was explained in the previous section.

### 5.7 Evaluation of $E_a$ from Thermal Scan

Arrhenius relationship (Eq 21) relates the rate constant,  $k$ , to the activation energy of reaction  $E_a$ , the absolute temperature of the reaction  $T$ , the ideal gas constant,  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$  and another constant such as  $z$  to describe the efficiency of the molecular collisions in a chemical reaction.

$$k = ze^{\frac{E_a}{RT}} \quad (21)$$

Combining Eq (2) and Eq (21) results:

$$r = ze^{-\frac{E_a}{RT}} w^n \quad (22)$$

The logarithmic form of Eq (22), linearly relates  $\ln r$  to the inverse of temperature,  $1/T$  (K):

$$\ln r = \ln z + n \ln w - E_a/RT \quad (23)$$

Fig. 6 represents the application of Eq (23) to TGA scan from  $120^{\circ}\text{C} - 333^{\circ}\text{C}$  and  $333^{\circ}\text{C} - 408^{\circ}\text{C}$ . The  $E_a = 229$  (Table 5)  $\text{kJ/mol}$  for initial weight loss,  $191 < t^{\circ}\text{C} < 203$  is comparable to the reported  $E_a = 225 \text{ kJ/mol}$  for initial decomposition step (0-10%) of rubber in nitrogen [51]. The calculated  $E_a = 255 \text{ kJ/mol}$  at  $333^{\circ}\text{C} < t < 415^{\circ}\text{C}$  (Table 5) for 55-61% region is comparable to the reported value  $E = 239 \text{ kJ/mol}$  of rubber for 10-100% region [51]. Both values are far smaller than the bond energy for decomposing of Cl-C bonds ( $331 \text{ kJ/mol}$  at  $25^{\circ}\text{C}$ ) and C-C single bond ( $346 \text{ kJ/mol}$  at  $25^{\circ}\text{C}$ ) by radical mechanism under standard conditions. However, at those high temperatures, the  $E_a$  will be lower than standard conditions as were observed by other researchers [45,46].

At the end of thermal scans ( $314$  to  $333^{\circ}\text{C}$ ), the estimated  $E_a$  values was negative meaning that only exothermic reactions are taking place and the amount of available energy was more than the amount of energy that the reactants could absorbed. At the end of scan, exothermic combination reactions such as formation of HCl and C=C must be the predominate reactions.

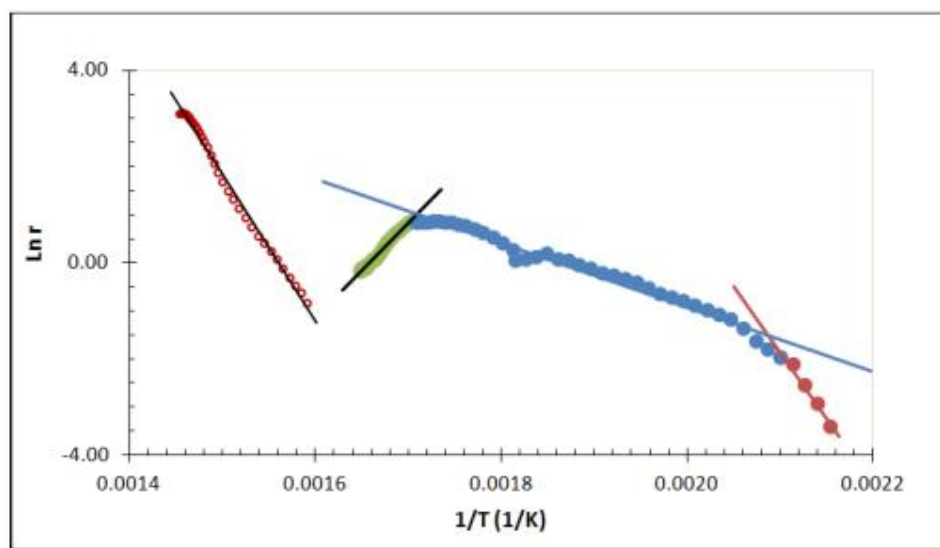


Fig. 6. Variation of logarithm of rate of decomposition of LG versus inverse of temperature

Table 5.  $E_a$  of the pyrolysis steps of LG, including initial time ( $t_i$ ), final time ( $t_f$ ), the duration of process ( $\Delta t$ ) time, initial and final temperatures ( $t_i$  and  $t_f$ ), and the range of temperature ( $\Delta T$ ), initial and final weight loss ( $w_i$ ,  $w_f$ ) and the amounts of weight loss ( $\Delta w$ )

Steps	$t_i$ (min)	$t_f$ (min)	$\Delta t$ (min)	$w_i$ %	$w_f$ %	$\Delta w$ %	$t_i$ ( $^{\circ}\text{C}$ )	$t_f$ ( $^{\circ}\text{C}$ )	$\Delta T$ ( $^{\circ}\text{C}$ )	$E_a$ (kJ/mol)
1	0.90	0.97	0.07	100	100	0.01	191	203	12	229
2	0.97	1.60	0.63	100	99.48	0.76	203	312	109	56
3	1.62	2.73	1.12	99.44	98.17	1.27	314	333	20	-165
4	91.40	92.27	0.87	61.79	55.05	6.74	333	414	81	255

## 6. CONCLUSIONS

The decomposition kinetics of LG at two isotherm 333 $^{\circ}\text{C}$  and 422 $^{\circ}\text{C}$  was studied by TGA. The obtained data showed that the decomposition of LG at 333 $^{\circ}\text{C}$  could be explain as a second order reaction where the slowest step be the abstraction of a hydrogen by chlorine radical from substrate. The order of reaction at 422 $^{\circ}\text{C}$  based on the polynomial curve fitted to all experimental data indicated the order of decomposition reaction at any given value of  $w$  was  $0.50 < n < 1.4$ . This is within expectation for a decomposition reaction at solid or liquid sated. The pyrolysis data was described well with the surface model reaction since the initial reaction order was first order, and as the reaction progressed, it became independent to the concentration of reactants. The experimental data showed that the initial rate can be described as first order, however, as reaction progressed, many simultaneous zeroth order reactions were observed. The occurrence of many simultaneous decomposition thermalizes reaction is in agreements with theoretical simulations. The

activation energy obtained from the thermal scan starting 333 $^{\circ}$  to 422 $^{\circ}\text{C}$  was well below of the standard bond energy of C-Cl and C-C which confirms the at higher temperatures occurs at lower  $E_a$  Values.

The TGA data shows that reactants in the first isotherm are different than in the second isotherm. Therefore, this work shows with tow step decomposition, it will be possible to decompose the waste gloves into useful chemicals. In the first step removal of chlorine occurs and in the next step chlorine-free remains thermalizes into useful chemicals. In other words, this work simulate a waste processing reactor. Keeping the temperature of reactor at lower to remove chlorine contain volatiles, then increase the temperature to a higher temperature for degrade the chlorine free remaining to petrochemicals useful as fuel.

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## COMPETING INTERESTS

Author has declared that no competing interests exist.

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