# Thermogravimetric and Kinetic of thermal degradation of Powdered Laboratory Examination Gloves: 1. Analysis of thermal Scan Traces from 310-440°C.


## ABSTRACT

The focus of this work is on developing the most energy efficient method to decompose powdered laboratory safety examination gloves (PLEG).Here we are reporting the results of thermogravimetric analysis (TGA) of PLEG, without catalyst.The study was done in the Department of Biological and Physical Sciences at South Carolina State University (SCSU), Orangeburg, SC, USA, during the spring and summer of 2014.Twelvesamples of PLEG were studies under three types of operating conditions: firsta sample was thermal scannedfrom 50ºC to 800ºCwith a heating rate of 10ºC/min while it were purged with 10 mL/min argon. The results of this study determine the thermal stability of PLEG, the highest weight loss rate was observed ~410 °C. The second approach was a dynamic thermal scan with a linear and fast (200°C/min)increase of the temperature over time, then stopped at a given temperature for a sequential isothermal step for 30 minutes. Afterward, the sample was heated fast again to the temperature of 410°C (the highest weight-loss rate) where the sample hold for another 30 min.From the thermal scans and isotherms,the highest rate of weight loss, the temperature at the maximum weight loss, the acceleration of weight loss by thermal scan, the deceleration of weight loss at the isotherms, the rate constant and activation energy of weight loss (Ea) were estimatedThe experimental results confirm that Ea of weight loss of PLEG samples depended on the temperature of operation. At temperature below 430°, the amount of Ea of weight loss of sample was higher than those above 430°C temperatures.



*Keywords: thermogravimetric studies of latex gloves, kinetics of thermogravimetry of laboratory safety gloves, environment; pollution; lab examination gloves; latex gloves, pyrolysis of gloves, thermolysis of neoprene; activation energy of pyrolysis, rate constant of laboratory safety glove pyrolysis.*


## DEFINITIONS, ACRONYMS, ABBREVIATIONS

**Term**:

PLEG: powdered laboratory examination glove, LSG: laboratory safety glove, PVC: poly(vinyl chloride); PMMA: poly(methyl methacrylate); PS: poly(styrene); PE: poly(ethylene); PET: poly(ethyleneterephthalate); RT: retention time, TIC: total ion chromatogram;GC-MS: gas chromatography-mass spectrometery, WHO: world health organization, Ea: activation energy, TGA: thermogravimetric analysis,

## 1. INTRODUCTION

The decomposition of polymeric materials has been of scientists' interests since the applied knowledge of polymeric materials gained relevance [1,2,3]. The decomposition kinetics of polymeric materials [4,5] and the mechanism of decomposition have been studied by many researchers [6,7]. Researchers have discovered that some widely used polymeric materials such as poly(methyl methacrylate) (PMMA), upon heating,

decomposed to original monomers [8] likewise polystyrene (PS) to styrene [9,10,11,12]. However, some other polymeric materials decomposed to smaller stable, and toxic molecules upon heating. For example, poly(vinyl chloride) (PVC), upon heating, first decomposed to hydrogen chloride and unsaturated polymers which decomposed later to other chemicals [13,14,15]. Pyrolysis of neoprene also is similar to PVC first produce HCl [16].

The decomposition of polymeric materials is also relevant and of interest to industries since plastic is used in many of today's commodities [17,18]. The pyrolysis of LEG has attracted the attention of the engineers for designing pilot plants [19]. The wide use of LEGs resulted in the accumulations of untraditional wastes not native to the mother earth life cycle [20]. The disposal of latex gloves in medical wastes, in particular, presents several problems as they are hazardous biologically, non-biodegradable, do generate HCl and chlorinated organic compounds upon incineration, thus the World Health Organization (WHO) is opposed to land filling or incineration of this waste. Therefore, a new technology that is both environmentally friendly and biologically safe would be required to process these wastes. There is still lack of data concerning the characteristics and the kind of product produced[21], therefore further studies will help to better understanding of the process. A study on kinetic properties of pyrolysis of selected medicals such as absorbentcotton, medical respirator, bamboo sticks [22] and cotton gauge, packaging boxes, capsule plates and transfusion tubes [25] were conducted by a number of researchers.

Kinetic models are proposed for polymer degradation, describing the pyrolysis process with simplified reaction pathways. Each individual reaction step considered can be representative of a complex reaction network. This single step approach is only adequate for describing the apparent kinetics of degradation, but dose not cover a wide range of heating rates, temperatures and conversion levels, with the same kinetic parameters. Consequently, this approach is not useful in understanding the decomposition behavior of polymer mixtures. Only a few detailed kinetic models describing the polymer degradation are reported in the literature, Recently, Kruse et al [23] presented a detailed mechanism of polystyrene (PS) pyrolysis based on population balance equations and method of moments in which up to 93 species and 4500 reactions are used to describe product distribution and average molecular weight. Similarly, detailed kinetic models of polyethylene (PE), polypropylene (PP) and PS pyrolysis were recently presented and discussed [24,25,26]. These kinetic models can be useful in the study and analysis of the role of mixing in the thermal degradation of polymer blends, The considerable attention was given the thermal degradation of plastic blends and their mutual interactions [eg 27,28]. These results do not completely agree and different effects were observed. The work of Westerhout et al [29], carried out in pure chemical conditions, states that the pyrolysis of' polymer mixtures behaves quite similarly to pure polymers and it claims that the additives rule is the correct approach for this problem.

Examination gloves or disposable gloves are used during medical examinations and procedures, and as safety protection in work to prevent contamination.[30,31]They are available in forms of un-powdered, or powdered with cornstarchto lubricate the gloves, making them easier to use [32].Cornstarch replaced tissue-irritating lycopodium powderand talc. The powders can impede healing if they get into tissues (as during surgery), and can contaminate experiments in laboratory procedures. Therefore, un-powdered gloves are being used more often. Surgical gloves have more precise sizing with a better precision and sensitivity and are made to a higher standard than examination gloves. The gloves that are used in chemistry laboratory as safety protection media are examination gloves (Fig 1a). This type of gloves was the one that they were pyrolyzed and reported here.

The examination gloves are made of diverse polymers including latex, nitrile rubber, vinyland neoprene. 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=$CH_2$).[33] 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.[34]

Actually, wastes of modern materials are accumulated without effective decomposition and recycling routes in the landfills. The increase of petroleum and petrochemical prices opened the ways for industries to invest in recycling of plastic wastes to petrochemicals [35,36,37].Literature abounds on the recycling of these none-traditional wastes to petrochemicals [38,39,40] and many industries are sustained and developed based on decomposition of natural and synthetic polymers [41,42]. 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 [43]. However, run-away plastic wastes are continuing to be a huge hazard on the surface and surface water such as waterways, seas and oceans, endangering safe life for both animals and humans [44].

Based on our previous experiments[45,46] and the results reported by other researchers, one possible process for recovering valuable chemical and petrochemical products from plastic waste is the stepwise thermal degradation of recovered waste plastics as mixtures polymers and plasticizers [47]. The aim of this paper is to investigate the effect of temperature on kinetic of thermolysis of plastic wastes particularly latex gloves, the one that made of chloroprene as rubber ingredient. Two types of operating conditions were adopted: (1) two dynamic thermal scans with a linear increase of the temperature over time, and (2) the latter consists of two sequential isothermal steps.

This study reports the results of non-catalytic conversion of examination gloves a neoprene based materials.

## 2. MATERIALS, INSTRUMENTATION, AND METHODS

### 2.1 Materials

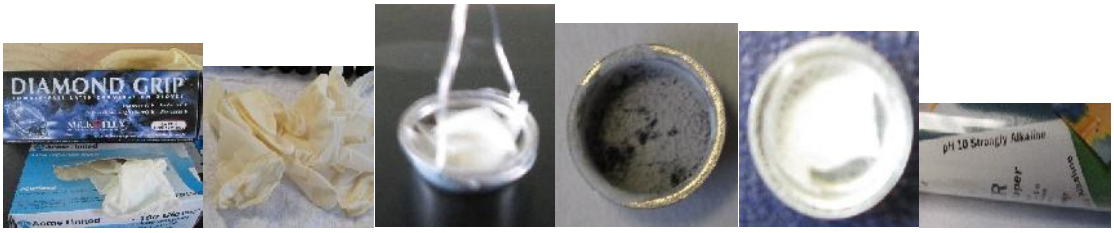
The material used (Figure 1a) was powdered examination gloves (PLEG) by Acme United Corporation (Fairfield CT, USA) which was purchased from Office Form and Supply, INC (Charlotte, NC, USA).The gloves was cut into small pieces (3 mm x 4 mm) to be fit into the pan of TGA analyzer (Fig 1b).

### 2.2 Instrumentation

#### 2.2.1 The Thermogravimetric Analyzer

A Perkin-Elmer (USA) thermogravimetric analyzer (TGA-7) was used to study the thermal stability of the PLEG from 50ºC to 800ºC with a heating rate of 10ºC/min while the sample was purged with 10 mL/min argon. 4-12 mg of a sample cut from an unused-PLEG was loaded into a TGA pan (Fig 1b). The experimental tests, both under dynamic and isothermal conditions, were performed in the same thermogravimetric analyzer (TGA-7) controlled by a Dell (USA) PC. The atmosphere was fluxed by argon with a flow rate of 10 mL $min^{-1}$. The heating rate in all the dynamic experiments was kept to the maximum capacity of the TGA instrument, 200°C $min^{-1}$, starting from 50°C and rising to the first isotherm. The isothermal tests were performed in two steps. First the sample was rapidly heated up(~ 200°C min) to the first temperature level ( e.g. 310°C) and then the temperature was kept constant for 30 min. In succession, the temperature was rapidly increased to the second isothermal step (410°C) which was the highest decomposition rate for PLEG, and therein the temperature was maintainedfor 30 min.Successively, the

temperature was rapidly increased to 800°C and maintained for two min; this lead to the complete degradation of the organic substances. The fast temperature ramps to the isothermal conditions did not show significant overheating. The initial sample weights varied between 4 and 12 mg, however, in calculation the weight percent of sample were used.




(a) (b) (c) (d) (e) (f)

**Figure 1. Step-by-step illustration of thermogravimetric of pyrolysis process of PLEG: (a) and (b) Unused LEG and PLEG; (c) TGA pan with PLEG; (d) the remains after heated to 600°C; (e) the products at 800°C, (f) alkaline pH of the aqueous solution of the ashes.**

Twelve samples were analyzed; seven samples has two isotherms, one blow 410°C and the second at 410°C. These experiments were designed to find the most effective temperature of pyrolysis of PLEG. The sample was heated up quickly (200°C/min) to first isotherm and kept at this temperature for 30 min. Depending on the isotherm temperature there was a partial weight loss of the PLEG at the first isotherm (5-60%), Next, the system was quickly heated up (200°C/min) to 410°C and left for another 30 min. during this isotherm up to 70% weight loss was appreciated (Fig 2). The mass of the PLEG and the temperature of the first isotherm are summarized in Table 1.These experiments were carried out with a practical interest in the PLEG decomposition under various temperatures and their impact on the activation energy of (Ea) of pyrolysis process.

Seven set of two-step isothermal experiments was performed in order to analyze the typical conditions of the pyrolysis of PLEG more closely and to investigate the best conditions for pyrolysis of the LEG. The sample was heated up quickly (200°C/min) to a temperature (for example to 310°C) and kept at this temperature for 30 min (first isotherm). After 30 min the temperature raised fast (200°C/min) to next isotherm at 410° and kept at this temperature for another 30 min, where up to 70% of the sample vaporized. These experiments were carried out with a theoretical interest in the LEGs thermolysis at molecular level and their impact on the reaction mechanisms.

## 3. RESULTS AND DISCUSSION

The detailed description of the overall degradation of the PLEGs is quite a complex process which involves a large number of chemical reactions and intermediate species. The TGA alone is not able to provide information about the nature of volatiles. Therefore, without chemical identification of the thermolysis products it would be rather hard to propose a mechanism for degradation. However, by the information

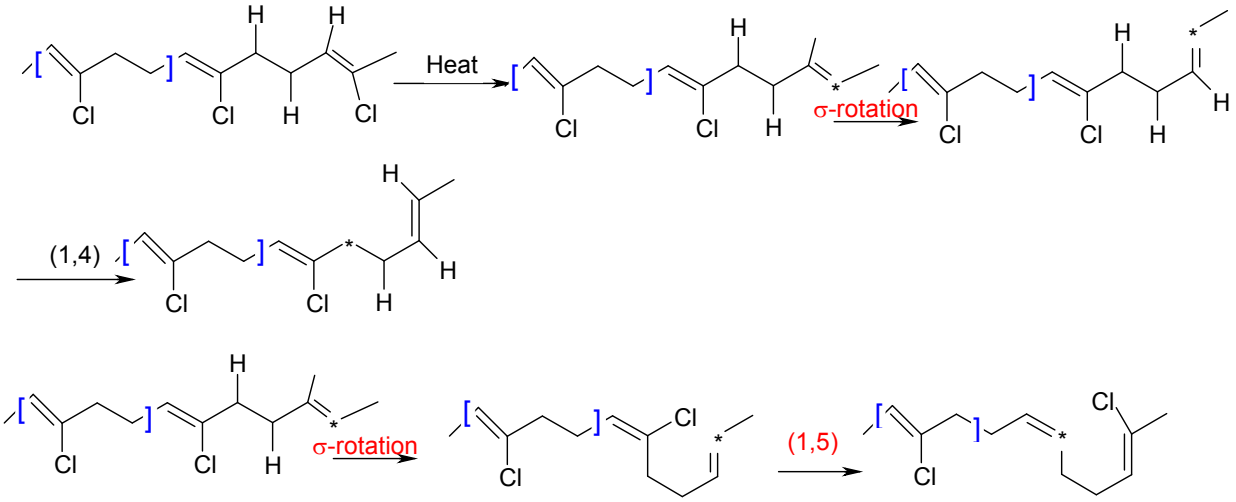
obtained from gas chromatography mass spectrometry analysis of the thermolysis products of LEGs [] and the results published byother researchers who have developed kinetic models with an in-depth discussion for the pure polymers [e.g. 24-26[48]] we may assume a type of radical degradation mechanism. Radical mechanism has three general steps, initiation, propagation and termination. Adopting these steps for neoprene degradation as the followings:

1. Initiation reactions of neoprenewith n number of polymeric segments to be the formation of the first pair of radicals by thermolysis:
   $[-CH_2-CCl=CH-]_n \rightarrow [-CH_2-CCl=CH-]_{n-1}-CH_2-C.=CH- + Cl.$
   Because of the relative lower amount of bond energy of C-Cl (331 kJ/mol) with respect to C-C (346 single bond and 602 C=C both in kJ/mol) bond, the first radicals set will be Cl radical and a neopreneradical. The unzipping of neoprene to the monomer by thermolysis was not observed; which confirms this assumption.

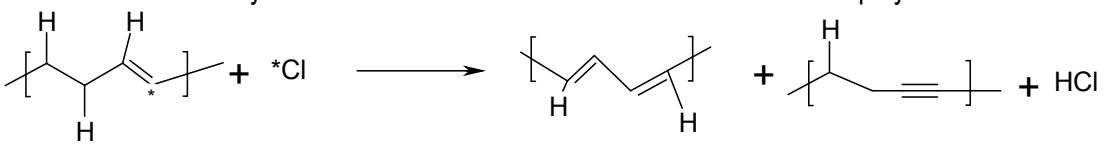
2. Propagation reactions of intermediate radicals:

The propagation step consisted in:

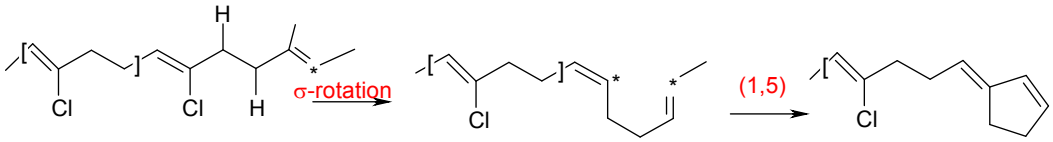
a. Formation of multi-radicals by H-abstraction reaction on the neoprene chain by Cl radicals. The observation of high amounts of HCl as one of the products of thermolysis confirm this assumption.
b. Chain transfer of radicals
c. Radicalization of new chains with no chlorine
d. Scission of radicals to form unsaturated small molecules such as ethylene, but-1,3-di-yne, benzene and cyclooctatetraen which were observed in the producats of pyrolysis.
e. New polymer radical isomerization via (1,4) and (1,5) H-transfer:




3. Termination reactions which consisted of the combination of all radicals formed during the degradation.
   a. Abstraction of H by Cl radical and formation of a new C=C bond in the polymeric backbone:



b. 1,5 and 1,6 -di-radical combination




### 3.1 Thermogravimetric Analysis

Figure 2 shows the results of thermogravimetric studies of a sample of PLEG. The thermogram showed a two-step weight loss of PLEG. The first weight loss step of PLEG started around 350°C reached the highest rate (13.1 $min^{-1}$) at 410°C. The first step of decompositions reaction was complete at a temperatures below 500°C; the residues of PLEG was ~30% of the total mass of PLEG containing stable carbon compounds (fig 1c). A second stage of decompositionbegun around 650° for PLEG (Fig 2) reached to the highest rate at (0.15 $min^{-1}$) ~ 655°C.

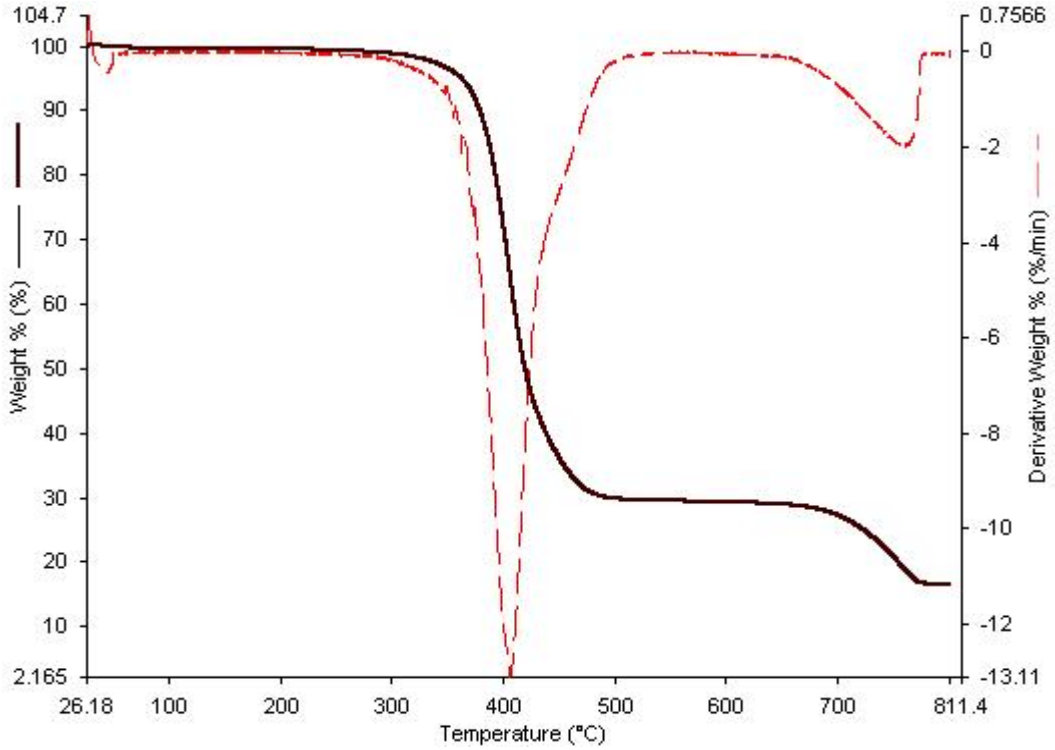
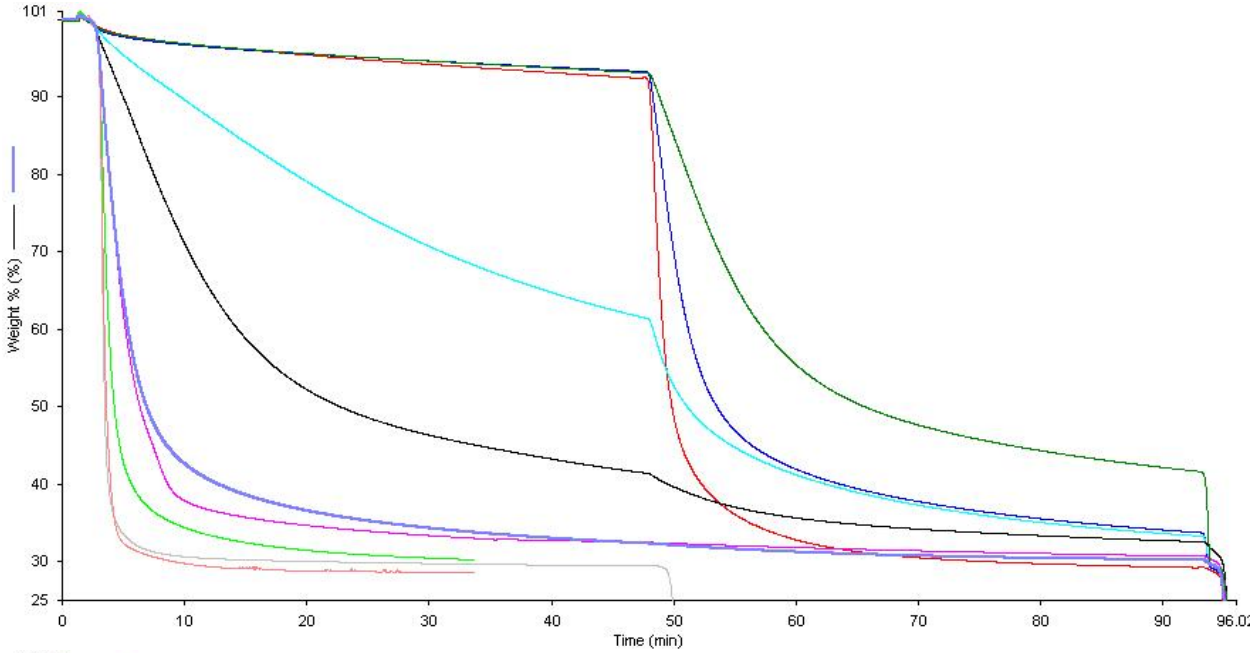
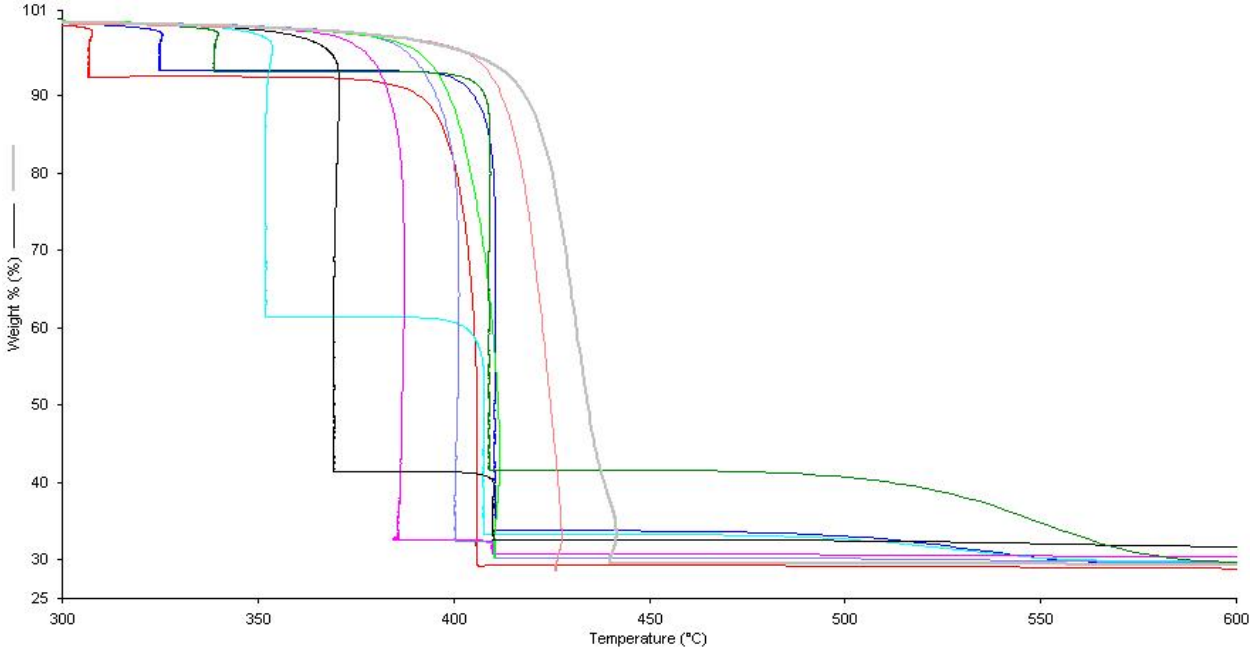



Fig 2. Thermogram of a sample of powdered glove from 50°C of 800°C under 10 mL/min Argone with heating rate of 10°C/min.

Fig 3a shows the thermograms of eleven samples of PLEG at eleven temperatures. The sample that was kept for 30 min at 330°C obtained higher thermal stabilities than any other samples. This due to the chemical changes in the structure of the material during 30 min at 340°C; such a change in thermal properties of PLEG was not observed for the samples kept in other temperatures. The weight loss of this particular sample at 410°C get slower than any other sample. The remains of this particular sample at 475°C was about 40% of its original weight, while for the any other sample at the same temperature the

remaining reached near to 30% of the original mass. The staying of the PLEG at the other isotherms also produce some stability to the secondary products of pyrolysis as was observed in Fig 3.


Weight % (%)
Time (min)


Weight % (%)
Temperature (°C)

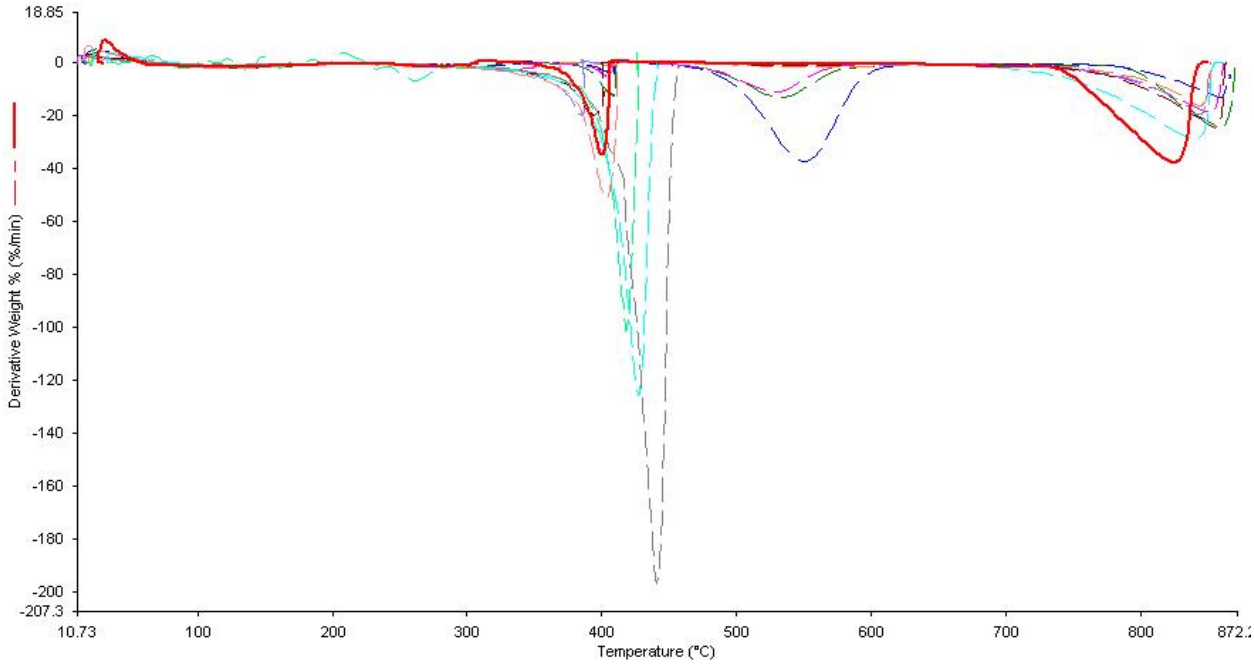



**Fig 3. Thermogravimetric analysis of PLEG: (a) weight-loss versus time for 11 samples of PLEG; (b) weight loss versus temperature for 11 samples of PLEG, and (c) derivatives of weight loss versus temperature.**

### 3.2 Kinetics of Pyrolysis of PLEG

Fig 3 shows a thermogram of thermolysis of powdered LEGs where the mass of PLEG decreasing by the time and temperature. The thermolysis process can be describe by a typical reaction such as reaction (1) where W is the unvaporized mass percent of the materials in the TGA reaction pan:

W → Products (1)

The reaction rate for a typical chemical reaction, such as reaction (1), with molecularity order of n, rate constant k at time t has been described by Eq (2);

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

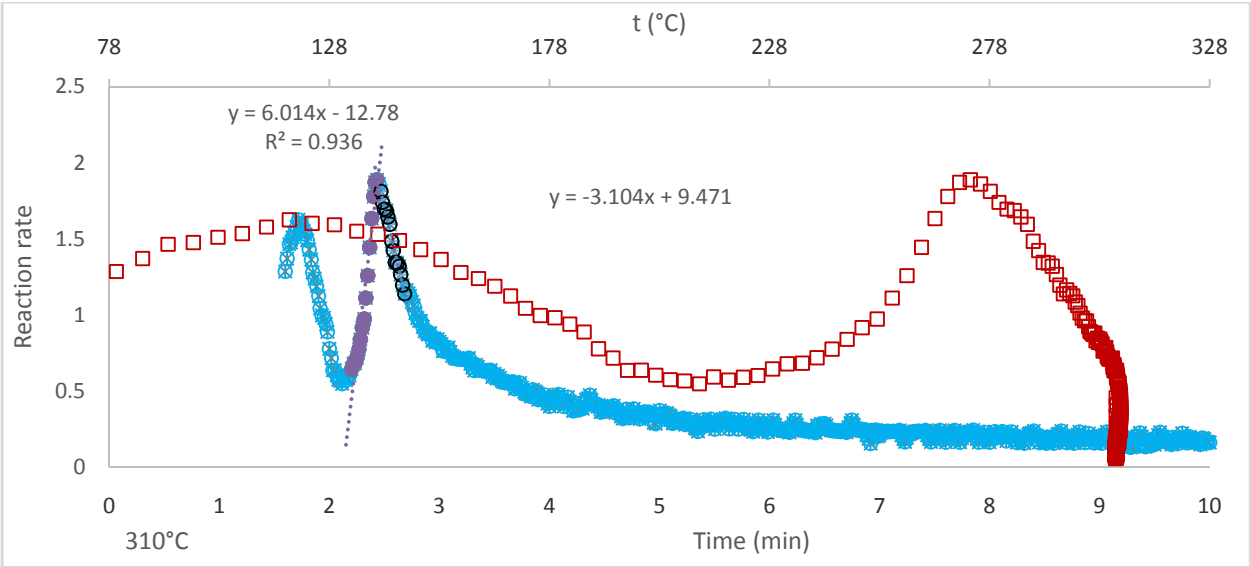
Arrhenius related the rate constant, k, to a factor such as z to describe the efficiency of the molecular collisions, the activation energy of reaction $E_a$, the absolute temperature of the reaction T, and the universal gas constant R = 8.314 J $mol^{-1}$ $K^{-1}$as shown by Eq (3):

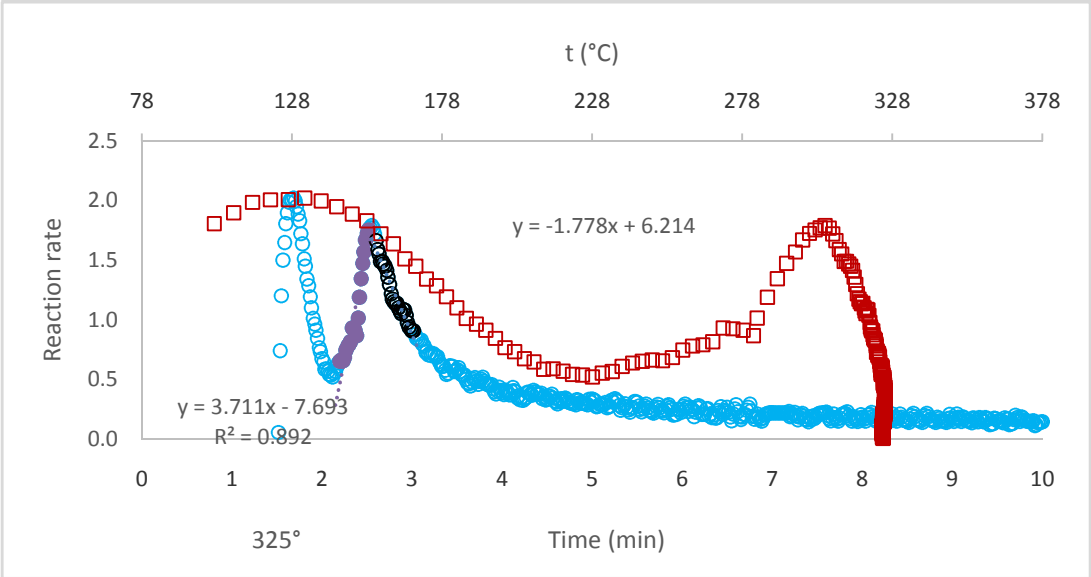
$$k = ze^{-\frac{E_a}{RT}} \qquad (3)$$

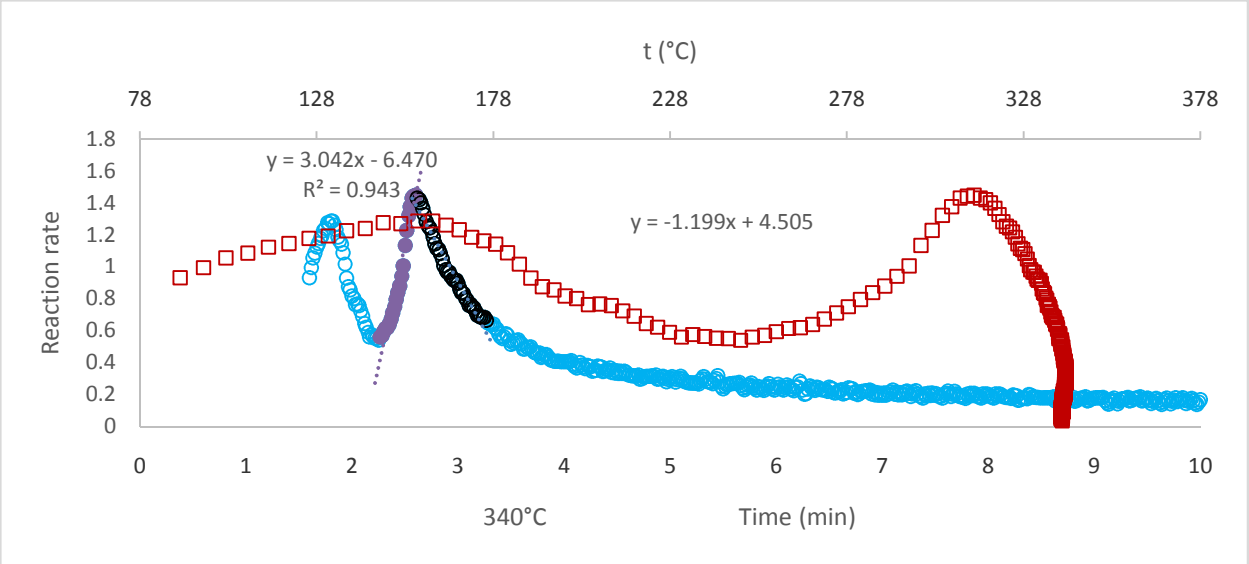
Combining and rearranging Eq (2) and Eq (3) results in:

$$Rate = -\frac{dw}{dt} = zw^n e^{-\frac{E_a}{RT}} \qquad (4)$$

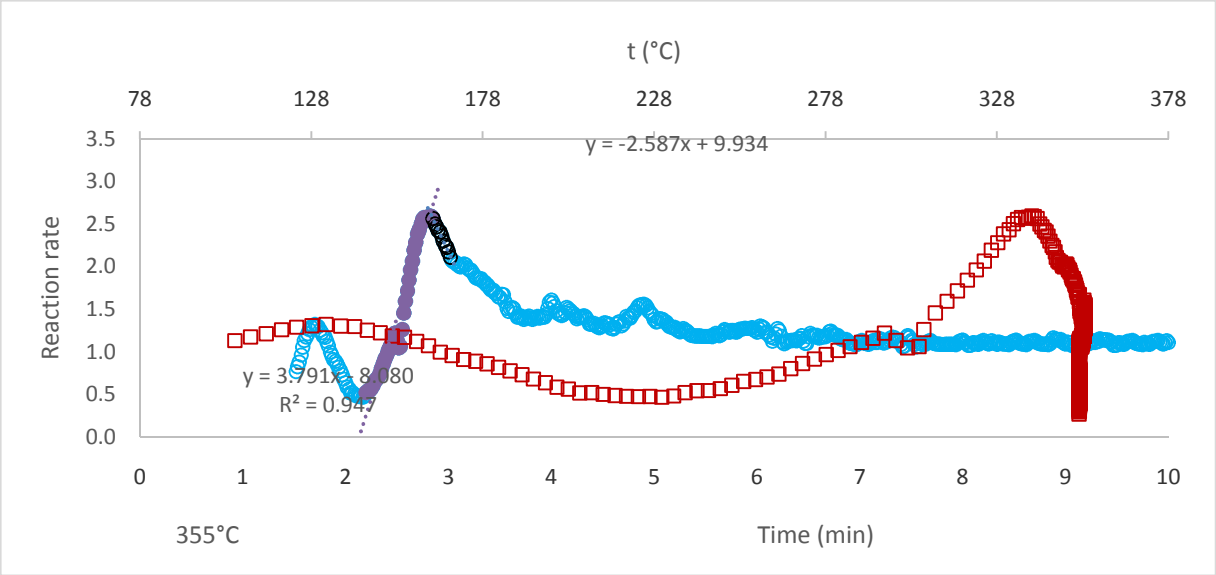
Fig 4 shows the variation of the initial rate of weight loss of eleven sample of PLEG over initial time and temperaturefor eleven samples of PLEG form 310°C to 455°C.



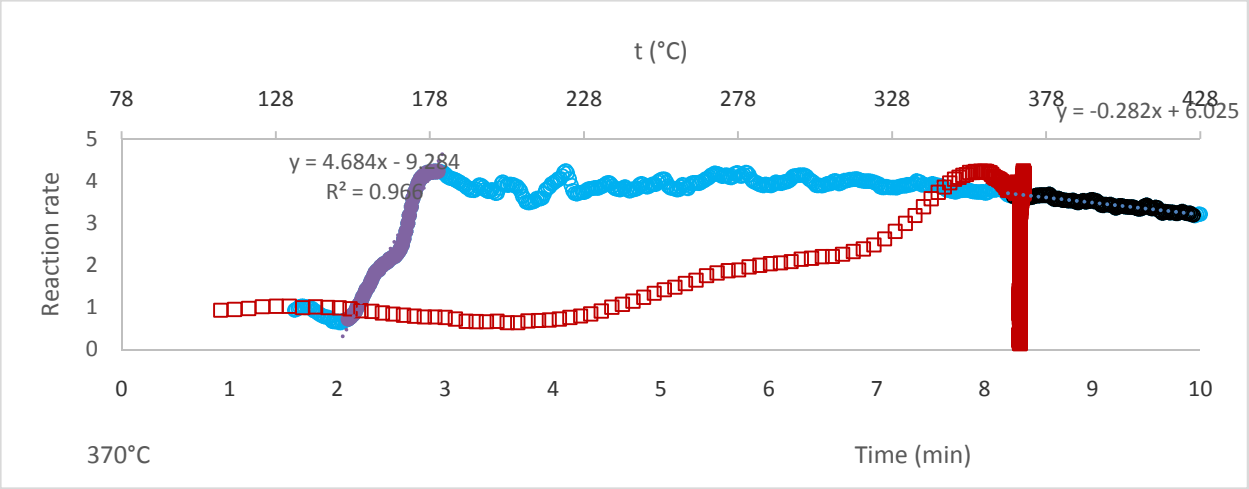




t (°C)
78
128
178
228
278
328
378
y = 3.042x - 6.470
R² = 0.943
y = -1.199x + 4.505
Reaction rate
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
1
2
3
4
5
6
7
8
9
10
340°C
Time (min)

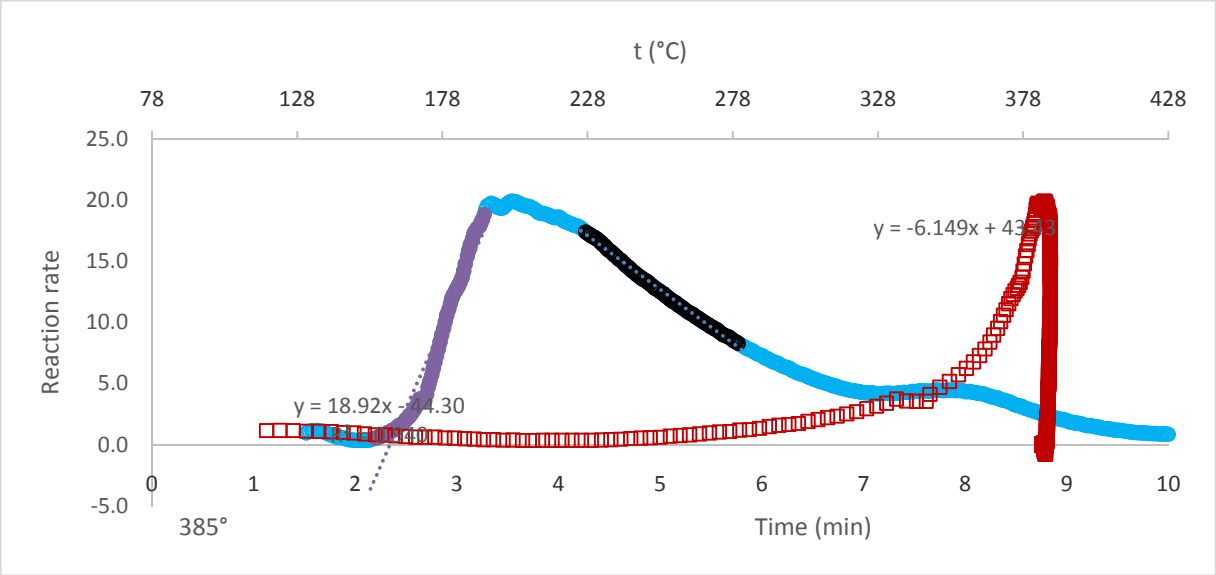
236


t (°C)
78
128
178
228
278
328
378
y = -2.587x + 9.934
Reaction rate
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
y = 3.791x - 8.080
R² = 0.947
0
1
2
3
4
5
6
7
8
9
10
355°C
Time (min)

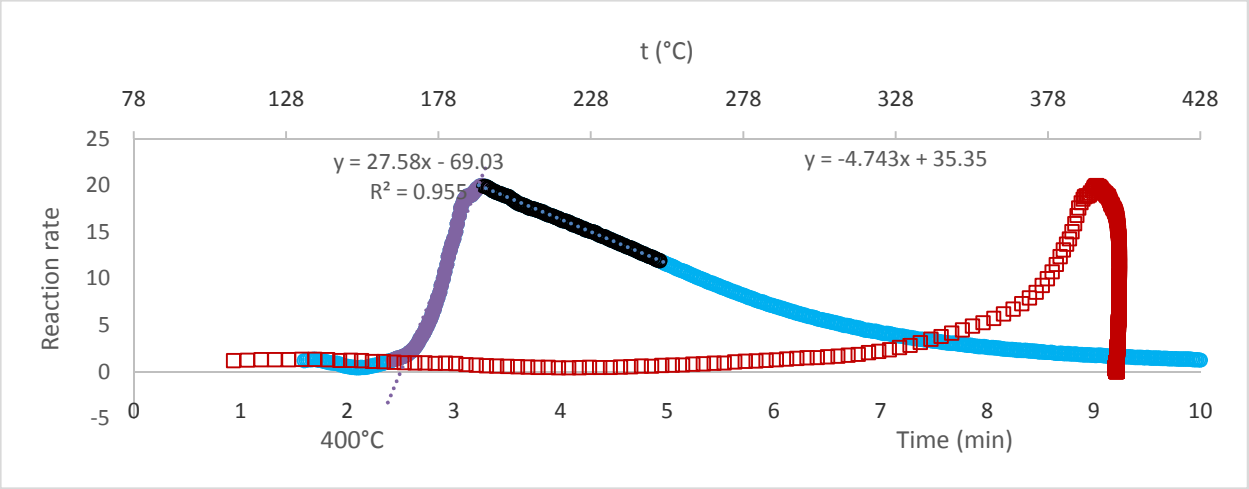
237


t (°C)
78
128
178
228
278
328
378
428
y = -0.282x + 6.025
y = 4.684x - 9.284
R² = 0.966
Reaction rate
5
4
3
2
1
0
0
1
2
3
4
5
6
7
8
9
10
370°C
Time (min)

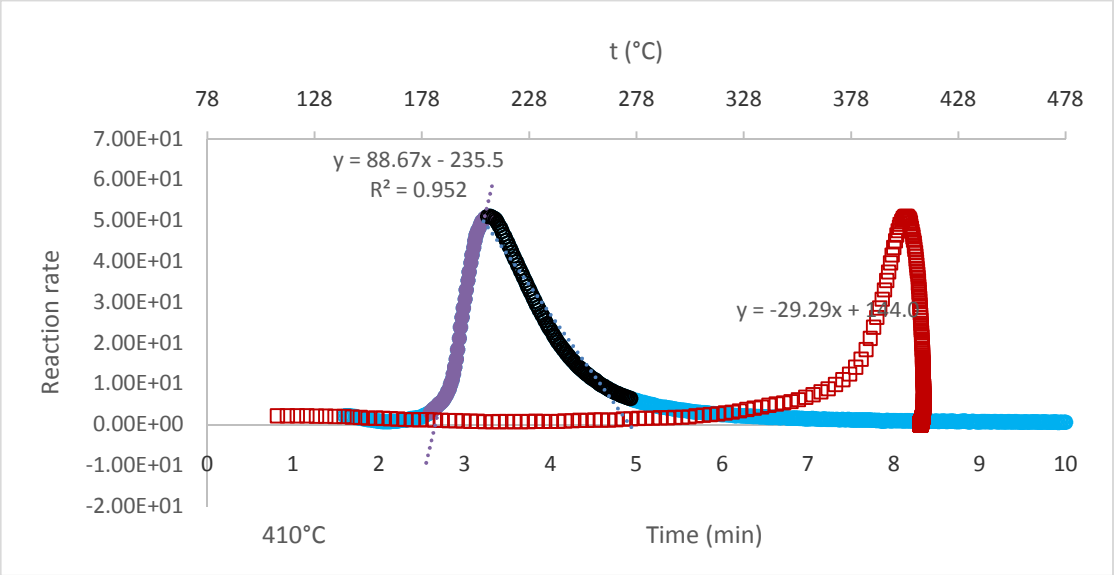
238


t (°C)
78
128
178
228
278
328
378
428
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
Reaction rate
y = -6.149x + 43.53
y = 18.92x - 44.30
0
1
2
3
4
5
6
7
8
9
10
385°
Time (min)

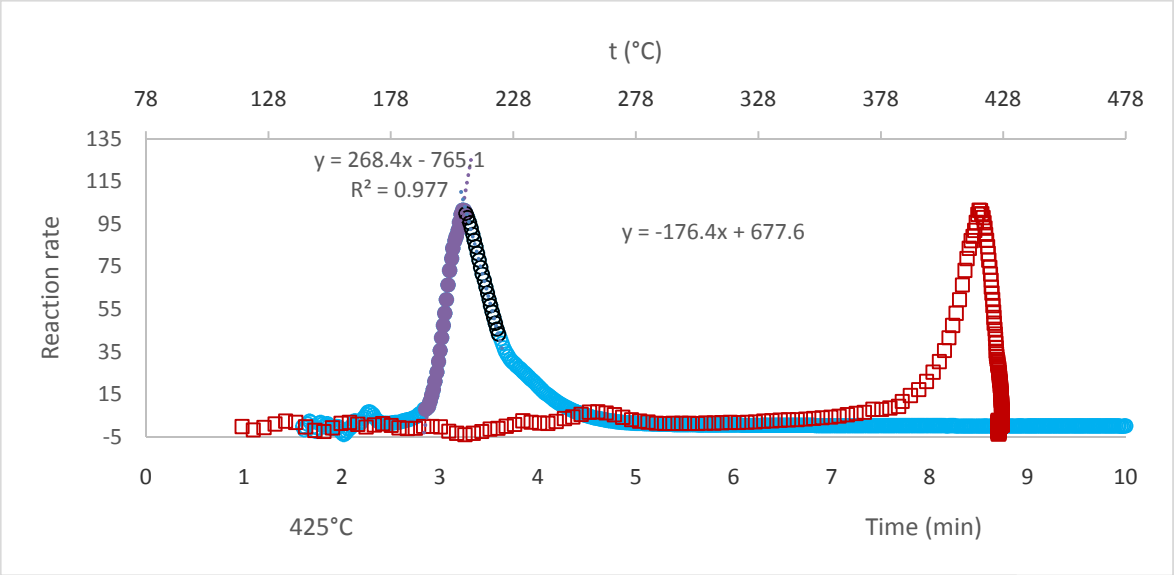
239


t (°C)
78
128
178
228
278
328
378
428
25
20
15
10
5
0
-5
Reaction rate
y = 27.58x - 69.03
R² = 0.955
y = -4.743x + 35.35
0
1
2
3
4
5
6
7
8
9
10
400°C
Time (min)

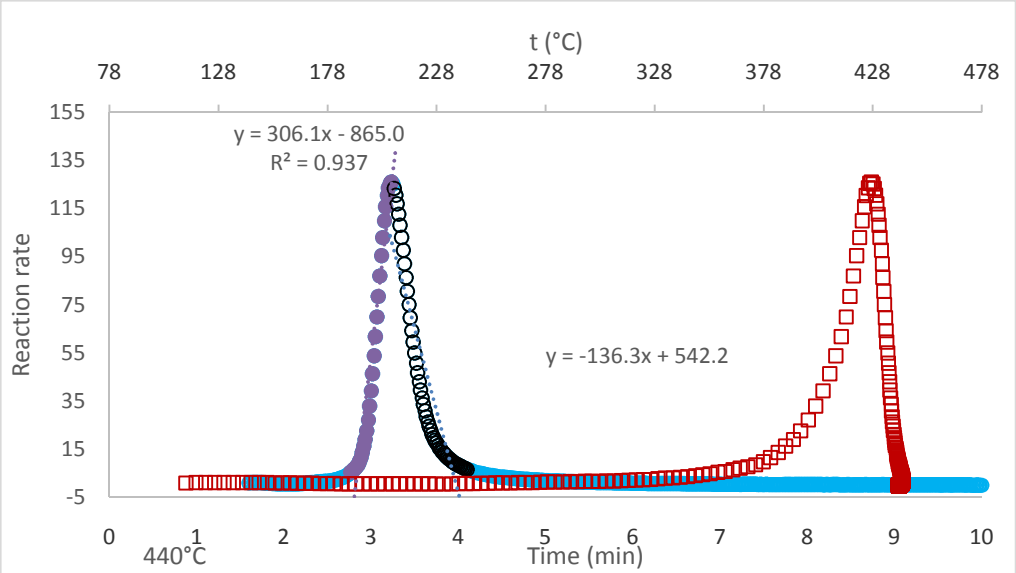
240


t (°C)
78
128
178
228
278
328
378
428
478
7.00E+01
6.00E+01
5.00E+01
4.00E+01
3.00E+01
2.00E+01
1.00E+01
0.00E+00
-1.00E+01
-2.00E+01
Reaction rate
y = 88.67x - 235.5
R² = 0.952
y = -29.29x + 194.0
0
1
2
3
4
5
6
7
8
9
10
410°C
Time (min)

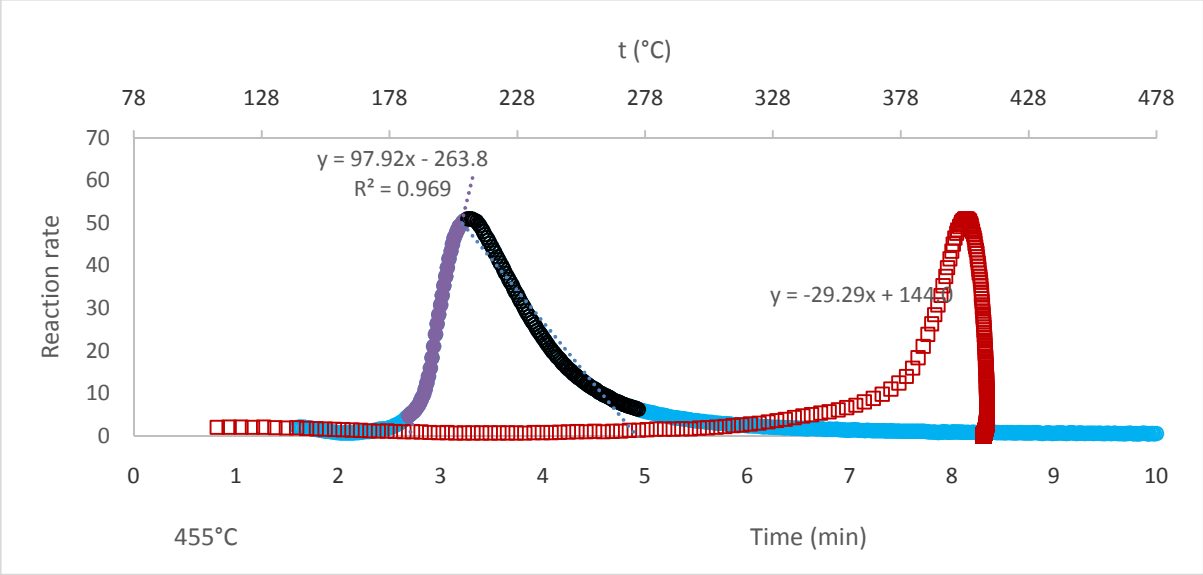
241


t (°C)
78
128
178
228
278
328
378
428
478
135
115
95
75
55
35
15
-5
Reaction rate
y = 268.4x - 765.1
R² = 0.977
y = -176.4x + 677.6
0
1
2
3
4
5
6
7
8
9
10
425°C
Time (min)

242


t (°C)
78
128
178
228
278
328
378
428
478
155
135
115
95
75
55
35
15
-5
Reaction rate
y = 306.1x - 865.0
R² = 0.937
y = -136.3x + 542.2
0
1
2
3
4
5
6
7
8
9
10
440°C
Time (min)

243


t (°C)
78
128
178
228
278
328
378
428
478
70
60
50
40
30
20
10
0
Reaction rate
y = 97.92x - 263.8
R² = 0.969
y = -29.29x + 1440
0
1
2
3
4
5
6
7
8
9
10
455°C
Time (min)

244

Fig 4. Variation of the initial rate of weight loss for eleven samples of LEG at eleven temperatures, the red color related to rate versus temperature upper horizontal ax. Other color represents rate of weight loss versus time of isotherm.

From graphs of Fig 4, the highest rate of weight loss, the temperature at the maximum weight loss, the acceleration of weight loss by thermal scan, the deceleration of weight loss after thermal scan when the system stays in an isothermal situation were estimated. These data were tabulated in table 1,

Table 1. The results of the two isotherm obtained from pyrolysis process of LEGs at various temperatures.

| | First isotherm | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Start | | | | | | | At Max | | |
| | t (mim) | T (K) | Accele-ration | Rate (max) | w% | k* | R.Ea(max) | t (min) | T (K) | Decele-ration |
| 1 | 2.13 | 215 | 7.60 | 1.89 | 99.64 | 1.89 | 8,823 | 2.43 | 274 | -3.10 |
| 2 | 2.17 | 238 | 3.71 | 1.79 | 99.24 | 1.80 | 5,449 | 2.55 | 306 | -1.78 |
| 3 | 2.27 | 251 | 3.71 | 1.45 | 99.26 | 1.46 | 6,185 | 2.60 | 314 | -1.28 |
| 4 | 2.17 | 230 | 6.44 | 2.56 | 98.80 | 2.60 | 4,997 | 2.85 | 340 | -2.57 |
| 5 | 2.10 | 220 | 9.88 | 4.23 | 97.87 | 4.32 | 3,355 | 2.93 | 358 | -0.28 |
| 6 | 2.20 | 246 | 17.9 | 19.9 | 86.70 | 23.0 | 10,409 | 3.53 | 385 | -7.42 |
| 7 | 2.43 | 289 | 34.5 | 20.0 | 91.71 | 21.8 | 8,581 | 3.27 | 394 | -4.72 |
| 8 | 2.60 | 323 | 117 | 51.0 | 83.04 | 61.4 | 17,153 | 3.27 | 403 | -45.2 |
| 9 | 2.60 | 327 | 325 | 98.0 | 74.57 | 131 | 27,524 | 3.27 | 419 | -170 |
| 10 | 2.77 | 357 | 436 | 120 | 69.67 | 173 | 8,772 | 3.27 | 429 | -249 |
| 11 | 2.10 | 352 | 838 | 209 | 70.72 | 296 | 6,079 | 3.17 | 439 | -156 |
| | Second isotherm | | | | | | | | | |
| 1 | 47.38 | 307 | 75.56 | 34.27 | 83.20 | 41.2 | 34,494 | 48.32 | 399 | -23.45 |
| 2 | 47.87 | 382 | 27.06 | 12.58 | 85.33 | 14.7 | 45,194 | 48.68 | 409 | -3.02 |
| 3 | 47.87 | 382 | 7.34 | 4.48 | 47.87 | 9.36 | 40,397 | 49.52 | 409 | -0.32 |
| 4 | 47.87 | 382 | 10.74 | 5.48 | 59.06 | 9.28 | 40,202 | 48.47 | 405 | -1.91 |
| 5 | 47.73 | 374 | 2.85 | 1.04 | 41.14 | 2.53 | 21,754 | 48.22 | 406 | -0.17 |
| 6 | 47.77 | 385 | 1.09 | 0.18 | 32.49 | 0.54 | 56,077 | 48.13 | 406 | -0.34 |
| 7 | 47.88 | 404 | 0.10 | 0.14 | 32.18 | 0.44 | 26,413 | 49.03 | 411 | -0.01 |

* Assuming a first order reaction

During the temperature scan, the rate of weight loss of PLEG increased by increasing the temperature (and therefore by time), reached to a maximum, then at the isotherm process it began to decrease. The variation of maximum of rate of weight loss versus temperature of isothermal process (Fig 5) followed the exponential form of$Rate = 4.73E+09e^{-1.25E+04/T}$. This equation has the same exponential form of Arrhenius equation [eq (4)] which it is within theoretical expectations.

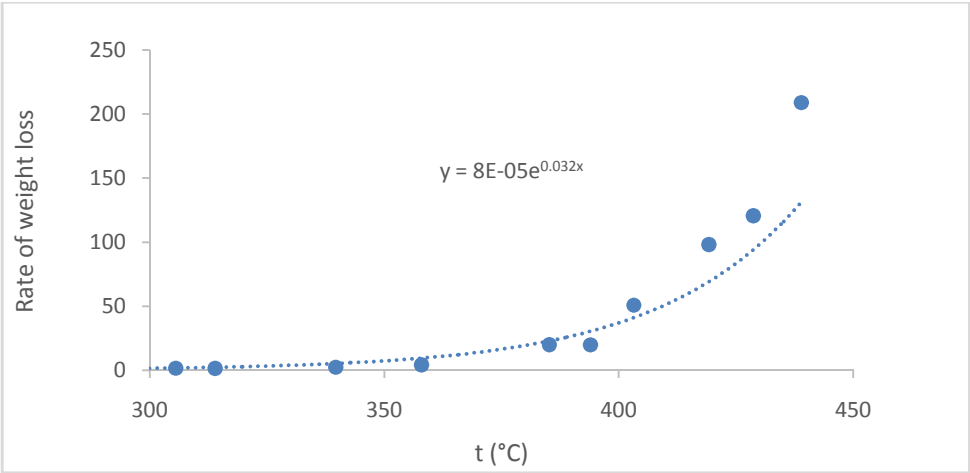



Fig 5. Variation of the values of the rate of weight loss of PLEG versus temperature.

The slope of the variation of rate of weight loss by time is acceleration of weight-loss (A) by the thermolysis process. As the temperature increases the weight loss accelerate, and A also increases when the temperature of the isotherm process increase (the data in 4th column of Table 1). The best line that describes the A values versus temperature is: $A = 1.04 \times 10^{10} e^{-1.25E+04/T}$ as showed in Fig 6. It has the exponential form similar to the Arrhenius relationship for the rate constant of a reaction, which is within expectation [eq (6)]. The derivative of Eq (2) with respect of time and temperature gives accounts for the A function which regains the exponential form again:

$$A = \frac{d}{dt}(Rate) = \frac{d}{dt}\left(-\frac{dw}{dt}\right) = \frac{d}{dT}\left[zw^n e^{-\frac{E_a}{RT}}\right] = -\frac{E_a}{TR} zw^n e^{-\frac{E_a}{TR}} \qquad (6)$$

Therefore, the data related to A are within expectations.

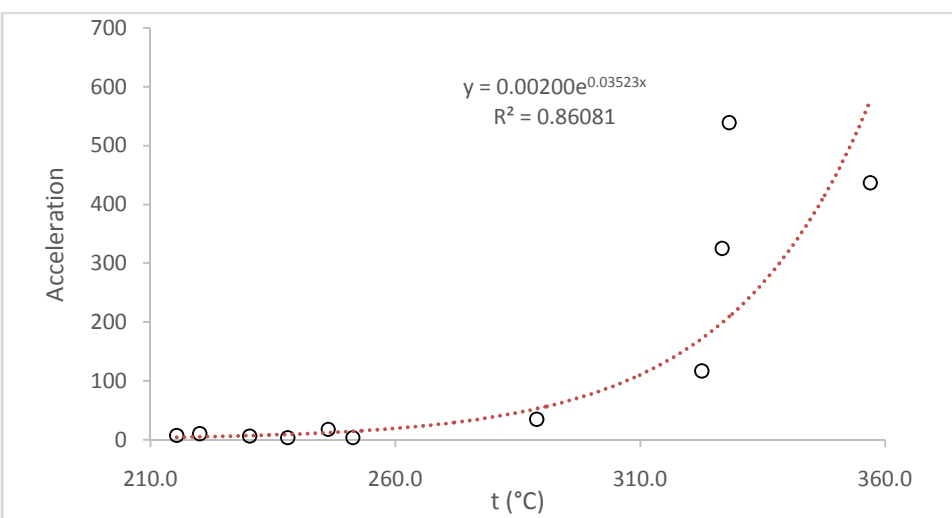
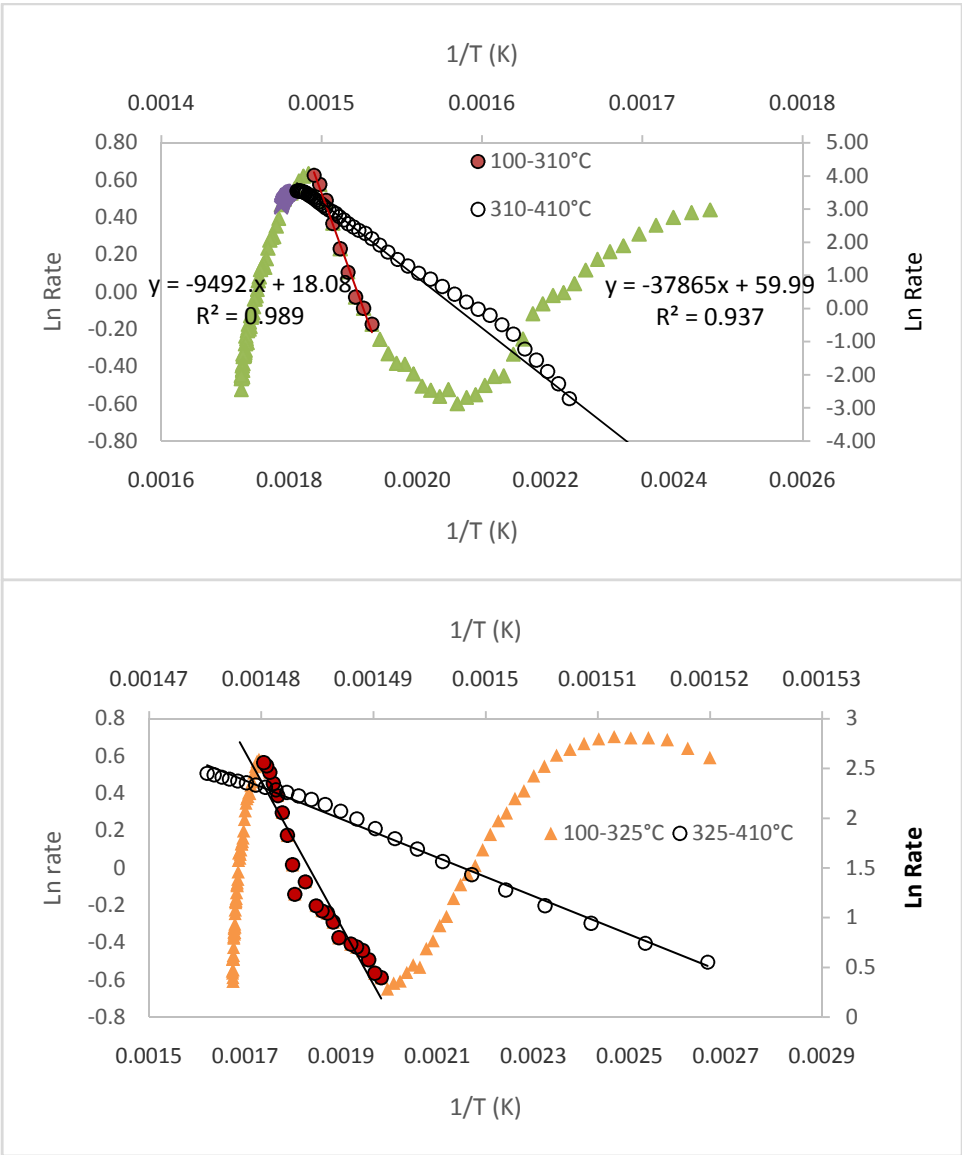


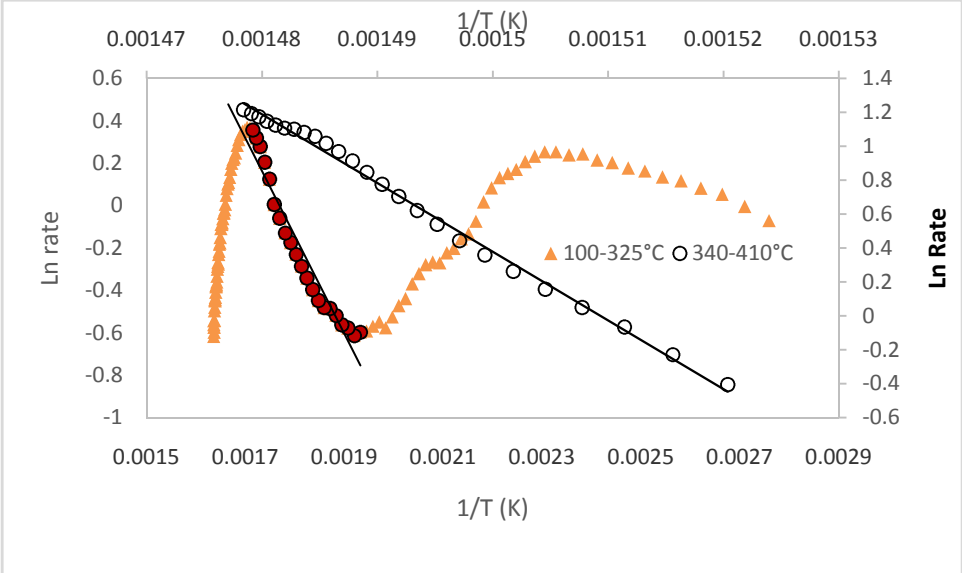
Fig 6. Representation of acceleration of weight loss of PLEG versus temperature of isotherms.

The logarithmic form of Eq (4) becomes Eq (7) which was applied to the results of thermogravimetric data collected during a thermal scan processes to calculated Ea of weight loss:

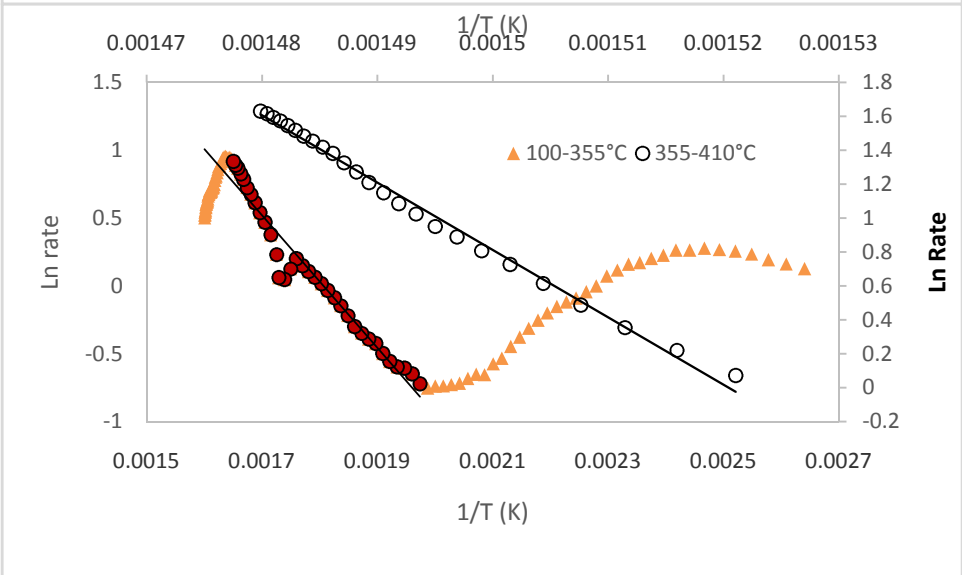
$$Ln\ Rate = -\frac{E_a}{RT} + Lnz + nLnw \qquad (7)$$

The slope of the graph of "Ln rate" versus "1/T" results in the value of "–Ea/R" (Fig 7).

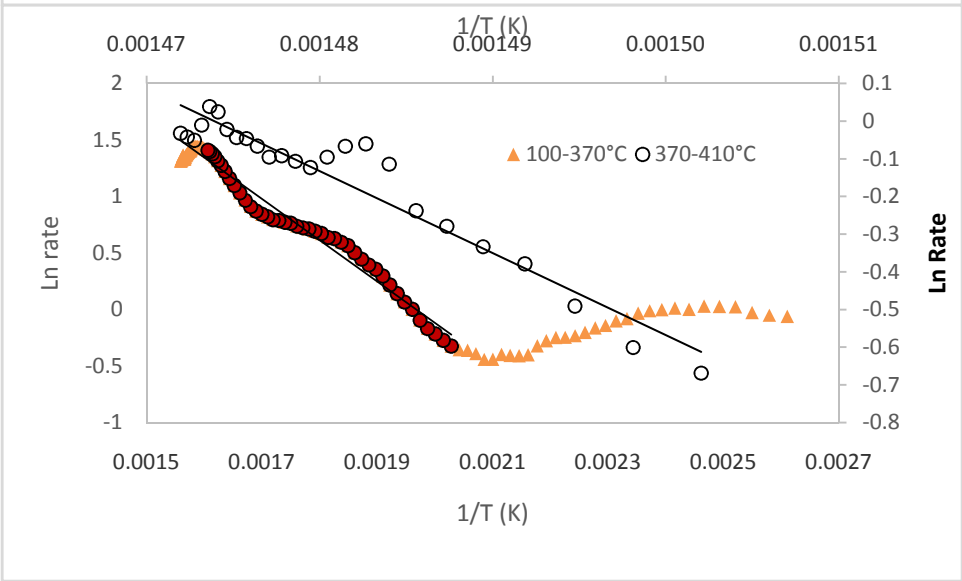



1/T (K)
0.00147
0.00148
0.00149
0.0015
0.00151
0.00152
0.00153
Ln rate
Ln Rate
100-325°C
340-410°C
0.0015
0.0017
0.0019
0.0021
0.0023
0.0025
0.0027
0.0029
1/T (K)

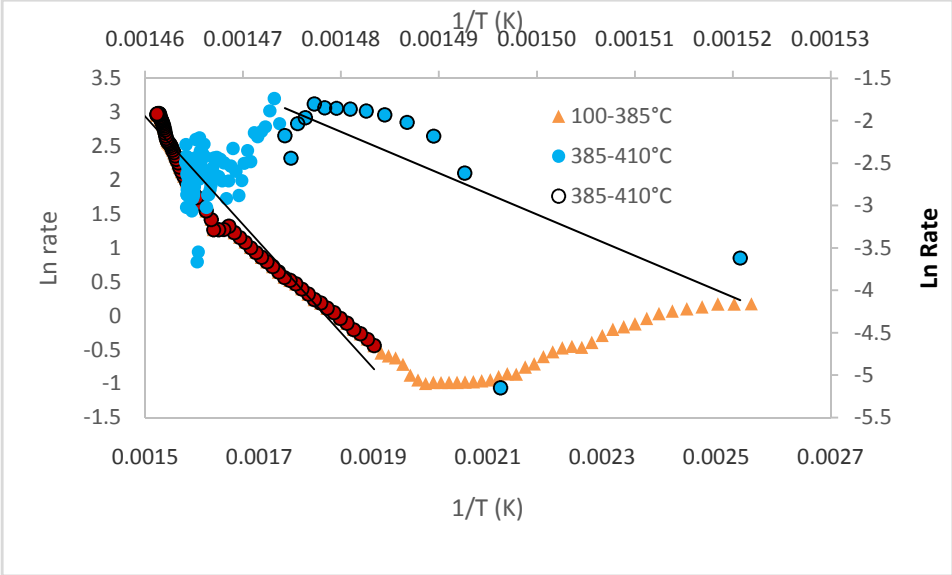
285


1/T (K)
0.00147
0.00148
0.00149
0.0015
0.00151
0.00152
0.00153
Ln rate
Ln Rate
100-355°C
355-410°C
0.0015
0.0017
0.0019
0.0021
0.0023
0.0025
0.0027
1/T (K)

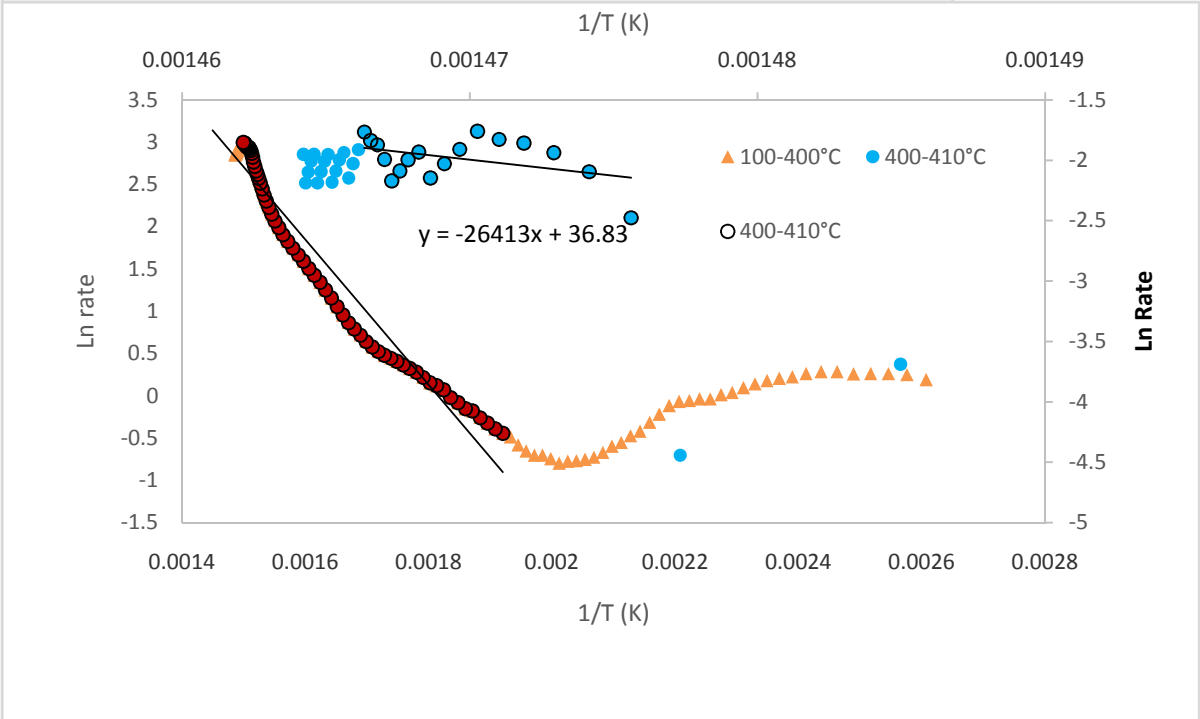
286


1/T (K)
0.00147
0.00148
0.00149
0.00150
0.00151
Ln rate
Ln Rate
100-370°C
370-410°C
0.0015
0.0017
0.0019
0.0021
0.0023
0.0025
0.0027
1/T (K)

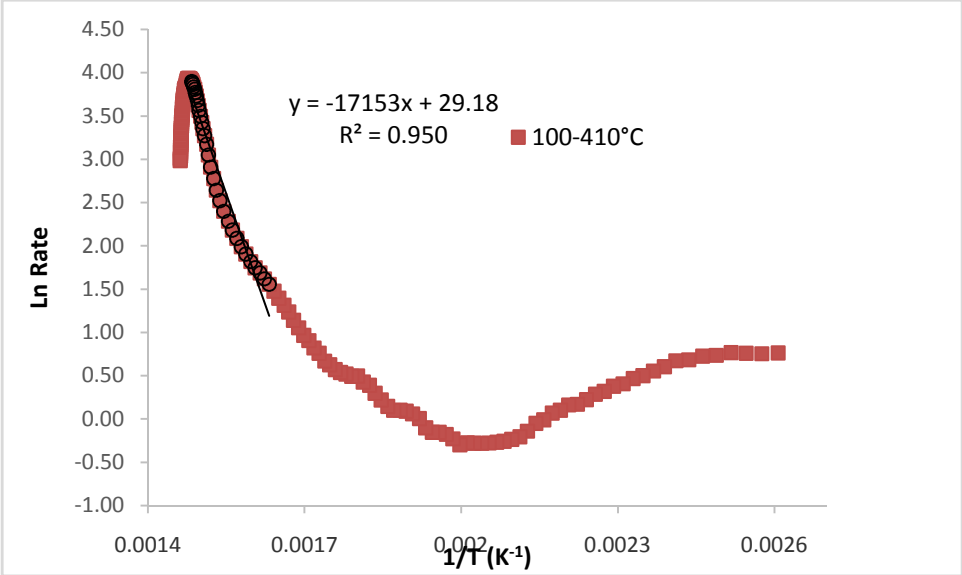
287

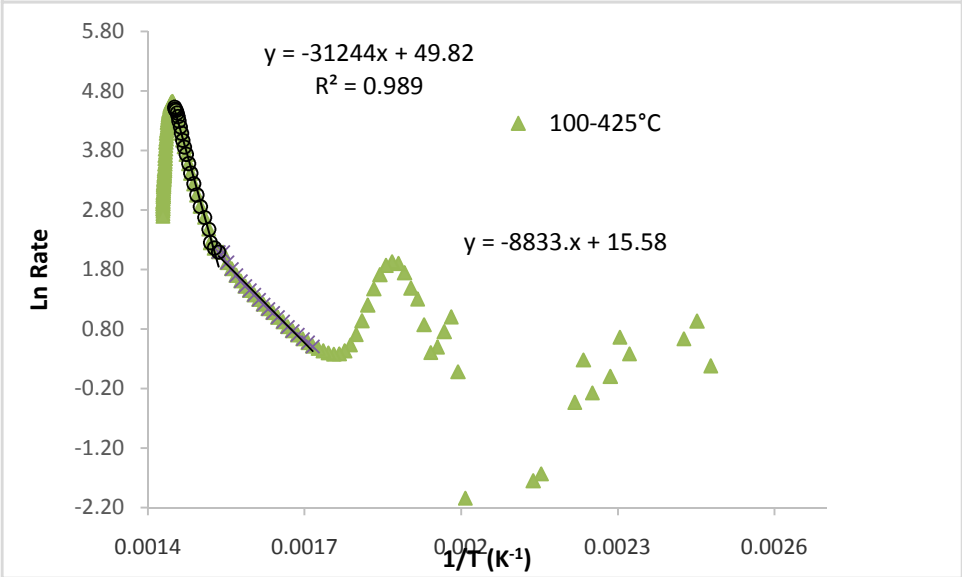

1/T (K)
0.00146
0.00147
0.00148
0.00149
0.00150
0.00151
0.00152
0.00153
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
Ln rate
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
-5
-5.5
Ln Rate
100-385°C
385-410°C
385-410°C
0.0015
0.0017
0.0019
0.0021
0.0023
0.0025
0.0027
1/T (K)

288


1/T (K)
0.00146
0.00147
0.00148
0.00149
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
Ln rate
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
-5
Ln Rate
100-400°C
400-410°C
400-410°C
y = -26413x + 36.83
0.0014
0.0016
0.0018
0.002
0.0022
0.0024
0.0026
0.0028
1/T (K)

289


y = -17153x + 29.18
R² = 0.950
100-410°C
Ln Rate
1/T (K-1)
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00
0.0014
0.0017
0.002
0.0023
0.0026


y = -31244x + 49.82
R² = 0.989
100-425°C
y = -8833.x + 15.58
Ln Rate
1/T (K-1)
5.80
4.80
3.80
2.80
1.80
0.80
-0.20
-1.20
-2.20
0.0014
0.0017
0.002
0.0023
0.0026

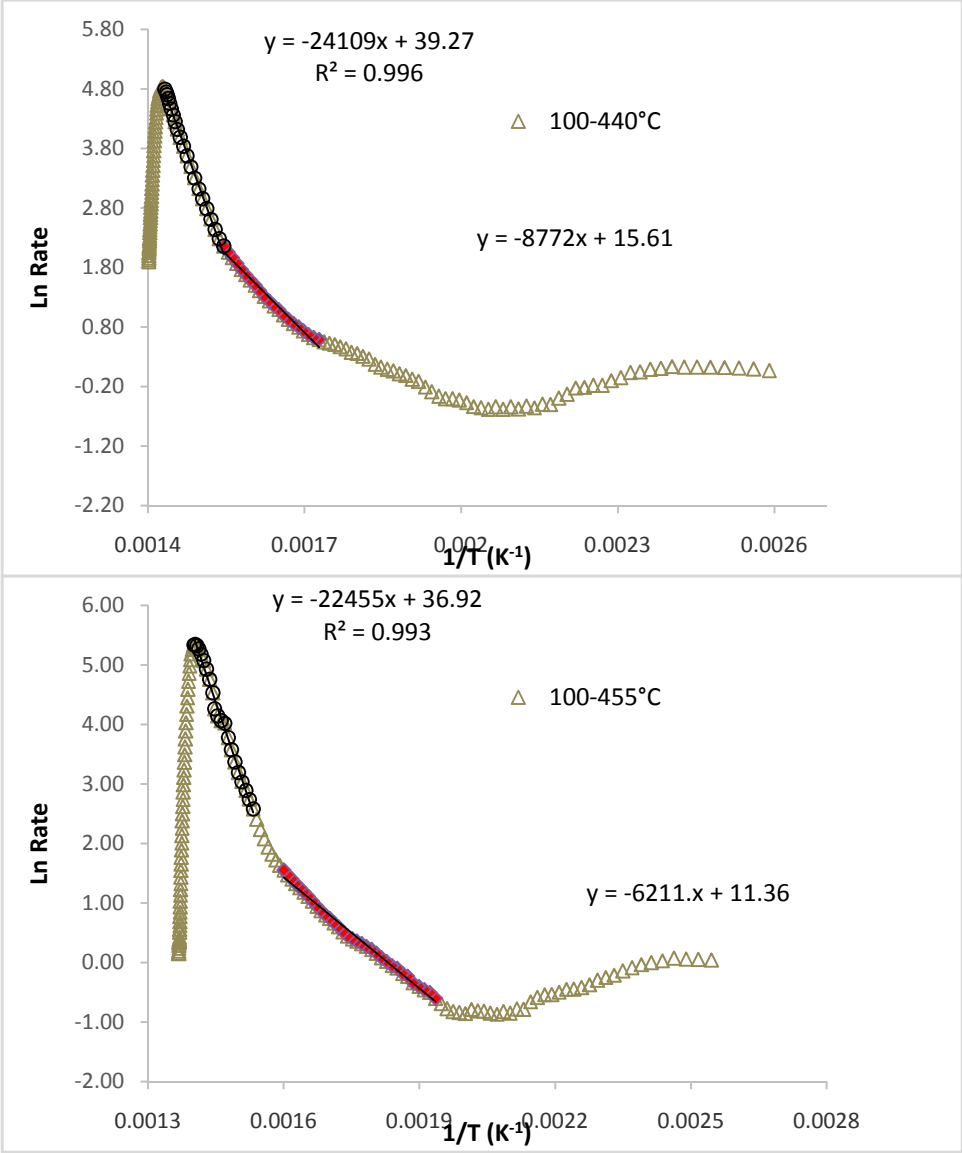



Fig 7. Variation of "Ln rate" of weight loss versus "1/T (K)" for the18 thermal scans of the samples of LEG from 308°C and 450 °C.

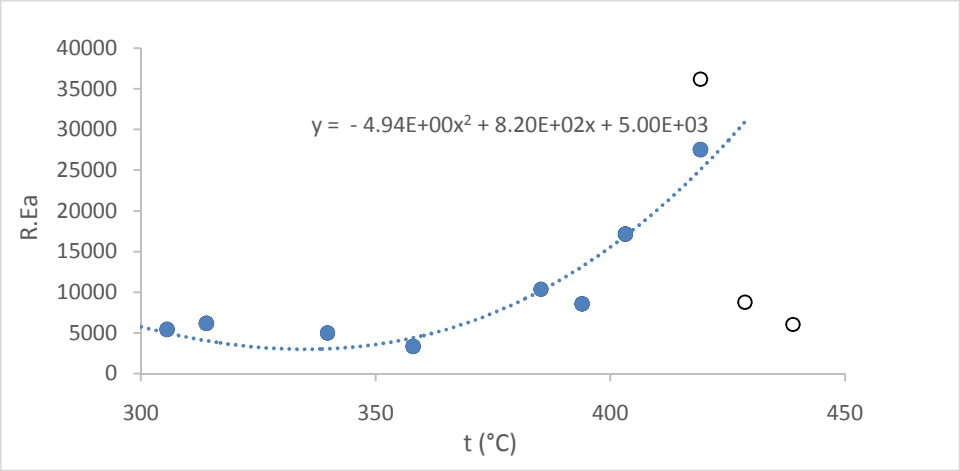
The variation of "Ln rate" of weight loss versus "1/T" based on Eq (6) must be a straight line with a negative slope (the value of Ea of any reaction expected to be positive). Fig 7 represents plots of variations of "Ln rate" weight loss versus "1/T" based on Eq (6). The entire range of thermal scan did not followed Eq (6) as was expected for a pure compound. For a complex mixture of materials such as PLEG; several traces with different slopes were observed. For example,let analyze the scan of thesample 1, covering ranges 100-310°C.Three traces with slopes positive, negative, positive; with minimum and maximum like an "N" shape was observed. The rate of weight loss decreasing from 100-238°C, then it began to increase reaching a max at 306° (1°C before the isotherm 307°). Afterward, it began to decrease;the decrease of the values of

the rate of weight loss continue during the entire range of isotherm at 307°C. Then at the next thermal scan (307-406°C) the rate of weight-loss increased, reached a maximum at 399°C (about 7°C before starting the isotherm temperature.) This kind of behavior was observed for all 11 samples as on can observe in Fig 7. The data obtained from this Fig also are tabulated in Table 1.

The weight loss at 355°C and higher takes another curse. Sixty percent and more of the materials are volatized during first isotherm. Keeping in mind that around 30% of the mass of the PLEG are substance stable over 550°C; thus, 70 % of the mass of PLEG are organic consisting both plasticizers and neoprene. Chlorine contributes 40% of pure neoprene mass, when it is eliminated from neoprene in form of HCl, 41.2% of weight loss occurs to neoprene materials. Therefore, useful organics contents of PLSG is less than 30% of its original weight. The isotherm at 355°C recorded (100-69 = )31% of weight loss in first stage of heating. If all weigh loss at this temperature be related of elimination of HCl, therefore,it will be a practical process to eliminated chlorinated compounds before complete degradation of PLEG to other chemicals.

The Ea obtained from the slope of "Ln rate" versus inverse of temperature "1/T"($K^{-1}$) also increased by increasing the temperature as indicated in 8$^{th}$ column of Table 1. Fig 8 shows the variation of Ea versus temperature. As temperature of the first isotherm process increased the value of Ea of weight-loss also increased. This is within expectation. If the weight loss' Ea was not an increasing function of temperature, a full weight loss must be observed at very first isotherm process. The increment of Ea versus T also has the exponential form (Fig 7). The variation of Ea for the thermal scans below 425°Cthough having the exponential form; also followed a third degree polynomial as well:

$$Ea= 0.00740t^3 - 4.94t^2 + 820x + 5000.$$




Fig

8. Variation of Ea versus T for eleven isotherms of PLEG.

It is worthy to mention that the Ea of weight loss at temperatures over 435°C is less than the temperatures below 435°C (Fig 8).

Also the value of k obtained from maximum of weight loss rate assuming the reaction be first order was tabulated in the 7$^{th}$ column of Table 1. The value of k estimated in this manner are not accurate since the weight-loss order was not uniform over all temperature range, and neither was it a first ordered reactions. The values of k also increase by temperature and it has the exponentials form as was expected.

The rate of weight-lossfor a thermolysis process has an exponential form with a maximum. At the maximum of rate of weight loss the order or reaction become zero; therefore, the maximum rate of weight loss, $R_{max}$ =k for the zeroth order reactions. These values also are tabulated in the Table 1.

The logarithmic from of Eq (3) results

$$\text{Ln } k = \text{Ln } z - E_a/RT \qquad (8)$$

Application of logarithmic form of Arrhenius Equation (Eq 8) to the 7th and 10th columns data of Table1 results to evaluation of Ea for the pyrolysis of the samples of PLEG.Fig 9 shows the variation of "Lnk" versus "$T^{-1}$" ($K^{-1}$) for eleven samples of PLEG. As Fig 9 shows, the Ea of lower temperature weight loss was lower, and hence the rate of weight loss at lower temperatures was very slow. As the temperature increases, the rate of weight loss also increases which was within expectation. The slope of the graph in Fig 8 is related to Ea of the weight loss process of sample of PLEG. At lower temperature the Ea of weight loss was lower. This is within expectation since in this stage main reaction was loss of HCl from the PLEG sample. Elimination of HCl (bp -89°C) from backbone of the chloroprene radical (328 kJ/mol) is less energy consuming than the elimination of carbon chains (347–356 kJ/mol) by chain scissoringof neoprene at high temperatures.

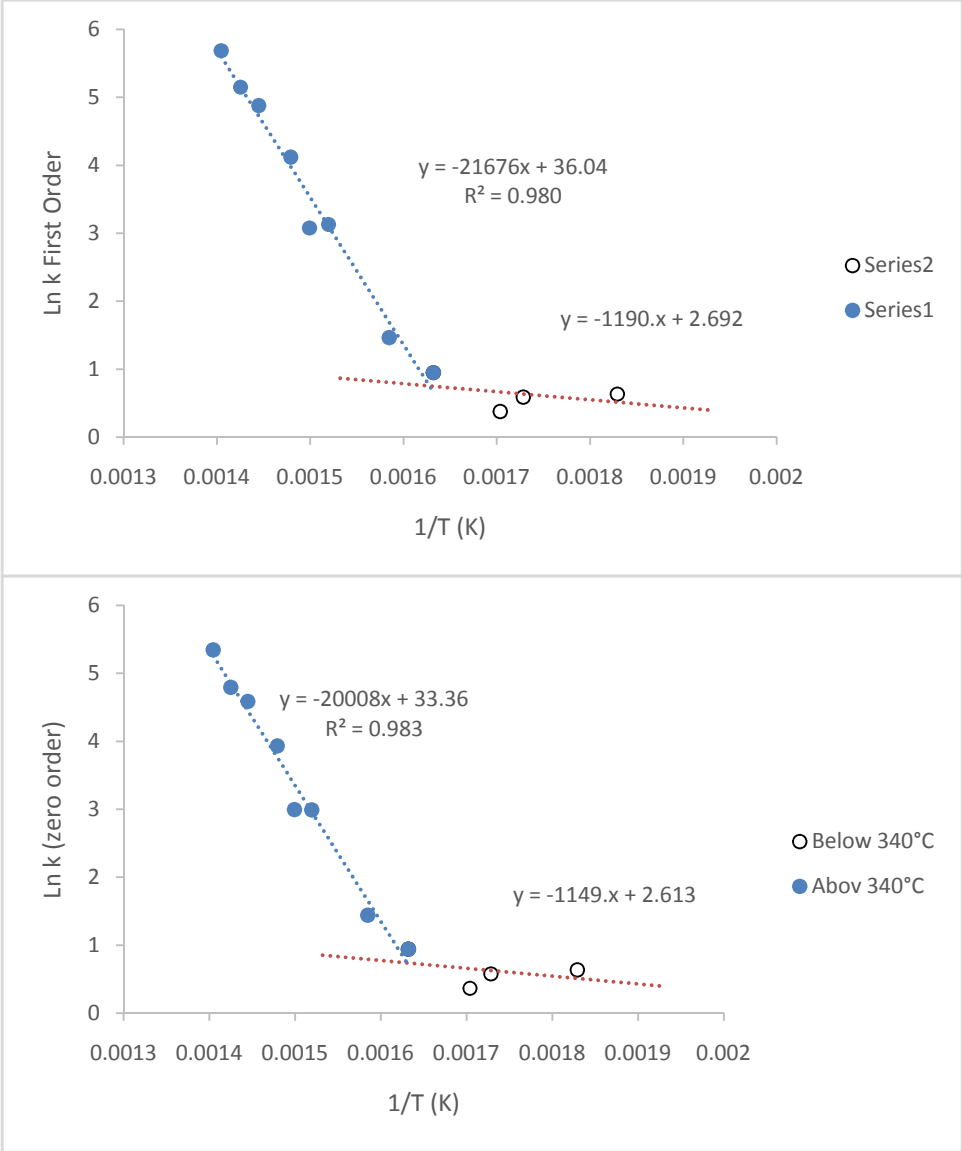
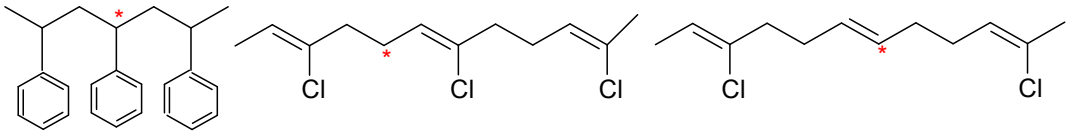



Fig 9. Variation of Ln k versus 1/T for eleven samples of PLEG.

## 4. CONCLUSION AND REMARKS

Thermogravimetry step-by-step pyrolysis degradation of PLEG showed that the thermolysis process of PLEG depends on the temperature of pyrolysis. Experimental thermogravimetric data performed at various temperature, confirm that at temperatures above 435°Cthe Ea for pyrolysis is less than that of the temperatures below it. The experimental results showed part of the pyrolysis products of LSGs are reached in many varieties of chlorinated compounds which are potentially hazardous for environment and human health. A large number of molecular and radical species are involved in this process. In the case of PLEG the presence of chlorine and double bonds favors the initiation reactions and this fact reduces the activation energy of decomposition comparing with polyethylene chains, similar to PS decomposition; because of the

allylic resonance of the resulting radical. The lower activation energy of PLEG similar to PS is due to the preferential formation of the long lived resonantly stabilized radicals,




(1) ( 2) (3)

Cl and H-abstraction reactions include both inter-and intramolecular or backbiting reactions. When compared with the analogous reactions in the gas phase, the latter are inhibited due to the higher density of the liquid phase which favors the bimolecular interactions. It should also be noted that the Cl- and H-abstraction reactions in the liquid phase are much faster than ß-decomposition reactions. In the typical temperature conditions (600-800 K), the ß-decomposition reaction becomes the rate-determining step and the smaller radicals formed generate the parent molecule before undergoing a new ß-scission. A particular case of ß-scission reactions of PS are the unzipping reactions, which play a fundamental role and explain the formation of a large quantities of the monomer. The formation of a large quantities of eight carbons compounds resulting of pyrolysis of LEGs is indications of ɣ-scissions of de-chlorinated neoprene.

## REFERENCES


[1] Lehmann, F.A. & Brauer, G.M. (1961). Analysis of pyrolyzates of polystyrene and poly(methyl methacrylate) by gas chromatography. *Analyatical Chemistry* 33(6) 679-676.

[2]Gargallo, L., Hamidi, N., Radic, D., & Tagles, L.H. (1989). Thermogravimetric Analysis of Poly(dialkylphenyl methacrylate)s, *Thermochimica Acta,* 143, 75-84.

[3]Gumula, T, Paluszkiewicz, C., & Blazewicz, S. (2009).Study on Thermal Decomposition Processes of Polysiloxane Polymers—From polymer to Nanosized Silicon Carbide. *Journal of Analytical and Applied Pyrolysis*, 86(2), 375–380.

[4]Insura, N., Onwudili, J.A. & Williams, P.T. (2010). Catalytic Pyrolysis of Low-Density Polyethylene over Alumina-Supported Noble Metal Catalysts. *Energy & Fuels*, 24(8), 4231-4240.

[5]Faravelli, T., Bozzano, G., Colombo, M., Ranzi, E., & Dente, M. (2003). Kinetic modeling of the thermal degradation of polyethylene and polystyrene mixtures. *Journal of Analytical and Applied Pyrolysis,* 70(2) 761 – 777.

[6]Koo, J.K., Kim, S.W., & Waste. (1993). Reaction Kinetic Model for Optimal Pyrolysis of Plastic Waste Mixtures. *Management & Research* 11(6) 515-529.

[7]Costa, P., Pinto, F., Ramos, A. M., Gulyurtlu, I., Cabrita, I., & Bernardo, M. S. (2010). Study of the Pyrolysis Kinetics of a Mixture of Polyethylene, Polypropylene, and Polystyrene. *Energy & Fuels.* 24(12), 6239-6247.

[8]Smolders, K., & Baeyens, J. (2004). Thermal Degradation of PMMA in Fluidized Beds. *Waste Management,* 24(8), 849-857.

[9] Straus, S & Madorsky, S. L. (1953). Pyrolysis of Styrene, Acrylate, and Isoprene Polymers in a Vacuum. *Journal of Research of the Notional Bureau of Standards,* 50(3), 2405.

[10]Cooley, J. H. & Williams, R. V. (2003). The Pyrolysis of Polystyrene. *Chem. Educator,* 8, 309-311.

[11]Onwudili, J.A., Insura, N., & Williams, P.T.(2009). Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: Effects of temperature and residence time. *Journal of Analytical and Applied Pyrolysis,*86(2), 293-303.

[12]Koo, J.K., Kim, S.W., & Seo, Y.H. (1991). Characterization of aromatic hydrocarbon formation from pyrolysis of polyethylene-polystyrene mixtures. *Resources, Conservation & Recycling,* 5(4), 365-382.

[13]Huggett, C. & Levin, B.C. (1987) Toxicity of the Pyrolysis and Combustion Products of Poly (Vinyl Chlorides): A Literature Assessment. *Fire and Materials,* VOL. II, 131-142.

[14]Miranda, R., Pakdel, H., Roy, C., & Vasile, C. (2001). Vacuum pyrolysis of commingled plastics containing PVC II. Product analysis. *Polymer Degradation and Stability*. 73(1), 47-67.

[15]Lee, K.H. (2011). Pyrolysis of waste polystyrene and High-Density Polyethylene. Korea Institute of Energy Research. South Korea.

[16]Li Chuantong, Liu Rong and Tang Bo, 2004. Study on Kinetic Properties of Pyrolysis for Hospital Solid Wastes, Proceedings, 3rd ICIPEC, Hangzhou, China, October.

[17]Achilias, D.S., Roupakias, C., Megalokonomos, P., Lappas, A.A., & Antonakou, E.V. (2007). Chemical recycling of plastic wastes made from polyethylene (LDPE and HDPE) and polypropylene (PP), *Journal of Hazardous Materials,* 149(3), 536-542

[18]Mastellone, M.L., & Arena, U. (2004). Bed Defluidisation during the Fluidised Bed Pyrolysis of Plastic Waste Mixtures. *Polymer Degradation and Stability*, 85(3), 1051-1058.

[19] Zakaria, N., Ani F. N., Yunus, M.N.M., and Husain, M.A.S. (2011) Oxidative pyrolysis of examination rubber gloves in the integral pyrolysis test plant, *International Journal of Mechanical and Materials Engineering (IJMME), Vol.6, No.1, 1-9*

[20]Environmental Protection Agency (EPA), (2010). Cycling: Frequent Questions. Retrieved July 2012, from http://www.epa.gov/epawaste/conserve/materials/ecycling/faq.htm and; http://www.epa.gov/epawaste/conserve/materials/plastics.htm

[21]Zakaria, N., Ani F. N., Yunus, M.N.M., and Husain, M.A.S. (2011) Oxidative pyrolysis of examination rubber gloves in the integral pyrolysis test plant, *International Journal of Mechanical and Materials Engineering (IJMME), Vol.6, No.1, 1-9*

[22]Zhu H. M., Yan J. H, Jiang X. G, Lai Y. E., Cen K. F. 2008. Study on pyrolysis of typical medical waste materials by using TG-FTIR analysis, Journal of Hazardous Materials, 153, 670-676.

[23] T.M. Kruse, O.S. Woo, Broadbolt, LJ. Chem. Eng. Sci. 56 (2001) 971.

[24] (9] Ranzi,E. Dente, M. Faravelli, T., Bozzano, G. Fabini, S. Nava, R. Cozzani, V., Toguotti, L. J, Anal. Appl. Pyrolysis 40-41 (1997) 305.

[25]Faravelli T, Bozzano, G, Seasa, C. Perego, M. Fabini, S. Ranzi, E.,Dente, M. J, Anal. Appl. Pyrolysis52 (1999) 87.

[26]Faravell, E. Pinciroli, M. Pizno, F. Bozzano, G. Dente, M. Ranzi. E J. Anal. Appl. Pyrolysis 60 (2001) 103

[27] Bouster,C., Vennande, P., Veron, J. J. Anal. Appl. Pyrolysis 15 (1989) 149.

[28]Koo, J.-K., Rim, S.-W., Seo, Y.-H. Resour. Conser. Recycling 5 (1991) 365. And Koo, I.-K., Kioo, S.-W., Waste Manag. Res. 13 (1993) 2;21

[29] Westerhout, R.W.J. , Waanders, J. Kuipers, I.A.M. van SWaaij, W.P.M, Ind. Eng. Chem. Res. 36 (1997) 1955.

[30]. "Medical Gloves and Gowns". FDA. Retrieved 2010-03-10.

[31]http://en.wikipedia.org/wiki/Medical_glove Retrieved 2013-6-5.

[32]"Glove manufacturing". Ansell.eu. Retrieved 2012-12-14

[33]Werner Obrecht, Jean-Pierre Lambert, Michael Happ, Christiane Oppenheimer-Stix, John Dunn and Ralf Krüger "Rubber, 4. Emulsion Rubbers" in Ullmann's Encyclopedia of Industrial Chemistry, 2012, Wiley-VCH, Weinheim.doi:10.1002/14356007.o23_o01

[34]Furman E. Glenn. "Chloroprene Polymers".*Encyclopedia of Polymer Science and Technology*.doi:10.1002/0471440264.pst053

[35]Sarker, M. Rashid, M.M. Rahman, R. & Molla, (2012). M. Conversion of Low Density Polyethylene (LDPE) and Polypropylene (PP) waste plastics into liquid fuel using thermal tracking process. *British Journal of Environment & Climate Change,* 2(1): 1-11.

[36]Williams, E.A., & Williams, P.T. (1997). Analysis of products derived from the fast pyrolysis of plastic waste. Journal of Analytical and Applied Pyrolysis, 40-41, 347-363.

[37]Williams, P.T., & Williams, E.A. (1999). Fluidised Bed Pyrolysis of Low Density Polyethylene to Produce Petrochemical Feedstock. *Journal of Analytical and Applied Pyrolysis,* 51(1), 107 – 126.

[38]Lee, K.-H.(2009). Thermal Degradation of Heavy Pyrolytic Oil in a Batch and Continuous Reaction System. *Journal of Analytical and Applied Pyrolysis*, 86(2), 348–353.

[39]Kaminsky, W., Predel, M.,& Sadiki, A. (2004). Feedstock Recycling of Polymers by Pyrolysis in a Fluidised Bed. *Polymer Degradation and Stability*, 85(3),1045-1050.

[40]Schmidt, H. & Kaminsky, W. (2001). Pyrolysis of Oil Sludge in a Fluidised Bed Reactor. *Chemosphere* 45(3), 285-290.

[41]For examples look at Envion (http://www.envion.com) or Agilyx (http://green.blogs.nytimes. com/tag/diesel) or Polymer Energy® (http://www.polymerenergy.com/technology)

[42]4R Sustainability, Inc., (2011). Conversion Technology: A Complement to Plastic Recycling, Portland, OR 97203

[43]Pinto F., Costa P., Gulyurtlu I., & Cabrita I. (1999). Pyrolysis of plastic wastes. 1. Effect of plastic waste composition on product yield, Journal of Analytical and Applied Pyrolysis, 51(1), 39-55.

[44]Bushnell, K. (2012). Plastic Bags: What About Recycling Them? The Sierra Club. Retrieved June 2010 from http://www.sierraclub.org/sustainable_consumption/articles/bags2.asp.

[45] . Hamidi,N., Massoudi, R., Shrestha, S., Lalmansingh, L., Pascoe, T., Oriakhi, C. and Whitesides, L. "Waste Plastics: Pyrolysis of Powdered and Powder-Free Laboratory Examination Waste Gloves" British Journal of Applied Science & Technology (2013) In Press

[46] Hamidi, N., Tebyanian, F., Massoudi, R., and Whitesides,L. "Pyrolysis of Household Plastic Wastes" British Journal of Applied Science & Technology 3(3): 417-439, 2013

[47] Faravelli, T., Bozzano, G., Colombo, M., Ranzi, E., & Dente, M. (2003). Kinetic modeling of the thermal degradation of polyethylene and polystyrene mixtures. *Journal of Analytical and Applied Pyrolysis,* 70(2) 761 – 777.

[48] Benson, S. The Foundations of Chemical Kinetics. McGraw-Hill, New York, 1960, pp. 130~155.

[21] M. Dente, G. Bozzano, G. Bussani, Compo Chem. Eng. 21 (1997) 1125.

[22] G. Bozzano, M. Dente, G. Bussani, Mechanistic models for liquid phase pyrolysis of complex hydrocarbon mixtures: the delayed coking process simulation., AIDIC Conf. Series, Selected papers, 2. 1997