

Original Research Article

Thermogravimetric and Kinetic of thermal degradation of Powdered Laboratory Examination Gloves: 2. Analysis of isotherm and thermal scan Traces from 307-450°C.

ABSTRACT

This study focused on the thermogravimetric analysis (TGA) of powdered laboratory safety examination gloves (PLEG) with the goal of finding the most economic approach to save the condensed energy within the PLEG waste in order to reduce the environmental pollution caused by an ever increasing amount of laboratory safety examination gloves (LEG) in the landfills. The study was conducted in the Department of Biological and Physical Sciences at South Carolina State University (SCSU), Orangeburg, SC, USA, during the spring and summer of 2014. Twelve TGA experiments were performed on twelve samples of PLEG. Three types of operating conditions were studied: The first condition was a thermal scan from 50°C to 800°C with a heating rate of 10°C/min while the samples were purged with 10 mL/min argon. The results obtained determined the thermal stability of PLEG, and the highest weight loss rate, which was observed ~410 °C. The second approach was two dynamic thermal scans with a linear and fast increase of the temperature over time (200°C/min), followed by two isotherms, one at 310°C < temperature < 410°C and the other at 410°C for 30 minutes. The third approach was one thermal scan and one isotherm above 410°C. From the thermal scans and isotherms, the highest rate of weight loss, the temperature at the maximum weight loss, the apparent order of reaction, (wlo) the apparent rate constant (k) and the apparent activation energy of weight loss (Ea) were estimated. The experimental results confirmed keeping the LEG in temperatures near to 340°C for a long time prior to decomposition resulted in production of new materials with more thermal stability than the original PLEG.

Keywords: thermogravimetry, latex gloves, kinetics, environment, pollution, pyrolysis of gloves, thermolysis of neoprene

DEFINITIONS, ACRONYMS, ABBREVIATIONS

Terms:

PLEG: powdered laboratory examination glove, LSG: laboratory safety glove, w: the non-vaporized mass percent of the materials in the TGA reaction pan; r: the rate of reaction, wlr: weight loss rate of reaction; wlo: weight loss order of reaction; 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 spectrometry, WHO: world health organization, Ea: activation energy, TGA: thermogravimetric analysis,

1. INTRODUCTION

This study was a continuation of a previous study on the thermogravimetric analysis (TGA) to study degradation of powdered laboratory examination glove (PLEG) [1]. The objective of the study was conversion of chlorine-containing plastic waste materials, such as neoprene, into 'clean fuels' and the residue to other industrial used materials such as metals and metal oxides [1]. This study reports kinetics results of non-catalytic thermal degradation of PLEG, a neoprene based material by thermogravimetric analysis (TGA). In the previous paper, the thermal scans were analyzed; here the thermal scans and isotherms were considered. Based on our previous experiments [2] 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 of polymers and plasticizers [3]. The aim of this study was to investigate the effect of temperature on the kinetics of thermolysis of PLEG, the one that is made of chloroprene rubber.

2. MATERIALS, INSTRUMENTATION, AND METHODS

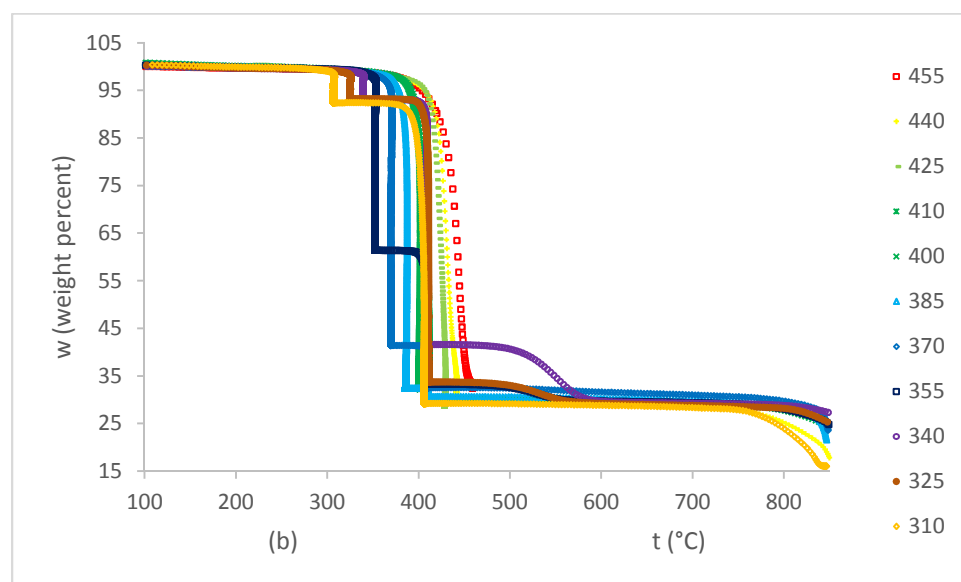
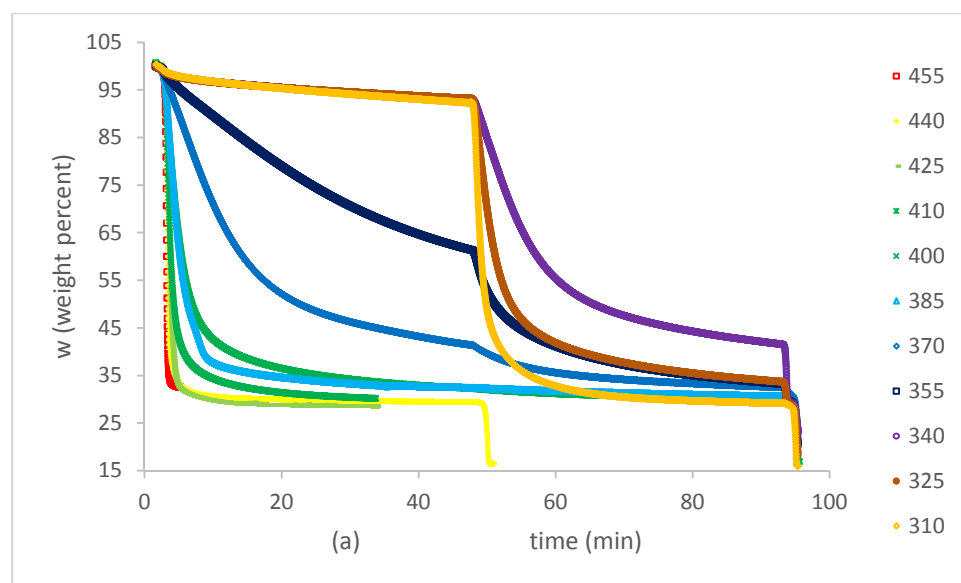
Materials, methods and instrumentation were described previously [Error! Bookmark not defined.]. The experiments were carried out with a practical interest in the PLEG decomposition under various temperatures and their impact on the kinetics of the pyrolysis process at various temperatures. Briefly, a Perkin-Elmer (USA) thermogravimetric analyzer (TGA-7) was used to study the thermal stability of the PLEG from 50°C to 850°C. The experimental tests, both under dynamic and isothermal conditions, were performed in the same thermogravimetric analyzer, TGA-7, and controlled by a Pyris program run on 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 at 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, the highest decomposition rate of PLEG) and maintained for 30 min. Successively, the temperature was rapidly increased to 850°C and maintained there for two min; this led to the complete degradation of the organic substances. The fast temperature ramps to the isothermal conditions did not show significant overheating.

Twelve samples were analyzed; one sample had one thermal scan from 50 to 800°, seven samples had two isotherms, one below 410°C and the second at 410°C; four samples had one thermal scan to a temperature above 410°C, and one isotherm at higher temperature. The initial sample weights varied between 4 and 8 mg; however, in calculations, the weight was normalized to the weight percentage of the samples. The experimental data, such as time (min), sample temperature (°C), weight percentage of sample, and derivative of weight loss over time (dw/dt), were downloaded from Pyris to Microsoft Excel 2000; then transferred to another PC for further analysis. Microsoft Office 2013 was used for calculation, graphs, and word processing.

3. RESULTS AND DISCUSSION

Fig 1a shows the thermograms of eleven samples of PLEG at eleven temperatures. The sample that was kept for 30 min at 340°C obtained higher thermal stabilities than any other sample. This was 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 other samples which were heated in other temperatures. The rate of weight loss of this particular sample at 410°C was slower than any other sample (Fig 1). The remains of this particular sample at 475°C was about 40% of its original weight, while for the other sample at the same temperature the remaining reached below of 30% of the original mass. Residues of the PLEG at the other isotherms (325 and 355) also produced some thermal stabilities but not comparable to that of 340°C (Fig1).



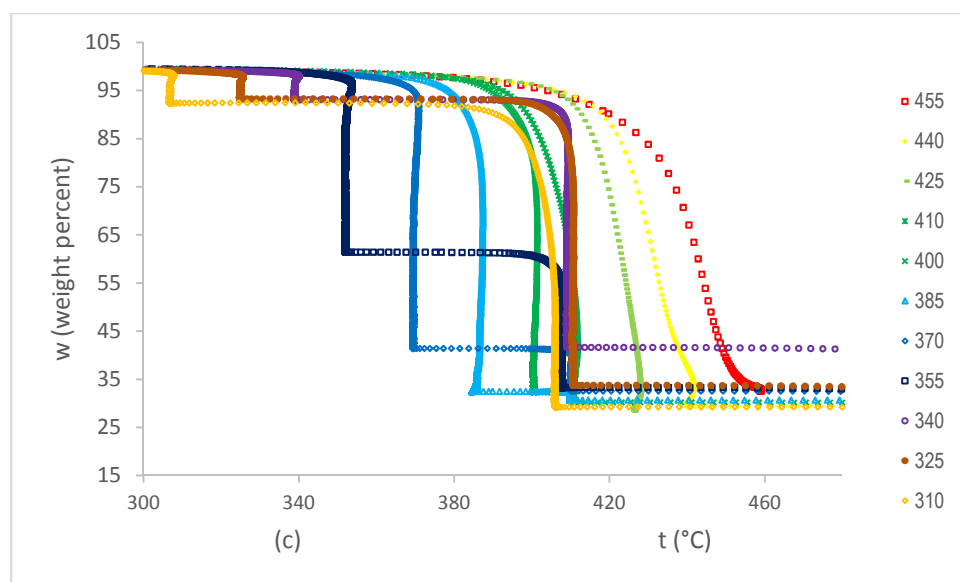


Fig 1. Thermogravimetric analysis of PLEG: (a) weight-loss versus time for 11 samples of PLEG; (b) weight loss versus temperature for 11 samples of PLEG, and (c) expansion of (b) 300-480°C.

3.2 Kinetics of Pyrolysis of PLEG

Fig 1 shows the thermograms of thermolysis of powdered PLEG where the mass of PLEG (w) decreased by time and temperature. The thermolysis process can be described by a typical reaction such as reaction (1) where w is the mass percent of reactants in the TGA reaction pan:



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

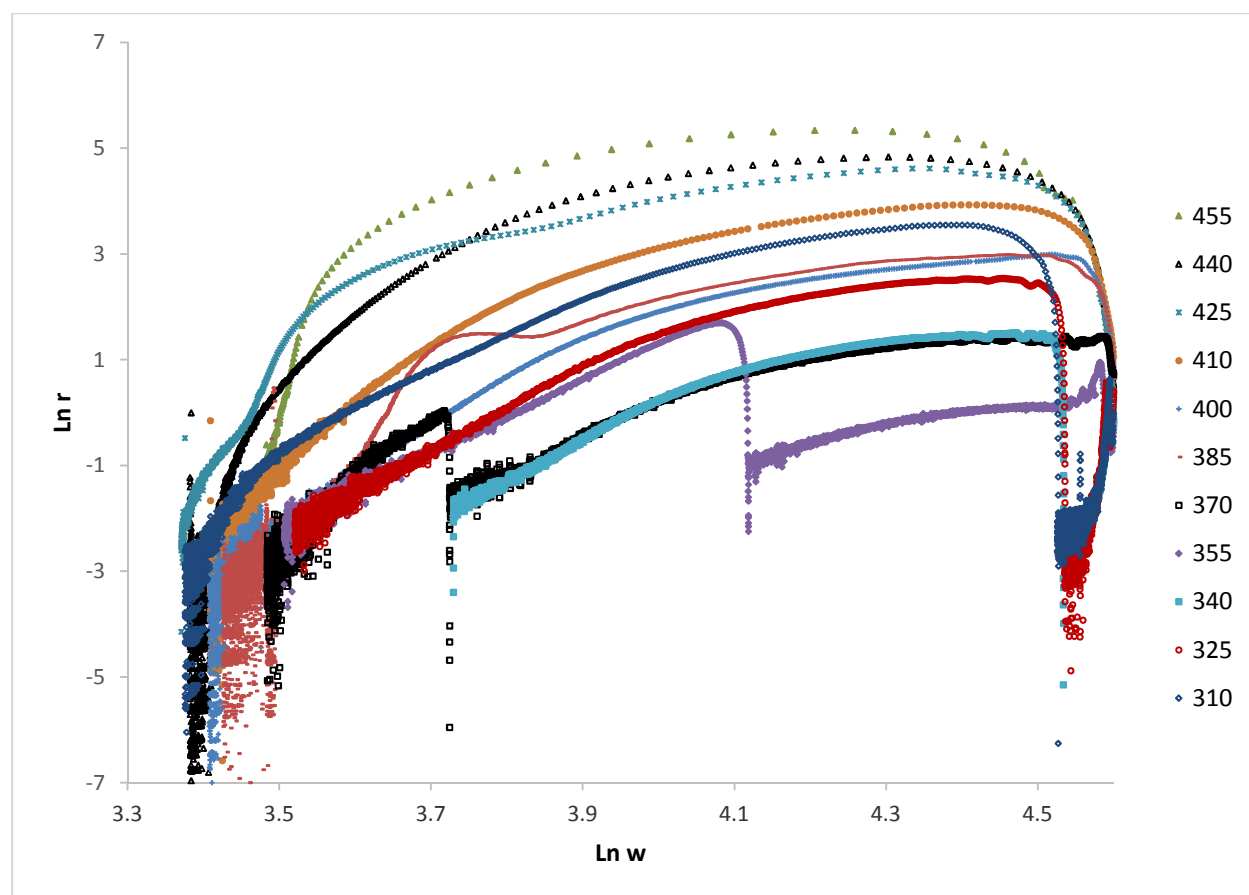
$$r = -\frac{dw}{dt} = kw^n \quad (2)$$

The logarithmic form of Eq 2 produces a linear function of $\ln r$ versus $\ln w$:

$$\ln r = \ln k + n \ln w \quad (3)$$

Fig 2 shows the double logarithmic plot of variation of rate of weight loss, $\ln r$, versus $\ln w$ for all eleven samples of PLEG. According to Eq (3), the slope of these graphs at any w represents the order of reaction, n , and the intercept of it represents the rate constant, k . As the temperature of the isotherm increased the rate of weight loss reaction (wlr) also increased. This was within expectations based on the Arrhenius equation, Eq (4). Four samples that had their first isotherm under 380°C (340, 355, 370, and 375 °C) had a very particular form in the double logarithmic plot (Fig 2). The sample of PLEG that was maintained for 30 min at 340°C underwent some kinds of internal chemical changes that led to production of thermal

109 resistance material. The samples that were held under 325°C and 355°C also gained some thermal
110 resistance but not as much as the previous sample.



111
112 Fig 2. Variation of 'Ln r' versus "Ln w" according to Eq(3) for 11 samples of PLEG.

113
114 **Analysis of the first thermal scans.** Fig 2 represents the variations of Ln r versus Ln w for the portion
115 of thermogram belonging to the first temperature scan, prior to the first isotherm process for 11 samples of
116 PLEG. This portion of the diagram was not very visible in Fig 2, so it was expanded for proper analysis (Fig
117 3). The variation of Ln r versus Ln w of the thermal scans below 370°C had the common feature of an "N"
118 form. At the initial state of thermal scan, as the temperature increased above 100 °C, the weight loss
119 reaction rate (wlr) decreased to a minimum; in this trace the order of weight loss (wlo) was a large positive
120 number although the amount of weight loss was well below 1% of the reactants. As the amount of reactants
121 (Ln w) decreased, suddenly, there was a change in course of wlr, creating a second trace where, the wlr
122 increased as the temperature increased (consequently, Ln w decreased); in this step the wlo value (the
123 slope of the line fitted by list-square into experimental data) was a large negative number. The increase of
124 wlr with Ln w (and consequently temperature) reached to a maximum where the third trace started to
125 appear. Afterward, the wlr decreased; by increasing Ln w, in this stage the initial wlo values were large
126 positive numbers which were decreased by increasing the value of Ln w. This behavior was more

pronounced in the first four samples where their thermal scans were below 355°C. In the samples that were heated to higher temperatures, therapid weight loss caused the compression of these sections(Fig 3).

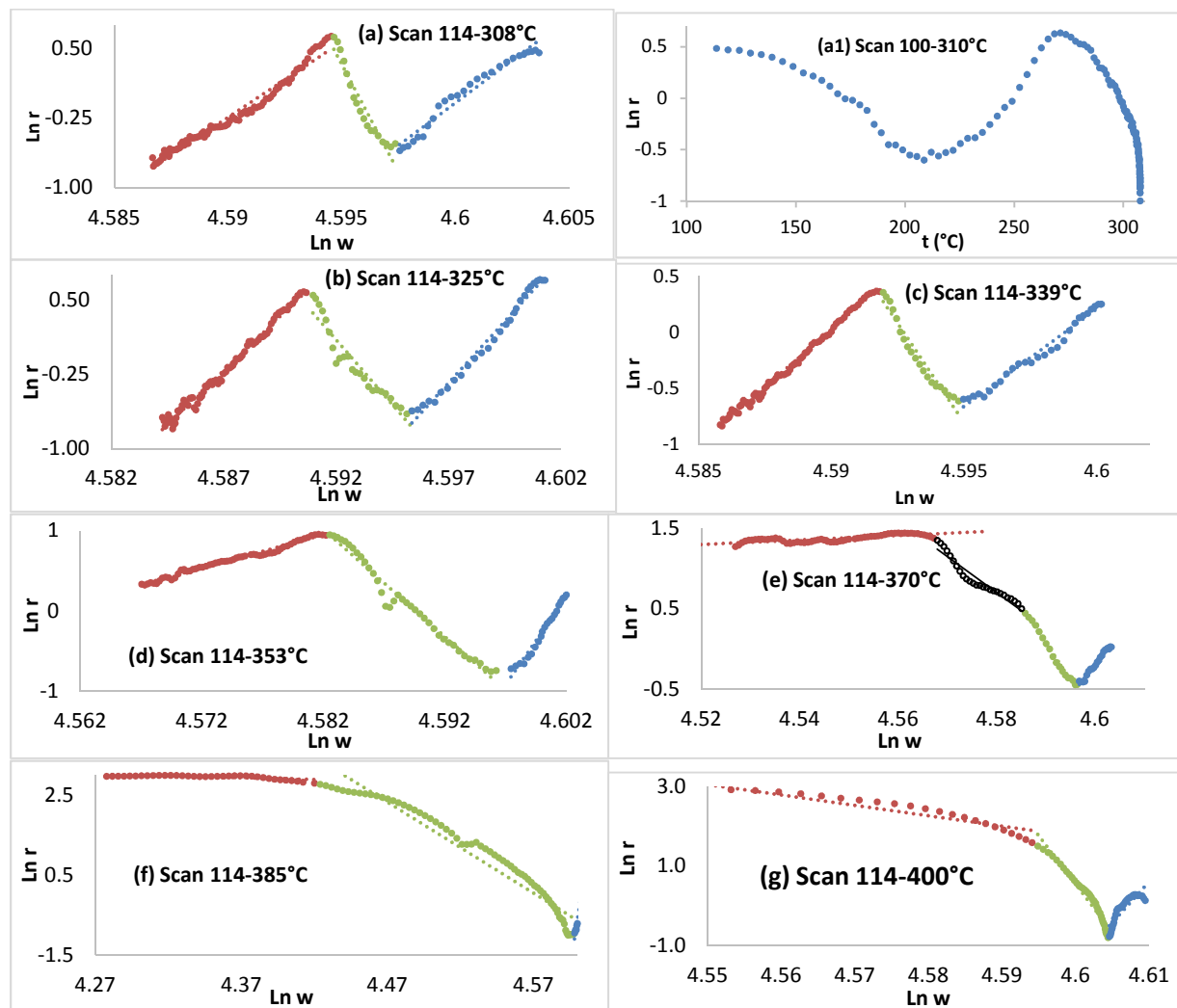
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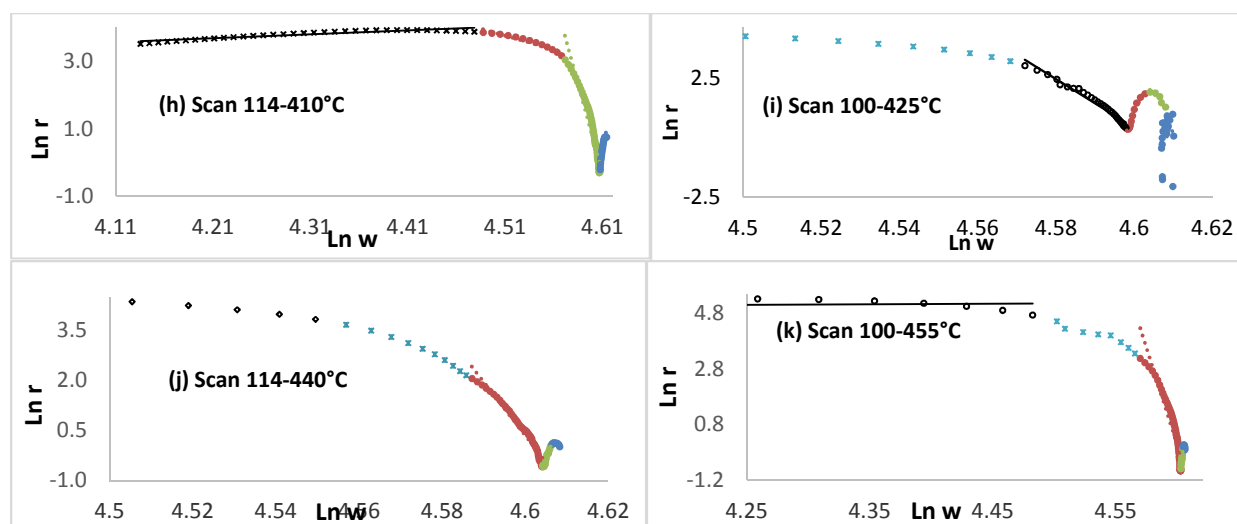


Fig3. Variation of Ln r versus Ln w of 11 samples of PLEG from 100°C to the isotherm temperatures. The temperature range is indicated on the plot.

At temperatures above 370°C, the plots of initial thermal scans took a different form, particularly at the third trace. The tail of the third trace, now, was a concave upward curve shape; and it was the bearer of highest wlr and therefore convergeto form a plateau where the slope of the tangent line to it was zero. As weight loss increased, the values of slope increased; it initiated with a large negative number and ended with positive numbers. The entire range of thermal scan did not follow Eq (3) as was expected for a pure compound. For a complex mixture of materials such as PLEG (in temperatures below first isotherm) three traces with different slopes were observed. The wlr that reached to its maximum at temperatures above 100°C < t < 200 °C may be related to evaporation of the moisture in the PLEG or other lower molar mass compounds that resulted from initial decomposing of PLEG. As the temperature increased (t > 200 °C), other volatile components of PLEG werereleased which caused the wlr in this step increase and reach its max, where negative values of wlo were observed at 271°C. Afterward, the rwl began to decrease since those volatiles were consumed, after which a positive wlo was obtained. The detailed study of each of these samples follows:

Sample 310. Fig 4 shows the plot of variation of rate of weight loss of the isotherms and thermal scans according to Eq (3) for sample PLEG 310. The sample was heated fast from room temperature to 307°C, maintained for 30 min in 307°C, and then heated fast to 407°C and held there for another 30 min.

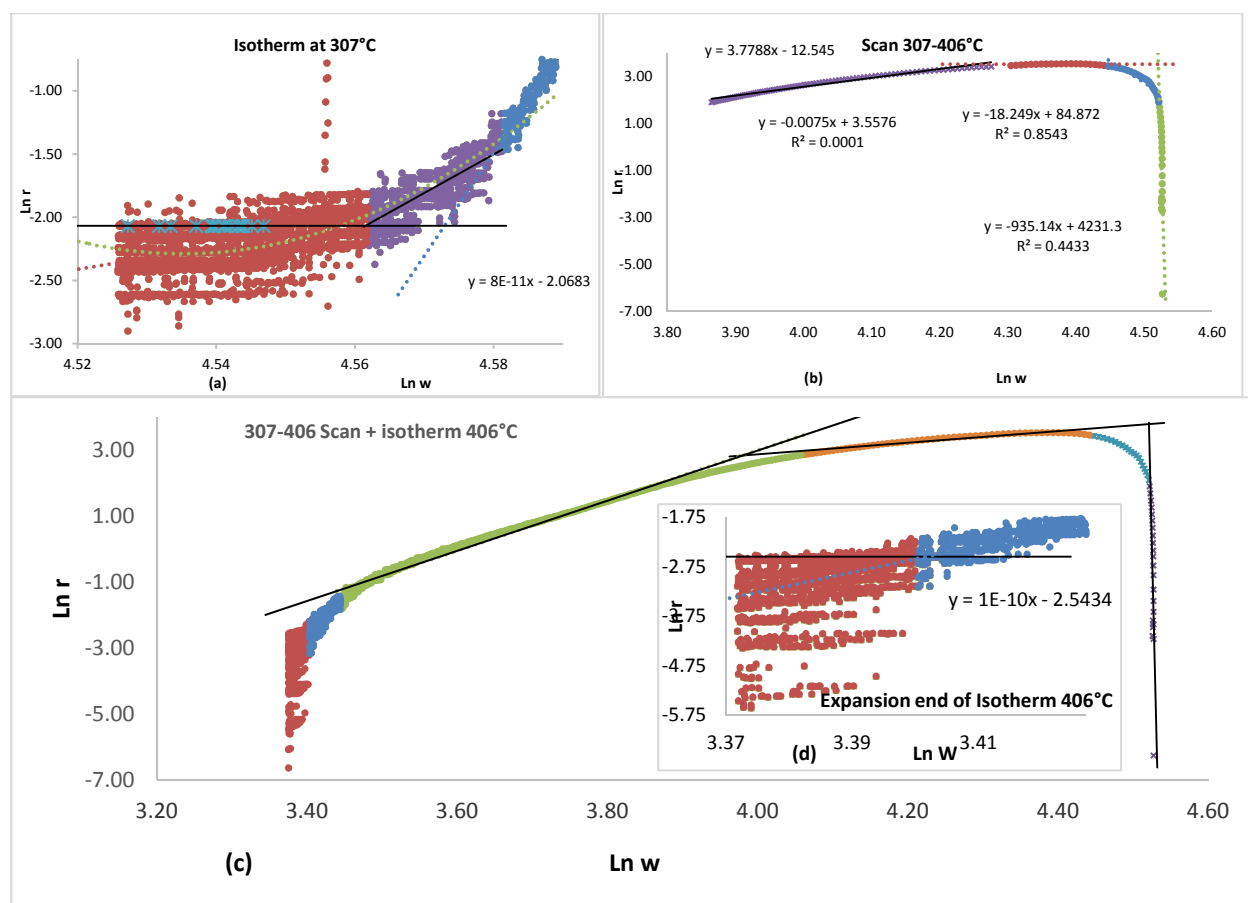


Fig 4. Variation of $\ln r$ versus $\ln w$ for sample LEG 310. (a) Isotherm at 307; (b) thermal scan from 307°C to 406°C; (c) combination of thermal scan from 307-407°C and the isotherm at 407°C; (d) expansion of the tail of isotherm at 407°C.

Thermal scan 100-307°C. Three traces with slopes positive, negative, and positive; with minimum and maximum like an "N" shape was observed (Fig 3a), and described in the text. The wlr decreased from 114-212°C, then it began to increase reaching a max at 273°C. Afterward, it began to decrease; this decrease of the values wlr continued during the entire temperature scan to 307°C. The initial wlo from the slope (~25 initial points) in the temperature range of 100-212°C was 184. This step is related to evaporation of volatile materials such as water, and other organic compounds in the PLEG sample. The wlr reached a minimum at 214°C, afterward wlr started to increase where the slope of $\ln r$ versus $\ln w$, the wlo , was a large negative number (-466). When the value of wlr reached to a max at 271°C, wlr started to decrease with initial wlo value of over 163. The wlo at the end of thermal scan decreased to 88; while the thermal scan had a lapse of 2.5 min. The total amount of weight loss in this process was 1.5% of the total mass of the sample (Table 1). Table 1 shows the initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the wlo , and $\ln k$ resulted from TGA analysis of PLEG sample 310.

176

177 Table 1. The initial and final time, the time of process, the initial and final temperature, and the change in
 178 temperature, the initial and final weight of sample and the weight loss amount, the wlo, and Ln k
 179 resulted from TGA analysis of PLEG sample 310.

Time (min)			Temperature (°C)			Weight Percent			wlo	Ln k
Initial	Final	Δt	Initial	Final	ΔT	Initial	Final	$-\Delta W$		
1.70	2.12	0.42	114	212	98	100.42	99.96	0.46	252	-1161
2.13	2.42	0.28	215	271	56	99.95	99.68	0.27	-495	2280
2.43	3.85	1.42	274	308	34	99.64	98.42	1.22	109	-501
3.87	5.53	1.67	308	308	0	98.41	97.81	0.61	88.2	-405
5.55	17.18	11.63	308	307	-1	97.80	95.76	2.04	33.4	-155
17.20	45.33	28.13	307	307	-0.04	95.76	92.56	3.20	9.33	-44.60
45.35	47.23	1.88	307	307	0.02	92.56	92.37	0.19	0.25	-3.44
47.25	47.92	0.67	307	378	71	92.37	91.98	0.39	-935	4231
47.93	49.22	1.28	380	405	25	91.87	58.10	33.76	-0.14	-5
50.32	64.90	14.58	406	406	0	46.55	31.32	15.23	8.27	-30
73.23	92.82	19.58	406	406	0	30.19	29.22	0.97	35.1	-122

180

181 **Isotherm at 307°C.** During 30 min of residency of the PLEG sample at 307° C, about 6% of total weight
 182 loss was observed. The wlo was started with the value of 88 and it decreased slowly to 33 when a kind of
 183 plateau was observed at the end with a slope near to zero (Fig 4a, Table 1).

184 The above results presents several inconveniences: first, the experimental data points are not following a
 185 simple plot, and second, the values of wlo do not appear to be within the values of a reaction order, since in
 186 a solid and liquid state a reaction order over 3 is rarely ever expected. The third concern is the variety of
 187 chemicals that are presented in the TGA pan, a mixture of a wide range of chemicals, both original
 188 components of the PLEG and products of degradation of PLEG during thermolysis. A close analysis of the
 189 experimental points indicates that their orientation is not a merely random distribution (Fig 4a & d). Many of
 190 the experimental points are oriented together forming parallel straight lines (similar wlo) with the value of
 191 slope near to zero, but their intercepts (k values) are different from each other. Therefore, the best
 192 hypothesis is that the value of k of w for the chemicals under TGA conditions is different while their wlo are
 193 near to zero. Filtering the data, regrouping and adjusting a list-square regression line to the experimental
 194 points that have a visual trend, yields the wlo and k for each separated hypothetical reaction. The kinetics
 195 characteristics of 28 hypothetical parallel reactions, such as the values of wlo, initial weight of sample (wi),
 196 final weight of sample (wf), and the amount of weight loss (δw) of pyrolysis of PLEG, sample 310 at 307°C
 197 are summarized in Table 2.

198

199 Table 2. The values of wlo, initial weight of sample (wi), final weight of sample (wf), and the amount of
 200 weight loss (δw) for the hypothetical weight loss reactions of PLEG during the isotherm 307°C.

Reaction	slope	intercept	min	max	dw
1	0.34	-3.36	95.05	95.75	0.70
2	-0.46	0.25	93.19	94.63	1.44
3	0.08	-2.23	94.49	94.82	0.33
4	-0.71	1.35	92.50	94.41	1.91
5	0.80	-5.58	95.27	95.76	0.48
6	0.03	-2.10	92.51	93.73	1.22
7	0.09	-2.40	92.51	94.63	2.12
8	0.10	-2.44	93.97	94.82	0.85
9	-0.01	-1.99	93.20	94.70	1.51
10	0.26	-3.20	93.58	95.48	1.90
11	0.16	-2.77	94.86	95.65	0.79
12	-0.16	-1.32	92.39	93.04	0.66
13	-0.21	-1.14	92.39	93.08	0.69
14	-0.43	-0.12	92.59	93.03	0.44
15	-0.36	-4.53	93.02	95.68	2.66
16	-0.04	-1.97	92.38	92.96	0.59
17	-0.09	-1.75	92.59	95.22	2.62
18	-0.63	0.66	92.51	93.46	0.95
19	-0.12	-1.70	92.37	92.76	0.39
20	-0.13	-1.68	93.27	94.02	0.74
21	-0.37	-0.60	92.39	93.23	0.85
22	0.07	-2.66	92.50	92.77	0.28
23	-1.05	2.40	92.39	93.52	1.13
24	-0.56	0.15	93.63	93.64	0.00
25	0.18	-3.23	92.37	93.51	1.14
26	-0.71	0.76	92.49	92.75	0.26
27	-0.22	1.54	92.54	93.90	1.36
28	0.41	-4.45	92.38	93.06	0.68

201

202 **Thermal scan 307 to 406 °C.** At the beginning of the thermal scan from 307-410°C, the wlr increased
 203 exponentially, which led to the decrease of the wlo to a high negative value (~ -935, 11th column Table 1).
 204 The wlr reached a maximum at 399°C, about 7°C before ending the heating scan. As the temperature
 205 increased, the wlr became slower; a plateau was observed with wlo near to zero around 398°C < t < 403°C,
 206 75 < w < 85. The plateau with wlo of zero covered 10 % of the total weight loss of sample. As thermal scan
 207 continued, the wlr decreased slowly, hence, the wlo increased gradually. At the end of the thermal scan the
 208 wlo ~ +3 was observed. The reaction order, one and two, in the liquid and solid state are well
 209 understandable, while higher orders are not so easy to interpret, particularly, when it is about
 210 decomposition and vaporization of a compounds. This kind of behavior was observed for all 11 PLEG
 211 samples (Fig 2); which was interpreted as simultaneous combination of many reactions at the same time
 212 rather than one simple reaction (Table 2).

213 **Isotherm at 406°C.** While the PLEG sample resided at temperature 406°C for 30 min, it lost more than
 214 61% of its original mass; the highest weight loss of the sample happened during this isotherm (10th column
 215 Table 1). The maximum value of wlr of this sample at 406°C was smaller than the maximum values of wlr
 216 of the sample of PLEG that was under 410°C isotherm (Fig 2). This was, primarily, due to differences in the

isotherm temperatures. Moreover, heating the sample for 30 min at 307°C caused internal structural changes of the PLEG sample. These internal changes also caused the reduction of the wlr of sample at 406°C. This kind of thermal retardation caused by degradation and recombination of materials at higher temperature was also observed for other samples of PLEG particularly sample 340.

The wlo ~3 which was inherited from previous thermal scan, began to increase in conjunction with decrease in wlr. Traces with wlo ~+8 and later on ~+34 were detected (11th column, Table 1).

A close inspection of an expanded section of the end of the isotherm (Fig 4c&d) showed a parallel array of many sets of experimental data that lined together forming a straight lines with a slope near to zero or very low values such as 1 or 2, but with different values of intercepts. Similar to the previous section, the experimental points that were aligned in straight lines were taken as references for a separated reaction. By this method, over 43 different reactions were recognized. Using total ion chromatogram of gas chromatography mass spectrometry, over 150 chemical were recognized in a sample collected by simple distillation of pyrolysis products [3]. Table 3 summarizes the values of wlo, wi, wf, and δw for the hypothetical weight loss reactions, calculated for hypothetical reactions took place in the tail of isotherm at 406°C.

Table 3. The values of wlo, initial weight of sample (wi), final weight of sample (wf), and the amount of weight loss (δw) for the hypothetical weight loss reactions of PLEG during the isotherm 406°C.

Reaction	Slope	intercept	w min	w max	dw
1	0.62	-7.43	29.25	29.56	0.31
2	1.21	-9.34	29.24	29.68	0.44
3	-0.98	-1.82	29.26	29.76	0.50
4	0.41	-6.34	29.22	29.87	0.64
5	2.26	-16.71	29.23	29.53	0.30
6	0.08	-4.64	29.24	29.61	0.37
7	-0.38	-3.06	29.23	29.67	0.44
8	0.83	-7.11	29.38	29.71	0.33
9	1.27	-8.51	29.22	29.71	0.49
10	-0.98	-0.90	29.23	29.83	0.60
11	-1.83	2.13	29.22	29.99	0.77
12	0.99	-7.19	29.23	29.55	0.32
13	-0.66	-1.58	29.25	29.58	0.33
14	0.92	-6.90	29.22	29.56	0.34
15	0.53	-5.53	29.24	29.68	0.44
16	0.23	-4.48	29.51	29.76	0.25
17	-1.48	1.41	29.22	29.87	0.65
18	0.29	-4.50	29.23	29.53	0.30
19	0.80	-6.18	29.23	29.69	0.46

20	1.03	-6.86	29.24	29.76	0.52
21	0.47	-4.91	29.23	29.87	0.64
22	0.25	-4.14	29.30	29.89	0.59
23	0.05	-3.39	29.24	30.02	0.78
24	1.51	-8.29	29.68	30.07	0.39
25	-0.47	-1.52	29.22	30.12	0.90
26	0.67	-5.35	29.24	29.68	0.44
27	-0.12	-2.63	29.22	29.76	0.54
28	1.47	-7.99	29.31	30.10	0.79
29	-0.71	-0.55	29.22	30.12	0.90
30	0.17	-3.47	29.24	30.10	0.86
31	0.84	-5.68	29.24	30.12	0.88
32	1.44	-7.59	29.23	30.10	0.87
33	1.68	-8.39	29.70	30.19	0.49
34	0.38	-3.92	29.54	30.10	0.56
35	-0.15	-2.11	29.22	30.18	0.96
36	-0.23	-1.81	29.24	30.07	0.83
37	0.34	-3.72	29.23	30.16	0.94
38	0.26	-3.39	29.30	30.19	0.89
39	0.49	-4.12	29.54	30.17	0.63
40	1.75	-8.37	29.75	30.18	0.43
41	0.83	-5.14	29.92	30.19	0.27
42	2.19	-9.71	29.92	30.18	0.26
43	-1.19	1.88	30.03	30.19	0.16

235

236 Observing over 150 chemicals simultaneously condensed in a sample of pyrolysis products of PLEG [3] is
 237 an indication that many reactions occur simultaneously. Postulating many chemical reactions at high
 238 temperatures for pure polymeric materials has been reported by other researchers [eg⁴]. Kinetic models are
 239 proposed for polymer degradation, describing the pyrolysis process with simplified reaction pathways. Each
 240 individual reaction step considered can be representative of a complex reaction network. This single step
 241 approach is only adequate for describing the apparent kinetics of degradation, but it is not able to cover a
 242 wide range of heating rates, temperatures and conversion levels with the same kinetic parameters.
 243 Consequently, this approach is not useful in understanding the decomposition behavior of polymer
 244 mixtures. Only a few detailed kinetic models describing the polymer degradation are reported in the
 245 literature. For example, Kruse et al [42] presented a detailed mechanism of PS pyrolysis based on
 246 population balance equations and method of moments in which up to 93 species and 4500 reactions were
 247 used to describe product distribution and average molecular weight. Similarly, detailed kinetic models of
 248 polyethylene (PE), polypropylene (PP) and PS pyrolysis were recently presented and discussed by other
 249 researchers [eg^{5,6,7}]. These kinetic models can be useful in the study and analysis of the role of mixing in
 250 the thermal degradation of polymer blends. In fact, the considerable attention given to plastic waste has
 251 seen several research projects focus on the thermal degradation of plastic blends and their mutual
 252 interactions [8,9]. These results do not completely agree and different effects were observed. Postulating
 253 many simultaneous reactions at higher temperatures, such as in the case of reactions shown in Tables 2
 254 and 3, is also occurred with the work of other researchers [10]. For example, Westerhout et al [10] results

indicated that in pure chemical conditions, the pyrolysis of polymer mixtures behaves quite similarly to pure polymers, thus, the additives rule is the correct approach for these kind of processes.

Evaluation of E_a by k and T . 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, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$:

$$k = ze^{-\frac{E_a}{RT}} \quad (4)$$

The logarithmic form of Eq (4), linearly relates $\ln k$ to the inverse of temperature, $1/T$ (K):

$$\ln k = \ln z - E_a/RT \quad (5)$$

Fig 5 represents the application of Eq (5) to the data tabulated in Table 1; the initial and final temperatures (5th and 6th column) of each trace and the $\ln k$ value belonging to that particular trace (12th column). The slope of the line fitted to these data represents E_a/R value for the weight loss process according to Eq (5). The highest values of k belonged to thermal scans from 215-271°C and 307-378°C. The k value of thermal scan of the trace at 114-212°C was the lowest k values in the Table, although it was in line with the other two highest k values (Fig 5). The slopes of lines fitted to these three extreme values of k (both negative and positives) in the graph of Fig 5 represents the $-E_a/R$ (9.9 to 9.5 MR) for the weight loss. These values are about five to eight times higher than the slopes of the lines representing the remaining k and T data (1.12 to 1.3MR). Ignoring the results of the thermal scan from 112-307°C (because of low value of weight loss), the $E_a/R = 21 - 24 \text{ kJ/mol}$ was obtained. Considering the values of bond energies of C-Cl (331 kJ/mol) and C-C (346 single bond and 602 C=C both in kJ/mol), the later value of E_a is smaller than the energy required for radical initiation reaction of neoprene and the former values is much higher than the E_a values.

Table 4 summarizes the values of E_a obtained for eleven samples of PLEG from the graphs similar to the Fig 5. One set of E_a values were calculated using initial temperature, and another set of E_a values were calculated considering the final temperature. Also, since the extreme values of k were arranged into a line by themselves, resulted to another set of E_a values which represent the extreme values. Each trace of the data had two temperatures, initial and final, for each sample two trends were observed (Fig 5) and the E_a was evaluated and tabulated in the Table 4.

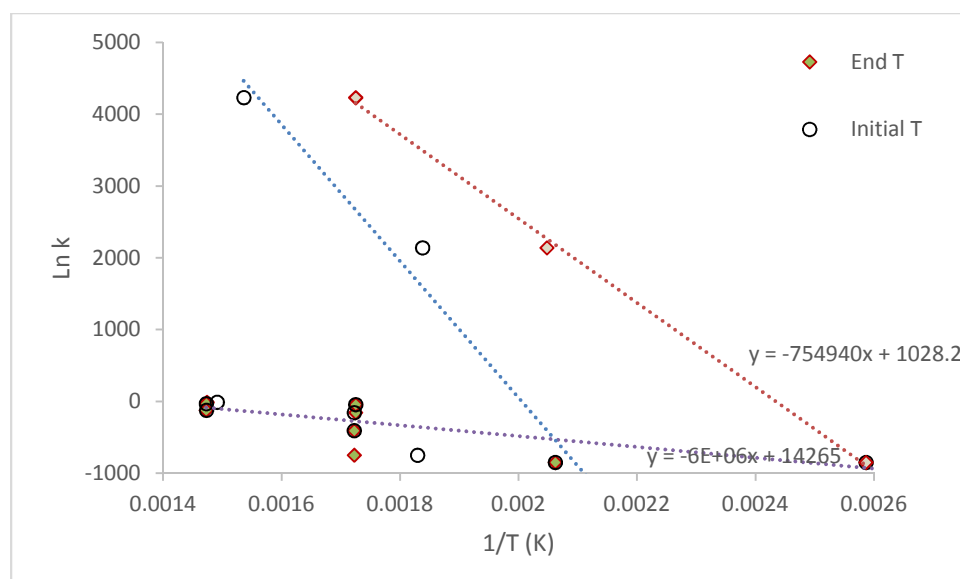


Fig 5. Variation of the values of the Ln k of weight loss of PLEG versus invers of initial and final temperatures (1/T in 1/K, data Table 1).

Table 4. Ea obtained from the slope of variation of Ln k versus 1/T (K) (Fig 7).

Sample	Lower Values of k		Higher Values of k	
	Initial T	Final T	Initial T	Final T
310	1.04	0.80	6.27	10.04
325	1.78	1.47	17.57	38.55
340	2.56	2.57	42.17	69.49
355	1.27	0.39	3.13	4.09
370	-0.02	0.02	20.67	29.81
385	1.07	2.67	1.36	2.80
400	0.82	1.72	3.30	4.67
410	0.57	1.09	2.16	1.96
425	2.13	4.88	-36.36	-18.03
440	-0.03	0.02	0.52	0.84

The values of Ea obtained from the slope of extreme k values were about 5-9 times higher than the values obtained using lower k values. Considering the lower k values belong to the regions that most significant weight loss of materials took place, was assumed that this Ea related to the weight loss of sample and vaporization of materials. Contrary to the extreme k values which belonged to the region that the material in the TGA pan were undergoing internal changes such as decomposition, rearrangements, and other possible chemical reaction including a significant vaporization. An important factor that must be recognized is the inaccuracy of the k values. One of the factors that make the value of k inaccurate is the extrapolation to the zero mass region; where the experiments never got.

As the temperature of the isotherm increased, the values of Ea of extreme k and the middle one got near to each other as was expected (Table 4).

Sample 325 This sample was heated fast (200°C/min) from room temperature to 325°C, retained for 30 min at 325°C, then heated fast to 411°C and held there for another 30 min. The variation of Ln r versus Ln w of this sample was similar to the previous one (310); therefore its presentation was omitted. Table 5 summarized the initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the wlo, and Ln k of sample PLEG 325. At the end of isotherm (at 411°C), 33.8% of materials remained contrary to the sample 310 which at the end of isotherm (407°C), 29.2% of the samples remained in the TGA pan. This suggested that keeping the PLEG in certain temperatures above 325 °C produced new materials (4.4%) which are more thermally resistant than the original compounds. In this experiment, the PLEG was kept for 30 min at 325 °C produce about 4% materials that were more thermal resistant than original sample. Keeping the sample for a longer time at the same temperature, perhaps, produces more thermal resistant material. The highest wlr of this sample was at ~533°C, while for the previous sample (310) the highest wlr was observed at ~402°C.

Table 5. The initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the wlo, and Ln k resulted from TGA analysis of PLEG sample 325.

Time (min)			Temperature (°C)			Weight Percent			wlo	Ln k
Initial	Final	Δt	Initial	Final	ΔT	Initial	Final	$-\Delta W$		
1.62	2.10	0.48	109	225	116	100	99.69	0.55	247.9	-1140
2.10	2.50	0.40	225	300	76	99.69	99.30	0.39	-272.7	612
2.53	3.77	1.23	300	325	25	99.33	98.17	1.16	217.7	-746
3.80	5.47	1.67	325	325	0	98.16	97.59	0.57	83.7	-385
5.48	17.12	11.63	325	325	-1	97.58	95.81	1.77	50.7	-234
17.13	42.37	25.23	325	325	0	95.80	93.63	2.17	15.7	
42.38	47.18	4.80	325	325	0	93.63	93.28	0.35	-0.1	-74
47.20	47.87	0.67	325	382	57	93.28	93.20	0.08	-4136	18757
49.38	48.20	-1.18	410	403	-7	93.18	91.41	1.76	-67.3	16109
48.20	48.63	0.43	403	409	5	91.07	85.96	5.11	-3.0	16
48.88	51.53	2.65	411	411	0	82.87	57.84	25.0	2.2	-7
48.90	51.55	2.65	411	411	0	82.66	57.74	24.9	2.2	-7
51.53	92.53	41.00	411	411	0	57.84	33.80	24.0	7.9	-30

The plot of Ln k versus 1/T of the values of Ln k and T in Table 5 were similar to those in Fig 4. However, the slopes were different. The differences in the values of Ea obtained from higher k values versus 1/T were about 18 to 39 times higher than the values of Ea obtained from lower k values (2nd row, Table 4).

The tails of the isotherms at 325°C and 411°C were similar to the tails of sample 310; therefore, to include a separated analysis here was omitted.

Sample 340 This sample was heated fast (200°C/min) from room temperature to 340°C, kept for 30 min at 340°C, then heated fast to 409°C and held there for another 30 min. The variation of Ln r versus Ln w for

this sample was also similar to the previous samples (Fig 2). Table 6 summaries the initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the wlo, and Ln k resulted from TGA analysis of PLEG sample 340. At the end of 409°C isotherm 41.7% of materials remained contrary to the previous samples. For example, the remaining of sample 310 at the end of its first isotherm was 29.2% and of sample 325 was 33.8%. This suggested that about 12.5% of the materials were not evaporated at 410°C; which was not within the expectations. The highest wlr of this sample was at 550°C instead of the expected temperature, 410°C. Therefore, some significant internal reactions took place during the isothermal process at 340°C. Those internal reaction produced some kinds of thermal resistance compounds during the 30 min at 340°C. Therefore, during the isotherm 340 a number of internal reactions occurred in the TGA pan, with no considerable weight loss, resulted in the formation of new materials with unique properties including higher thermal resistance than PLEG itself.

Table 6. The initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the wlo, and Ln k resulted from TGA analysis of PLEG sample 340.

Time (min)			Temperature (°C)			Weight Percent				
Initial	Final	Δt	Initial	Final	ΔT	Initial	Final	$-\Delta W$	wlo	LnK
1.80	2.23	0.43	157	244	88	99.96	99.59	0.38	259	-1192
2.25	2.57	0.32	248	310	62	97.11	99.31	-2.20	-392	1802
2.58	3.80	1.22	312	339	27	99.29	98.32	0.97	129	-591
3.83	5.50	1.67	339	340	0	98.30	97.74	0.56	82.2	-378
5.52	17.15	11.63	340	339	-1	97.74	95.88	1.86	41.6	-192
17.17	47.20	30.03	339	339	0	95.88	93.11	2.77	10.4	-50
46.57	47.93	1.37	361	390	29	93.12	93.04	0.08	-3580	16228
47.95	46.68	-1.27	392	404	13	93.02	91.97	1.06	-1600	380
48.37	48.90	0.53	405	408	4	91.90	89.66	2.24	-1.21	6.89
48.92	50.58	1.67	408	409	1	89.59	82.37	7.23	0.25	0.34
50.60	55.60	5.00	409	409	0	82.29	64.11	18.19	1.91	-6.88
55.58	92.82	37.23	409	409	0	64.11	41.66	22.45	7.11	-28

The appearance of the variation of Ln r versus 1/T of the data in Table 6 was similar to the two previous samples (310, 325); therefore its graphic representation was omitted. Table 4 summarizes the values of Ea obtained for this treatment (4th row).

The list-square line fitted to the trace $98.55 < w < 93.11$ showed a slope = 10.4. However, this trace, similar to the previous case, was made of many parallel reactions with slopes near to zero. The list-square fitting to all of these data is not appropriate for such condition when numerous simultaneous reactions were taking place but one weight loss was recorded.

Sample 355. This sample was heated fast (200°C/min) from room temperature to 355°C, kept for 30 min at 355°C, then heated fast to 410°C and held there for another 30 min. The plot of variation of $\ln r$ versus $\ln w$ for this sample was different from the three previous samples (Fig 4). At the end of the first isotherm at 352°C the weight of this sample reached to 61.2% of its original mass. This was contrary to the weight of samples 310, 325, and 340 where they held 92.4%, 93.3%, and 93.1 % of their total mass at the end of their first isotherm isotherm. The sample of PLEG at 355°C had lost about 38.4% of its weight. These data are summarized in Table 7. The appearance of the variation of $\ln r$ versus $1/T$ of this sample was also similar to the previous samples (310, 325,...); therefore, the graphs were omitted and the resulted E_a values were tabulated in Table 4, 5th row.

Table 7. The initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the wlo, and $\ln k$ resulted from TGA analysis of PLEG sample 355.

Time (min)			Temperature (°C)			Weight Percent				
Initial	Final	$\Delta\tau$	Initial	Final	ΔT	Initial	Final	-DW	wlo	$\ln k$
1.65	2.10	0.45	119	217	97	100.2	99.82	0.42	217.2	-999
2.12	2.77	0.65	220	335	115	99.82	99.02	0.80	-135.3	631
2.78	3.75	0.97	336	353	17	99.02	97.13	1.90	41.3	-187
3.78	7.73	3.95	353	353	0	97.08	92.11	4.97	5.9	-26
7.75	17.10	9.35	353	352	-1	92.09	81.91	10.18	0.6	-3
17.12	47.15	30.03	352	352	0	81.90	61.63	20.27	3.5	-15
47.52	47.92	0.40	352	389	37	61.49	61.32	0.17	-793.6	-382
47.92	48.35	0.43	389	404	15	61.32	59.70	1.63	-42.2	175
48.35	48.55	0.20	404	405	2	59.70	58.61	1.09	0.5	0
48.57	92.77	44.20	406	408	2	58.52	33.33	25.19	7.1	-27

A sample of PLEG held about 30% of its mass above 550°C (Fig 1). This mass may contain inorganic fillers and other higher temperature resistant materials that were added to neoprene for processing, and some thermally resistant organics, products of internal reactions. Pure neoprene also contains about 40% chlorine by mass. Therefore, chlorine makes about 28 to 29 % mass of PLEG. If the entire weight loss at this stage is related to the loss of water, and HCl from PLEG, the remains of the reaction are chlorine free materials. Further research will be conducted to identify the content of the remains of the reaction after PLEG was held for 30 min at 355°C.

Sample 370 This sample was heated fast (200°C/min) from room temperature to 370°C, kept for 30 min at 370°C, then heated fast to 410°C and held there for another 30 min. At the end of being 30 min in 370°C, the weight of the sample was 41.5% of its original mass (Table 8). At the end of 30 min, the process of weight loss was active; in other words, if the sample was kept longer at this temperature, more weight-

loss would be observed. Perhaps one of the most economical ways to decompose the PLEG is to keep it at 370°C for longer time. The variation of $\ln r$ versus $\ln w$ for this sample was different than the previous samples (Fig 4), since, at end of isotherm more than 3/5 of PLEG materials were lost. These values are summarized in Table 8 for PLEG sample 370. At the end of isotherm at 410°C $w = 32.58\%$. Therefore, heating the sample at 370° did not produced appreciable amount of thermally resistant materials at 410°C as in case of sample PLEG 340 (see above).

Table 8. The initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the w_{lo} , and $\ln k$ resulted from TGA analysis of PLEG sample 370.

Time (min)			Temperature (°C)			Weight Percent			w_{lo}	$\ln k$
Initial	Final	Δt	Initial	Final	ΔT	Initial	Final	$-\Delta W$		
1.70	2.00	0.30	137	200	63	100.3	100.0	0.25	189.6	-874
2.02	2.30	0.28	203	261	58	100.0	99.74	0.27	-363	1673
2.32	3.73	1.42	264	370	105	99.71	94.74	4.97	2.8	-12
3.77	7.72	3.95	370	370	0	94.63	79.10	15.52	-0.2	2
7.73	17.08	9.35	370	369	-1	79.10	55.52	23.58	2.9	-11
17.10	47.13	30.03	369	369	0	55.50	41.55	13.94	6.6	-26
47.67	47.90	0.23	370	393	23	41.45	41.43	0.02	4675	17410
47.90	48.23	0.33	395	406	11	41.42	41.12	0.29	-55.3	206
48.25	49.13	0.88	406	410	4	41.11	40.31	0.80	9.1	-34
49.15	54.13	4.98	410	410	0	40.30	37.38	2.92	8.9	-33
54.15	92.73	38.58	410	410	0	37.37	32.58	4.79	16.2	-60

The appearance of the variation of $\ln r$ versus $1/T$ of this sample was also similar to the previous samples (310, 325,...); therefore its graphic representation was omitted. Table 4 summarized the values of E_a obtained from this treatment (6th row).

Sample 385 This sample was heated fast (200°C/min) from room temperature to 385°C, kept for 30 min at 385°C, then heated fast to 410°C and held there for another 30 min. At the end of 30 min at 385°C, the weight of sample was 33.0% of its original mass (Table 9). Most of sample was decomposed, and evaporated at 385°C during the 30 min period. After 30 min at 385°C, while the weight loss was active, the sample was scanned to 410°C. After being 30 min at 410°C, $w = 31\%$ of its original mass was observed. During 30 min at 410, only about 2% of weight loss was observed. Therefore, a temperature near to 385°C is a suitable and economical way to decompose the PLEG at lower temperatures.

The variation of $\ln r$ versus $\ln w$ for this sample was different than the previous samples (Fig 2); since at the end of isotherm at 385, the thermal scan began with a smooth and gentle increase on the rate of

reaction as is visible (Fig 4). These values are summarized in Table 9 for PLEG sample 385. The appearance of the variation of “Ln r” versus “1/T” of this sample was also similar to the previous samples (310, 325,...); therefore the graphic presentation of the data was omitted and the resulted Ea were tabulated in the Table 4 7th row.

Table 9. The initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the wlo, and Ln k resulted from TGA analysis of PLEG sample 385.

Time (min)			Temperature (°C)			Weight percent			slope = n	intercept
Start	End	Δt	start	end	ΔT	start	end	-ΔW		
1.57	1.98	0.42	108	202	94	100.22	99.88	0.34	355.5	-1637
2.00	3.12	1.12	206	379	174	99.88	94.54	5.33	-71.2	328
3.13	3.55	0.42	380	385	6	94.27	86.37	7.90	-1.8	11
3.13	7.23	4.10	387	387	-1	94.27	32.72	61.55	2.3	-7
7.25	8.32	1.07	387	386	0	45.72	41.06	4.67	0.6	-1
8.33	34.32	25.98	386	386	-1	40.99	32.96	8.03	16.9	-62
34.33	48.72	14.38	386	409	23	32.96	32.44	0.52	29.6	-107
48.72	92.65	43.93	409	410	1	32.44	30.71	1.74	18.4	-67

The wlo was around -2 at the end of scan to 385°C. The isotherm beginning wlo was the same as previous thermal scan (~ -2). However, the wlo increased as weight of the sample decreased, reached to zero and continued to increase. A large trace of data, 94.2 < w < 32.7, about 61% of total mass of the sample, had awlo ~ 2 (Table). Afterward, the wlo began to decrease; a trace of data with wlo ~ 0.6 was characterized at the 46 < w < 41% of weight of the sample. Later on, the wlo continued to increase, wlo ~ 17, and 30, then decreased to 18. Considering the high wlo values for the reactions at the end of isotherm is not understandable. Perhaps many reactions with order zero and one were occurred simultaneously. In cases similar to this, adjusting a list-square line to all data is not an appropriate procedure to find the wlo. For example consider the expansion of end tail at 410° in the Fig 6:

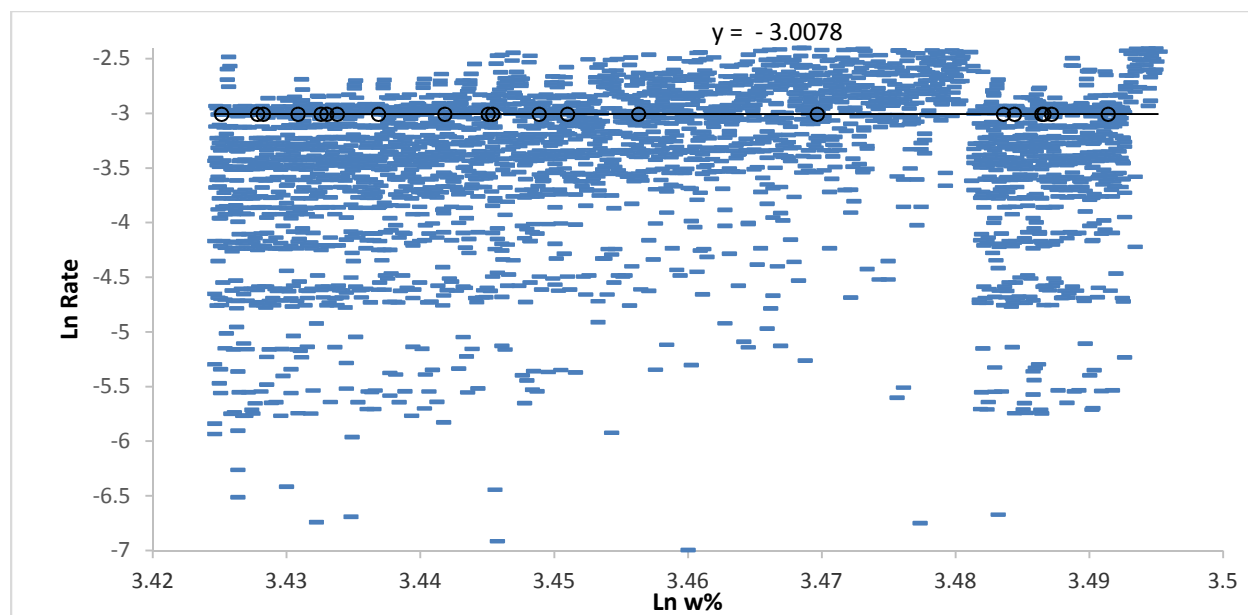


Fig 6. Expansion of a small section of Fig 4, the section related to the PLEG sample 385 under 410°C isotherm for 30 min.

By looking at Fig 6, many reactions of order zero, such as the one depicted, and others with very low $w_{lo} \sim 0$ were visible. About 48 of such hypothetical concurrent reactions are charted and tabulate in the Table 10.

Table 10. The values of w_{lo} and k for the hypothetical weight loss reactions of PLEG during the isotherm at 410°C.

	<u>slope</u>	<u>intercept</u>	<u>min</u>	<u>max</u>	<u>$\delta\omega$</u>
1	2.75	-11.54	32.29	32.51	0.21
2	-0.42	-0.74	32.37	32.48	0.12
3	0.63	-4.47	32.24	32.91	0.66
4	-0.12	-2.02	31.99	32.09	0.10
5	0.15	-2.99	32.47	32.50	0.03
6	0.08	-2.79	31.31	31.78	0.47
7	-0.19	-1.91	30.74	32.01	1.27
8	-0.08	-2.36	31.24	32.53	1.29
9	0.10	-3.03	32.08	32.88	0.79
10	-0.11	-2.34	32.02	32.12	0.10
11	-0.29	-1.75	30.74	31.19	0.45
12	0.20	-3.52	30.95	31.73	0.78
13	-0.22	-2.10	31.28	32.35	1.07
14	0.02	-2.98	31.45	32.83	1.38
15	-0.10	-2.60	30.71	31.01	0.30
16	0.08	-3.24	31.08	31.93	0.85
17	-0.05	-2.83	32.36	32.48	0.12

18	-0.14	-2.56	30.71	31.07	0.37
19	0.09	-3.40	31.22	32.03	0.81
20	0.01	-3.16	30.71	31.16	0.46
21	-0.10	-2.85	30.74	31.12	0.38
22	-0.05	-3.07	31.46	32.68	1.22
23	0.00	-3.28	30.76	31.15	0.39
24	-0.06	-3.10	30.72	30.84	0.12
25	-0.01	-3.33	30.71	31.58	0.87
26	-0.03	-3.29	31.07	32.04	0.97
27	0.00	-3.45	30.70	31.05	0.34
28	-0.27	-2.57	31.32	31.63	0.30
29	0.00	-1.93	32.13	32.89	0.76
30	0.12	-4.05	31.82	32.83	1.00
31	-0.05	-3.57	30.71	31.76	1.06
32	0.10	-4.17	30.72	31.43	0.71
33	-0.71	-1.52	31.90	32.04	0.13
34	0.13	-4.55	30.85	31.42	0.57
35	0.28	-5.15	30.92	32.73	1.81
36	-0.25	-3.44	30.72	30.75	0.03
37	0.25	-5.32	30.88	31.98	1.11
38	0.40	-5.96	30.77	32.64	1.87
39	-0.35	-3.42	30.71	30.87	0.16
40	0.17	-5.32	30.70	31.05	0.35
41	2.86	-14.80	31.04	32.01	0.98
42	0.15	-5.69	31.01	31.29	0.27
43	0.01	-5.40	31.44	32.66	1.23
44	-0.31	-4.47	30.72	30.72	0.00
45	-0.24	-4.79	31.06	31.07	0.01
46	0.11	-6.10	30.90	32.52	1.62
47	0.44	-7.29	30.71	32.60	1.89
48	-0.10	-5.59	30.71	30.76	0.05

427

428 **Sample 400** This sample was heated fast (200°C/min) from room temperature to 400°C, kept for 30 min
 429 at 400°C, then heated fast to 410°C and held there for another 30 min. At the end of being 30 min at 400°C,
 430 the weight of the sample was 32.3% of its original mass (Table 11). Compared with the previous samples
 431 after 30 min at 385° the w ~33.0% and the other at 370°C for 30 min w ~41.6%, there is not too much
 432 advantage in increasing the decomposition temperature of pyrolysis if time is not a factor. As the
 433 temperature increased the rate of the weight-loss increased as was observed in the graphs of Fig 2. The
 434 variation of Ln r versus Ln w for this sample was different than the previous samples (Fig 2), since, at end of
 435 isotherm at 400°C almost 32.3% of PLEG materials remained. These values are summarized in the Table
 436 11 for PLEG sample 400.

437

438 Table 11. The initial and final time, the time of process, the initial and final temperature, and the change in
 439 temperature, the initial and final weight of sample and the weight loss amount, the wlo, and Ln k
 440 resulted from TGA analysis of PLEG sample 400.

Time (min)			Temperature (°C)			Weight Percent				
Initial	Final	Δt	Initial	Final	ΔT	Initial	Final	$-\Delta W$	wlo	Ln k
1.58	2.08	0.50	106	217	111	100.4	99.95	0.48	194.8	-897
2.10	2.73	0.63	221	350	129	99.94	98.97	0.97	-245	1127
2.75	3.15	0.40	353	391	38	98.90	93.98	4.92	-46.0	122
2.77	3.17	0.40	357	392	35	98.81	93.67	5.15	-23.3	205
3.02	3.18	0.17	386	392	6	96.36	93.35	3.01	-6.9	34
3.20	3.37	0.17	392	396	3	93.03	89.72	3.31	0.1	3
3.38	4.17	0.78	396	401	5	89.40	75.77	13.63	1.3	-3
4.18	5.67	1.48	401	401	0	75.51	57.65	17.86	2.3	-7
5.70	47.78	42.08	401	400	-1	57.51	32.32	25.20	9.3	-35
47.92	48.47	0.55	405	410	4.66	32.32	32.24	0.08	66.06	-232
										-
48.48	54.30	5.82	410	410	0.42	32.05	31.64	0.41	17.24	62.0
54.32	92.80	38.48	410	411	0.13	31.64	30.19	1.45	51.13	-179

441

442 The appearance of the variation of “Ln r” versus “1/T” of this sample was also similar to the previous
 443 samples (310, 325,...); therefore the graphic presentation of it was omitted. Table 4 summarized the values
 444 of Ea obtained from this treatment (8th row).

445

446 **Sample 410** This sample was heated fast (200°C/min) from room temperature to 410°C, and held there
 447 for 30 min. After 30 min at 410°C, the weight of sample was 30.2% of its original mass (Table 12). This is
 448 the maximum amount of weight loss that could be reached at temperatures below 550°C. Also, this is the
 449 temperature at which the highest decomposition rate of PLEG was reached in a dynamic scanning from
 450 room temperature to 850°C [1]. As the temperature increased the wlr increased as was observed in the
 451 graphs of Fig 4.

452 Based on the variation of Ln r versus Ln w for this sample, the order of reaction during the thermal scan was
 453 similar to the previous one, large positive values, reaching to zero, followed by large negative values that
 454 increased gradually reached to zero, and continued afterward in positive values. The highest rate of weight
 455 loss occurred when w ~ 83.0%. Two traces of the isotherm at 410 °C were selected to analyze the order of
 456 reaction (Fig 4 & Table 12). The first, at 88% < w < 61% of its original mass where the weight loss order
 457 obtained was 1.0. Afterward, the order began to increase, the trace 61% < w < 44 had the average order of ~
 458 4. From this point the order increased and the last trace w < 44% had the average wlo of 25 and
 459 higher. These values are summarized in Table 12 for PLEG sample 410. Similar to previous cases,
 460 adjusting a list-square line to the data that belong to a wide range of reactions is not appropriate for
 461 calculation the order of reactions.

462

Table 12. The initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the wlo, and Ln k resulted from TGA analysis of PLEG sample 410.

Time (min)			Temperature (°C)			Weight Percent			wlo	Ln k
Initial	Final	Δt	Initial	Final	ΔT	Initial	Final	$-\Delta W$		
1.58	2.02	0.43	106	201	94.6	100.9	100.2	0.66	147.8	-681
2.02	2.93	0.92	204	387	182.9	100.2	96.68	3.52	-106	487.6
2.40	3.15	0.75	282	400	117.6	99.79	88.87	10.92	-8.29	41.16
3.17	3.25	0.08	400	403	2.42	88.06	83.89	4.17	-0.97	8.21
3.27	3.32	0.05	403	404	1.12	83.04	80.48	2.56	0.07	3.63
3.17	3.47	0.30	405	407	2.25	79.63	73.14	6.50	1.19	-1.28
3.18	3.48	0.30	405	407	2.16	85.58	59.83	25.75	2.01	-4.78
3.78	4.83	1.05	410	412	1.89	60.86	43.90	16.96	4.02	-13.0
4.85	19.83	14.98	412	410	-1.40	43.78	31.48	12.30	12.37	-44.4
19.85	33.75	13.90	410	410	0.12	31.48	30.23	1.24	24.54	-86.5

466

The appearance of the variation of Ln r versus 1/T of this sample was also similar to the previous samples (310, 325,...); therefore, the graphic presentation of it was omitted. Table 4 summarized the values of Ea obtained from this treatment (9th row).

470

Sample 425 This sample was heated fast (200°C/min) from room temperature to 425°C, then it was held there for 30 min. After it was heated for 30 min at 425°C, it lost all the volatiles (w ~ 28.6% Table 13). This is the maximum amount of weight loss that could be reached at temperatures below 550°C. Keeping in mind that this temperature is about 15° above the temperature at which the highest decomposition rate of PLEG was reached in a dynamic scanning from room temperature to 850°C (Fig 2).

The only factor that can be judged well is the wlr since the TGA does not provide information about the nature of products nor the reactants. The highest value of wlr was obtained when 78.0% mass of PLEG remained, where the wlo was zero. Based on the variation of Ln r versus Ln w for this sample, the wlo during the thermal scan was similar to the previous ones, large negative values at very beginning, reaching to zero, following with positive values. In continuation, the positive values converging to zero, and afterward large negative values observed. The trace continues with converging negative values to zero then continuing to positive wlo values (Table 13). Two traces of the isotherm 425 °C were selected to analyze to find the wlo. The first, when the mass of the sample was 91-80% of its original mass where wlo was ~ -3. The next trace was 78% <w <36% where the wlo was +3. Also the traces in-between these two traces were analyzed and tabulated in Table 13.

486

Table 13. The initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the wlo, and Ln k resulted from TGA analysis of PLEG sample 425.

Time (min)			Temperature (°C)			Weight Percent			wlo	Ln k
Initial	Final	Δt	Initial	Final	ΔT	Initial	Final	$-\Delta W$		
2.22	2.28	0.07	249	262	14	100.3	99.88	0.40	-412	756
2.30	2.47	0.17	266	300	34	99.76	99.29	0.46	313	1441
2.48	2.90	0.42	303	387	83	99.27	97.53	1.74	-113	521
2.92	3.07	0.15	390	410	20	97.30	92.23	5.07	25.5	119
3.08	3.20	0.12	411	417	6	91.22	81.35	9.87	-2.9	17
3.22	3.27	0.05	418	419	2	79.77	74.57	5.20	-0.1	5
3.28	3.32	0.03	420	420	1	72.89	69.68	3.21	1.2	0
3.33	3.47	0.13	421	423	2	68.15	57.74	10.41	1.9	-4
3.48	3.65	0.17	423	425	2	56.68	48.56	8.12	3.4	-10
3.67	4.23	0.57	425	427	2	47.96	35.80	12.16	4.0	-12
4.22	5.53	1.32	427	427	0	35.98	31.77	4.21	22.9	-79
5.57	13.75	8.18	427	426	-1	31.74	29.15	2.59	24.0	-83
13.75	33.75	20.00	426	426	0	29.15	28.57	0.58	48.2	-163

The appearance of the variation of “Ln r” versus “1/T” of this sample was also similar to the previous samples (310, 325,...); therefore, the graphic presentation of it was omitted. Table 3 summarized the values of Ea obtained from this treatment (10th row).

Sample 440 This sample was heated fast (200°C/min) from room temperature to 440°C, then held there for 30 min. The highest weight loss occurred during the thermal scan to 440°C, and before reaching the isotherm at 440°C (w ~32%). During 6.8 min of thermal scan to 440°C, the sample lost most of its weight w~ 31.5% (Table 14) where during the 30 min time period in the isotherm at 440°C, a small amount of wl (31.6% < w <29.5% , Table 14) was reached. This was within expectation since this temperature is about 30° above the temperature at which the highest decomposition rate of PLEG was obtained in a dynamic scanning from room temperature to 850°C (Fig 1). As the temperature increased the rate of the weight-loss increased as was observed in the graphs of Fig 4. The highest wlr ~ 126 min⁻¹ was reached at w ~ 73.9% and t = 427.4°C, where the wlo became zero.

Based on the variation of Ln r versus Ln w for this sample, the order of reaction during the thermal scan was similar to the previous one, large negative values, reaching to zero, followed by large positive values reaching to zero, followed with large negative values that increased fast passing zero at the max wlr and continued to high positive values. Seven traces of thermal scan and three traces of the isotherm 440 °C were selected to analyze (Table 14). At the 80% < w < 61% the wlr was the highest and the wlo was near

to zero ($n = 0.4$). As w_l values decreased the order of reaction increased. At the next trace, 44-60 %, order of $n = 3.6$ was calculated. All relevant data related to this experiment are tabulated in Table 14.

Table 14 The initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the w_l , and $\ln k$ resulted from TGA analysis of PLEG sample 440.

Time (min)			Temperature ($^{\circ}\text{C}$)			Weight percent			slope =	
Start	End	Δt	start	end	ΔT	start	end	$-\Delta W$	n	intercept
1.58	1.72	0.13	109	143	34	100.31	100.16	0.15	-64.8	299
1.73	2.03	0.30	147	208	61	100.14	99.90	0.24	335.6	-1546
2.05	2.85	0.80	211	374	163	99.90	98.08	1.82	-155.8	717
2.87	3.17	0.30	378	424	46	97.93	82.23	15.70	-13.3	64
3.18	3.33	0.15	425	431	6	80.23	61.82	18.42	0.4	3
1.68	3.60	1.92	431	436	5	60.04	44.01	16.03	3.6	-10
3.62	40.17	36.55	437	441	4	43.48	31.57	11.92	13.5	-47
7.73	14.00	6.27	441	440	-1	31.55	30.27	1.28	62.0	-214
14.08	24.33	10.25	440	439	-2	30.27	29.90	0.37	55.2	-191
24.33	47.33	23.00	440	440	0	29.90	29.45	0.45	118.8	-407
47.35	50.25	2.90	440	853	413	29.45	16.75	12.70	658.5	-2231

The appearance of the variation of " $\ln r$ " versus " $1/T$ " of this sample was also similar to the previous samples (310, 325,...); therefore, the graphic presentation of it was omitted. Table 3 summarized the values of E_a obtained from this treatment (11th row).

Sample 455 This sample was heated fast ($200^{\circ}\text{C}/\text{min}$) from room temperature to 459°C , then it was hold there for one min. After one min in 459°C $w \sim 32.5\%$ (Table 15) was reached which is equivalent in weight loss of keeping the sample for 30 min in 400°C . The pyrolysis temperature was about 45°C above the temperature at which the highest decomposition rate of PLEG was reached in a dynamic scanning from room temperature to 850°C (Fig 1). The TGA alone does not provide information about the nature of products neither the reactant. The only factor that can be judge well is the rate of weight loss. The highest rate of weight loss was reached (209 min^{-1}) when 70.7% mass of PLEG was remained at $t = 439^{\circ}\text{C}$, where the w_l became zero. Based on the variation of $\ln r$ versus $\ln w$ for this sample, the w_l of thermal scan was similar to the previous one (Fig 3), a large negative value, flowed with a high positive value, immediately followed with negative values. The negative slope gradually increased to zero, and highest positive values (Table 15). At $88\% < w < 47\%$ the w_l was near to zero ($n = 0.2$) where there was the highest w_l . As w_l values decreased the order of reaction increased. At the next trace, 35-43 %, $w_l \sim 8$ was calculated. All relevant data related to this experiment are tabulated in the Table 15.

Table 15. The initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the wlo, and Ln k resulted from TGA analysis of PLEG sample 455.

Time (min)			Temperature (°C)			Weight percent			slope = n	intercept
Start	End	Δt	start	end	ΔT	Start	end	$-\Delta W$		
1.55	1.68	0.13	106	142	36	100.10	99.96	0.14	-60.8	280
1.70	1.97	0.27	145	200	54	99.94	99.76	0.18	397.4	-1830
1.98	2.92	0.93	203	394	190	99.75	96.52	3.23	-140.4	646
2.93	3.05	0.12	397	420	23	96.10	97.20	-1.10	-15.1	72
3.07	3.30	0.23	423	447	23	88.43	47.03	41.40	0.2	4
3.32	3.62	0.30	448	453	5	43.83	35.25	8.58	7.8	-25
3.58	4.47	0.88	454	459	5	35.04	32.93	2.10	52.6	-184
4.48	5.23	0.75	459	459	0	32.92	32.54	0.38	42.8	-150

The appearance of the variation of “Ln Rate” versus “1/T” of this sample was also similar to the previous samples (310, 325,...); therefore, the graphic presentation of it was omitted. Table 3 summarized the values of Ea obtained from this treatment (12th row).

Analysis of the weight losses of the first thermal scans. Fig 7 shows the variation of the temperature versus weight loss of the 11 samples of PLEG at the end of the first thermal scan. The shape of plot (Fig 7) is similar to Fig 3 where a sample of PLEG was scanned from room temperature to 850°C, which again confirmed the accuracy of calculated values. The two graphs are similar in the initial weight loss temperatures and the end of weight loss temperatures under 500°C.

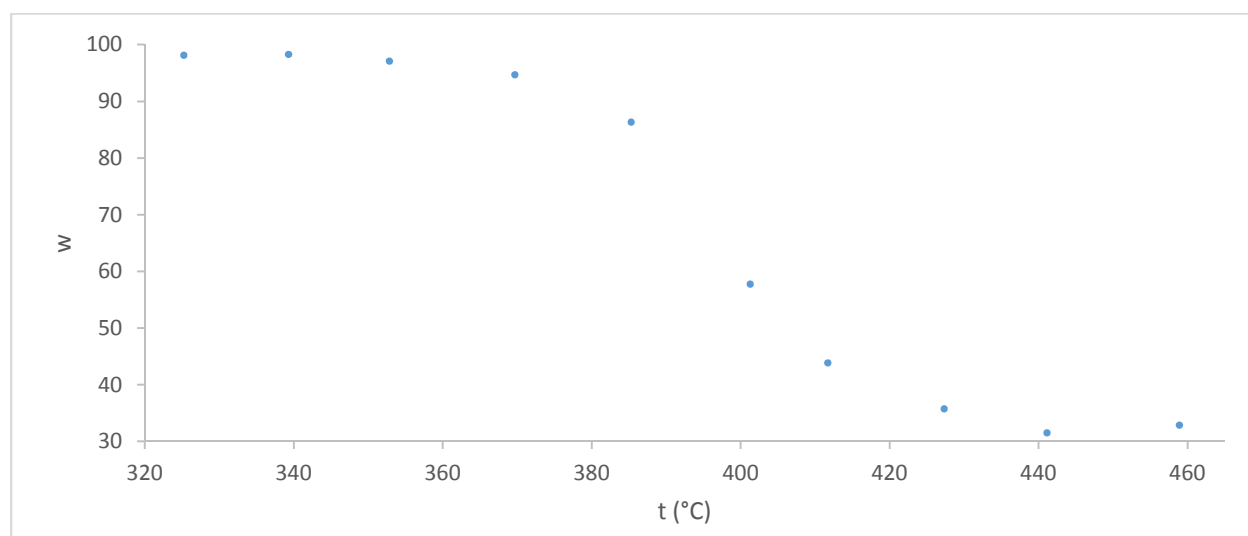


Fig 7. Variation of the weight loss at the end of the first thermal scans versus temperature for eleven samples of PLEG.

Variation of w versus w and t . Fig 8a shows the variation of calculated w versus the w , mass of un-reacted sample. The larger values of w were observed at the initial time, where the sample had preserved 90% or higher amounts of its mass. At $w < 90\%$ seems the w had lower values such as 0, 1, 2, ... which are within expectations for a liquid phase thermolysis process.

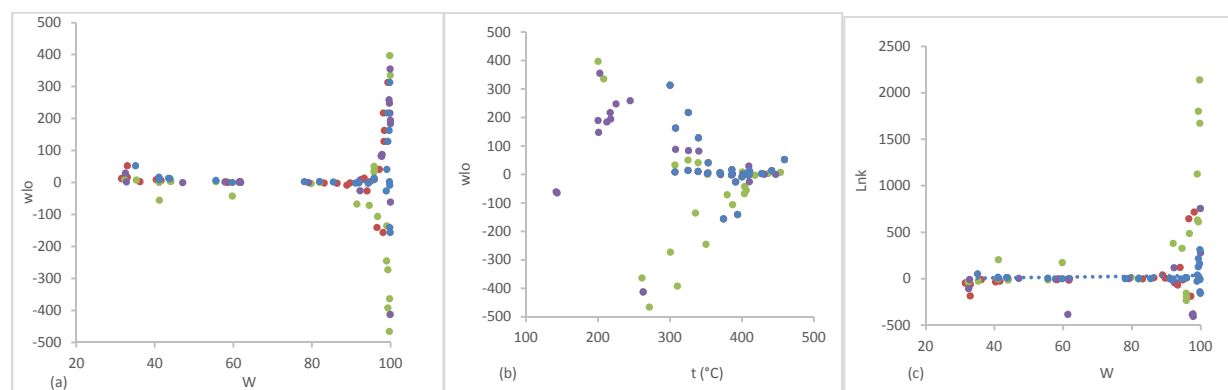


Fig8. Variation of order of w versus (a) w , (b) temperature, and (c) variation of $\ln k$ versus w , for eleven samples of PLEG.

The variation of w by temperature was well scattered. It is hard to establish a clear tendency or a mathematical relationship between w and temperature (Fig 8b). However, at a higher temperature, a lower w was possible.

The variation of the values of k by w (Fig 8c) was very similar to the variation of w with w ; in the sense that extreme high values of k were observed at the beginning of the reaction where more than 90% of initial mass remained in the TGA pan.

Reaction Rate Constant and Temperature. Fig 9 shows the application of the logarithmic form of Arrhenius relationship, Eq (5) to the values of $\ln k$ versus $1/T$ (K) using all values of k and t from the above Tables. The data are scattered; however, a list-square adjusted line to these data helped to calculate E_a of weight loss from the slope of the line, $-E_a/R$ (Fig 9).

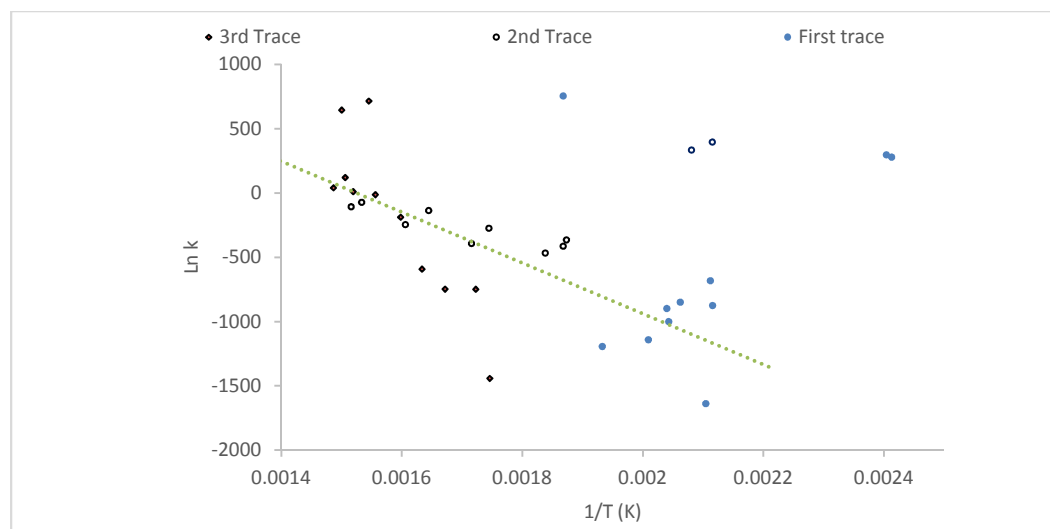


Fig 9 variation of all “Ln k” versus “1/T” (K⁻¹).

Considering that all of these k values belong to the same thermolysis process of PLEG, the straight line adjusted to these data has the negative slope which resulted in $E_a = 1.57$ MR which could be considered as the average E_a for the thermolysis process.

4. CONCLUSION AND REMARKS

The variation of Ln r versus Ln w of the first thermal scans showed three distinguished tendencies (Fig 2), which was analyzed accordingly. The weight losses of the first and second traces were negligible; the third trace bear the highest weight-loss of the process of the thermal scan. This by no means indicates that there were no physical and chemical changes in the structure of the materials under study at higher temperatures. In fact, prior to any visible weight loss in TGA many chemical and physical changes had already occurred to the structure of materials at high temperatures. These changes are the precursors to posterior wlr detected in TGA.

The variation of Ln r versus Ln w of the thermal scans had a concave downward curve form; they were converged to a plateau before reaching to the final temperature; thus, the intermediate trace was always a curve. Adjusting a straight-line to it produced inaccurate and arbitrary results which are reflected in the scatterings of the data (Fig 9).

It is universally accepted that the detailed description of the overall degradation of materials at high temperatures, particularly PLEG which is composed of a complex mixture of minerals, polymers, organic plasticizers, and inorganic fillers, is quite a complex process involving a large number of chemical reactions and intermediate species at high temperatures. The TGA alone is not able to provide a complete set of information about the nature of volatiles at a given temperature. Therefore, without chemical identification of the thermolysis products it is hard to propose a mechanism for degradation. However, from the information obtained from gas chromatography mass spectrometry analysis of the thermolysis products of

LEGs [Error! Bookmark not defined.] and the results published by other researchers who have developed kinetic models with an in-depth discussion for the pure polymers [e.g., 11,5-7], we may assume a type of radical degradation mechanism. Radical mechanism has three general steps, initiation, propagation and termination. Let's adopt these steps for neoprene degradation:

1. Initiation reactions of neoprene with n number of polymeric segments to be the formation of the first pair of radicals by thermolysis:

$$[-CH_2-CCl=CH-CH_2-]_n \rightarrow [-CH_2-CCl=CH-CH_2-]_{n-1}-CH_2-C\cdot=CH-CH_2\cdot + Cl\cdot$$

Because of the relative lower amount of bond energy of C-Cl (331 kJ/mol) with respect to C-C (346 kJ/mol) and C=C (602 kJ/mol), and C-H bond (413 kJ/mol), the first radicals set will be Cl radical and a neoprenyl radical. The unzipping of neoprene to the monomer by thermolysis was not observed [19]; which confirms this assumption.
2. Propagation reactions consisted but not limited to:
 - 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 [3].
 - b. Chain transfer of radicals
 - c. Radicalization of new chains with no chlorine
 - d. Scission of radicals to form unsaturated smaller molecules such as ethylene, but-1,3-diene, benzene and cyclooctatetraene which were observed in the products of pyrolysis [19].
 - 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

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 compared with polyethylene chains, similar to PS decomposition [Error! Bookmark not defined.]; because of the allylic resonance of the resulting radicals. The lower activation energy of PLEG similar to PS is due to the preferential formation of the long lived resonantly stabilized radicals.

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