Thermogravimetric and Kinetics of Thermal Degradation of Powdered Laboratory Examination Gloves: 1. Analysis of Thermal Scan Traces from 310-455℃

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Authors' contributions

This work was carried out in collaboration between all authors. Author NH designed and set-up the experiments, selected the materials, performed the experiment, operated the TGA instrument and, analyzed the results, wrote the first draft and finalized the manuscript. Author RM provided kinetics and thermodynamics expertise; participate on the revision of the manuscript. Authors SS, MM, and SC participated in performing the experiments, collecting the data, and analyzing the results. Author LW had the original idea and supported the work in all steps. All authors read and approved the final manuscript.

Original Research Article

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ABSTRACT

The aim of this study was to develop an energy efficient method to decompose powdered laboratory safety examination gloves (PLEG). This paper reports on the results of thermogravimetric analysis (TGA) of PLEG without a catalyst. The study was conducted in the Department of Biological and Physical Sciences at South Carolina State University (SCSU), Orangeburg, SC, USA, during the spring of 2014. Twelve samples of PLEG were studied under three types of operating conditions. First a sample was scanned from 50°C to 800°C with a heating rate of 10°C/min while it was purged with 10 mL/min argon. The results of this study determined the thermal stability of PLEG and the temperature of highest weight loss rate (~410°C). The second approach used two sequential dynamic thermal scans with a linear and fast (200°C/min) increase of the temperature over time, and two sequential isothermal steps for 30 minutes; one below 410°C and the other at 410°C. The third approach used a dynamic thermal scan and a sequential isothermal step for 30 minutes at a temperature over 410°C. 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 the activation energy of weight loss (Ea) were estimated. The experimental results confirmed that Ea of weight loss of the PLEG samples depended on the temperature of operation. At temperatures below 430°, the amount of Ea for the weight loss of sample were higher than those above 430°C temperatures. Also, internal reactions of the sample of PLEG at 340°C resulted on thermally stable materials, which slowed down the thermolysis rate of the sample at higher temperatures.

ABBREVIATIONS

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 (ethylene terephthalate); 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

The decomposition of polymeric materials has been of interest to scientists 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 [eg,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 [9-12]. However, some other polymeric materials decomposed to smaller stable toxic molecules upon heating. For example, poly (vinyl chloride) (PVC), upon heating, first decomposed to hydrogen chloride and unsaturated polymers which later decomposed to other chemicals [13-15]. Pyrolysis of neoprene also is similar to PVC producing HCl first [16].

The decomposition of polymeric materials also is relevant and of interest to industries since plastic is used in many of today's commodities [17,18]. The pyrolysis of laboratory safety examination gloves (LEG) has attracted the attention of engineers for designing pilot plants [19]. The wide use of LEGs has resulted in accumulation of untraditional wastes not native to the mother earth life cycle [20]. The disposal of latex gloves presents several problems as they are hazardous biologically, non-biodegradable, and generate HCl and chlorinated organic compounds upon incineration. Therefore, the World Health Organization (WHO) is opposes land filling or incineration of these wastes. A new technology that is both environmentally friendly and biologically safe would be required to process these wastes. There is not sufficient data concerning the characteristics and the kind of products produced [19]; therefore, further studies will help to increase understanding of the process. A study on kinetic properties of pyrolysis of selected medical products such as absorbent cotton, medical respirators, bamboo sticks [21,22] cotton gauges, packaging boxes, capsule plates and transfusion tubes were conducted by a number of researchers [eg 14].

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 does 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 were 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 [24-26]. These kinetic models can be useful in the study and analysis of the role of mixing in the thermal degradation of polymer blends. Considerable attention was given to the thermal degradation of plastic blends and their mutual interactions [eg 27-29]. These results do not completely agree with each other and different effects were observed.

The LEGs are made of diverse polymers including latex, nitrile rubber, vinyl, and 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 ($CH_2=CCl-CH=CH_2$) [30]. 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 [31].

Wastes from modern materials are accumulated without effective decomposition and recycling routes in the landfills. The increase of petroleum and petrochemical prices has opened the way for industries to invest into the recycling of plastic wastes to petrochemicals [32-34]. Literature abounds on the recycling of these none-traditional wastes to petrochemicals [35-37] and many industries are sustained and developed based on the decomposition of natural and synthetic polymers [38]. 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 [39]. 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 [40].

Based on our previous results [41,42] 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 [43]. The aim of this paper was to investigate the effect of temperature on the kinetics of thermolysis of plastic wastes, particularly latex gloves, the ones that are made of chloroprene as rubber ingredient.

2. MATERIALS AND METHODS

The material used was powdered examination gloves (PLEG) produced by Acme United Corporation (Fairfield CT, USA) and purchased from Office Form and Supply, INC (Charlotte, NC, USA). The gloves were cut into small pieces (3 mm x 3 mm) in order to fit into the TGA's pan.

2.1 The Thermogravimetric Analyzer

A Perkin-Elmer (USA) thermogravimetric analyzer (TGA-7) was used to perform experiments both under dynamic and isothermal conditions. The TGA-7 was controlled by a Dell (USA) PC running Pyris software version 3.8 for Windows.
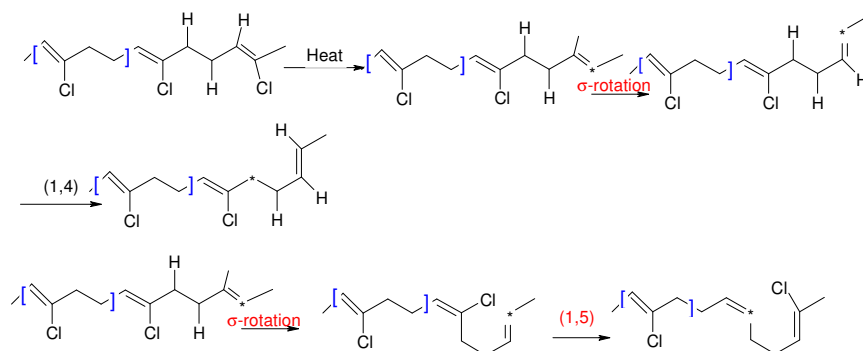
2.2 Experimental Procedure

The experimental tests were performed in a TGA-7, both under dynamic and isothermal conditions. The atmosphere was fluxed by argon with a flow rate of 10 mL min^{-1}. The heating rate in all dynamic experiments was kept at the maximum capacity of the TGA instrument, 200°C min-1, 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 the temperature was maintained for 30 min. Successively, the temperature was rapidly increased to 850°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 8 mg, however, in calculations, the weight percentage of the samples was used. 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.
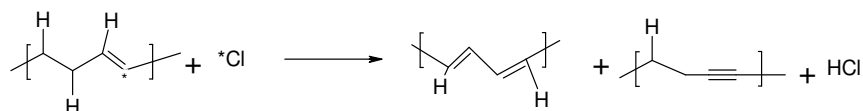
3. RESULTS AND DISCUSSION

The detailed description of the overall degradation of the PLEG 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, from the information obtained from gas chromatography mass spectrometry (GC-MS) analysis of the thermolysis products of a random mixture of PLEGs and LEGs [42], and the results published by other researchers who have developed kinetics models with an in-depth discussion for the pure polymers

[eg,24-26], we may assume a type of radical degradation mechanism. Radical mechanism has three general steps: initiation, propagation, and termination. Adopting these steps for neoprene polymeric materials, degradation process was as follows:
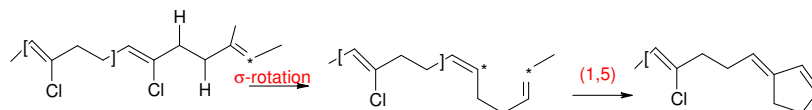
1. Initiation reactions – neoprene (with n number of polymeric segments) forms the first pair of radicals by thermolysis:
    $[-CH_2-CCl=CHCH_2-]_n \rightarrow [-CH_2-CCl=CHCH_2-]_{(n-1)}-CH_2-C.=CHCH_2- +Cl.$
    Because of the relative lower amount of bond energy of C-Cl (331 kJ/mol) with respect 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 neoprene radical. The unzipping of neoprene to the monomer by thermolysis was not observed [42]; which confirmed this assumption.
2. Propagation reactions of intermediate radicals - The propagation steps consisted of:
    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 predominate products of thermolysis, confirmed this assumption [42].
    b. Chain transfer of radicals
    c. Radicalization of new chains with no chlorine
    d. Scission of radicals to forms unsaturated small molecules. This assumption was confirmed by observation of products such as buta-1,3-di-ene, benzene and cyclooctatetraene in the pyrolysis process [42].
    e. New polymer radical isomerization via (1,4) and (1,5) H-transfer:

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

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

3.1 Thermogravimetric Analysis

Twelve samples were analyzed; one sample was scanned from 50 – 800 °C, seven samples had two quick thermal scans and two isotherms, one below 400 °C and the second at 410 °C, and five samples only had one thermal scan and one isotherm above 410 °C. The goal was to find the most adequate temperature of pyrolysis for PLEG.

3.1.1 Scan from 50 to 800 °C

Fig. 1 shows the results of thermogravimetric studies of a sample of PLEG scanned from 50º to 800 °C. The thermogram showed a two-step weight loss of PLEG. The first weight loss step of PLEG began around 350 °C, and reached the highest rate (13.1 min-1) at 410 °C. The first step of decomposition reactions was completed at a temperature below 500 °C, with 30% weight. The ashes of PLEG at 500 °C contained dark dots of materials immersed in an off-white solid. This visual inspection indicated that some stable carbon-compounds remained in the TGA pan. The second step of decomposition began around 650 °C Fig. 1 attaining the highest rate (0.15 min-1) at ~ 655 °C. The ashes at 800° (w = 16.5%) were white, soluble in hot water, and the solution was strongly basic, pH > 10, tested by pH paper.
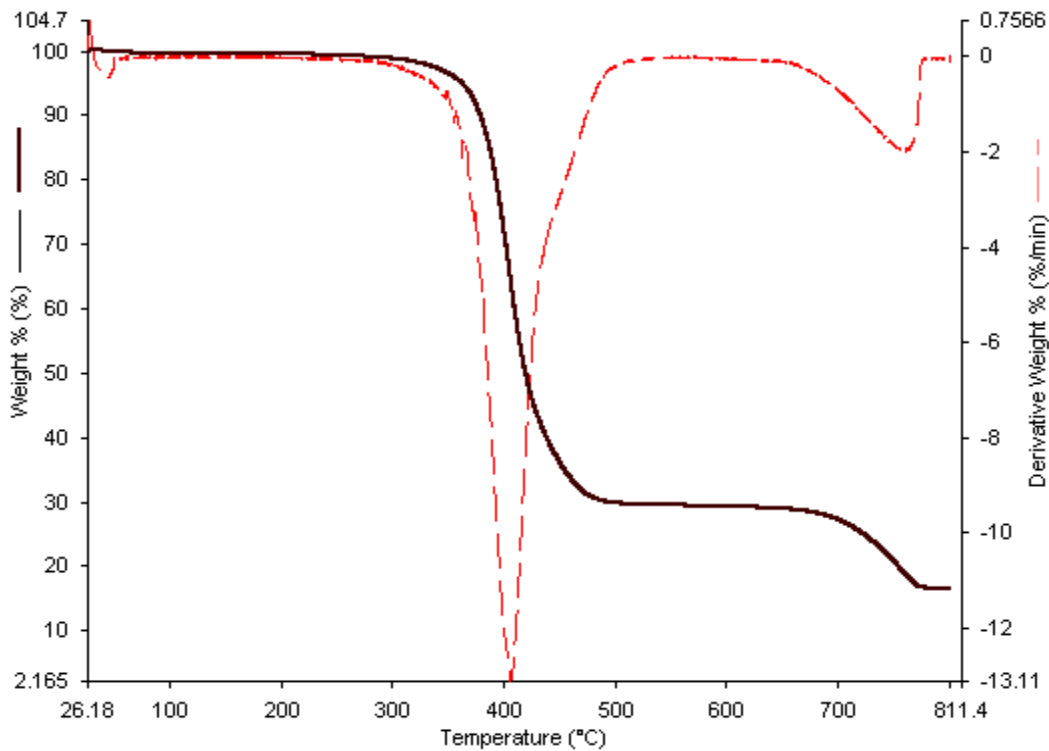

Fig. 1. Thermogram of a sample of PLEG from 50 °C of 800 °C under 10 mL/min argon with heating rate of 10 °C/min

3.1.2 Scans and Isotherms

Fig. 2a shows the thermograms of eleven samples of PLEG. Seven sets of two-step thermal scans and isothermal experiments were performed in order to analyze the specific conditions of the pyrolysis of PLEG more closely and to investigate the best conditions for pyrolysis of the PLEG at lower temperatures. These experiments were carried out with a theoretical interest in the PLEGs thermolysis at the molecular level and their impact on the reaction mechanisms. The samples were 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 maintained at this temperature for another 30 min, where up to 70% of the sample vaporized.

The sample that was kept for 30 min at 340°C gained higher thermal stabilities than any other samples. This was due to the chemical changes in the structure of the material during the 30 min at 340°C; such a change in thermal properties of PLEG was not observed for the other samples. The weight loss of this particular sample at 410°C was slower than other sample. The remains of this particular sample at 475°C was about 40% of its original weight, while for the other samples, at the same temperature, the remains were nearly 30% of the original mass. Heating the samples of PLEG at the other isotherms also caused some stability due to the secondary products of pyrolysis (Figs. 2a, b and c).

3.2 Kinetics of Pyrolysis of PLEG

Fig. 1 shows a thermogram of thermolysis of PLEG where the mass of PLEG decreased by time and temperature. The thermolysis process can be described by a typical reaction such as reaction (1) where W is the non-vaporized mass percent of the materials in the TGA reaction pan:

$$W \rightarrow Products \tag{1}$$

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);

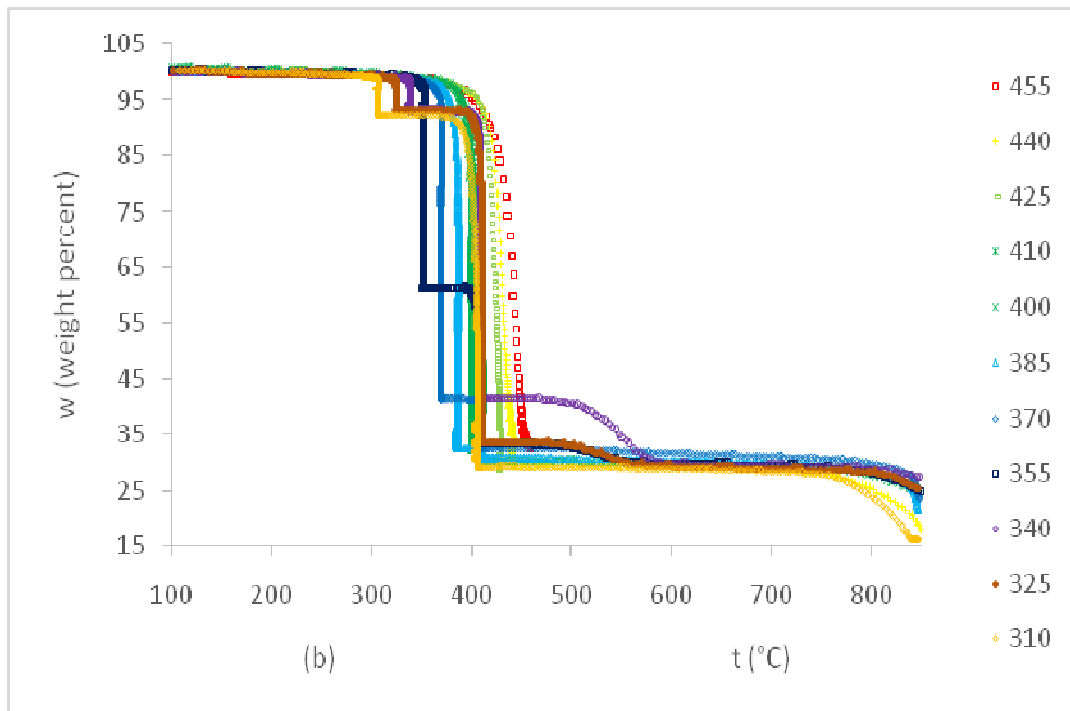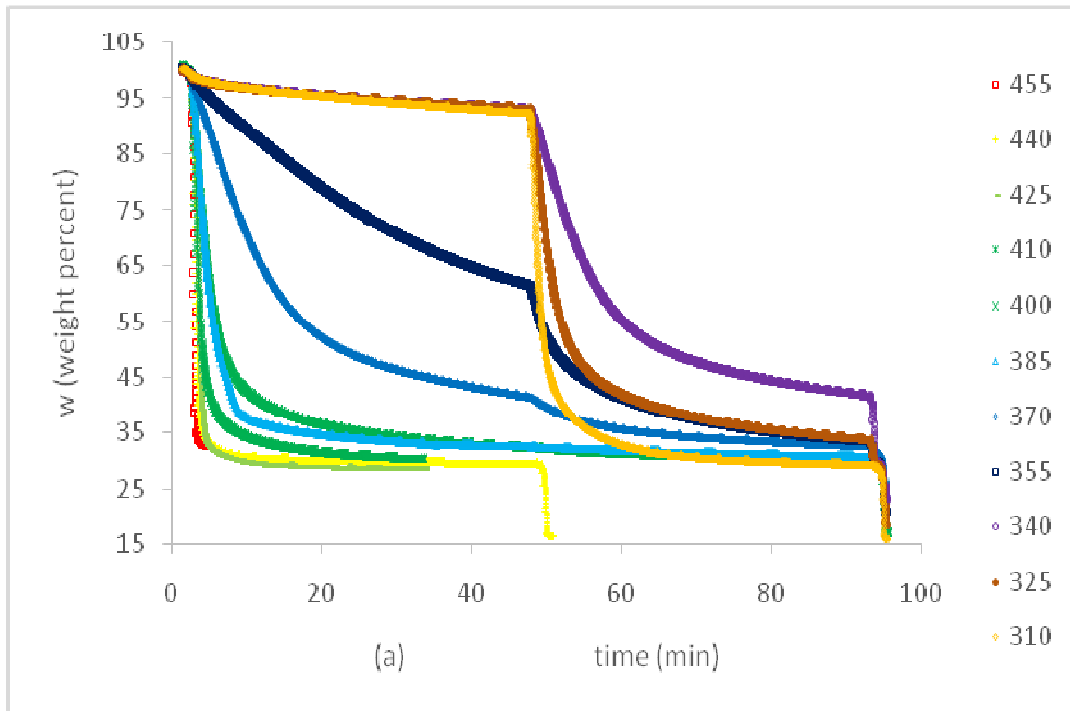$$Rate = -\frac{dw}{dt} = kw^n \tag{2}$$

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 Ea, the absolute temperature of the reaction T, and the universal gas constant R = 8.314 J mol-1 K-1as shown by Eq (3):

$$k = ze^{-\frac{E_a}{RT}} \tag{3}$$

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

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

Fig. 3 shows the variation of the initial rate of weight loss of eleven samples of PLEG over their initial time period (first 10 min) and related temperatures.
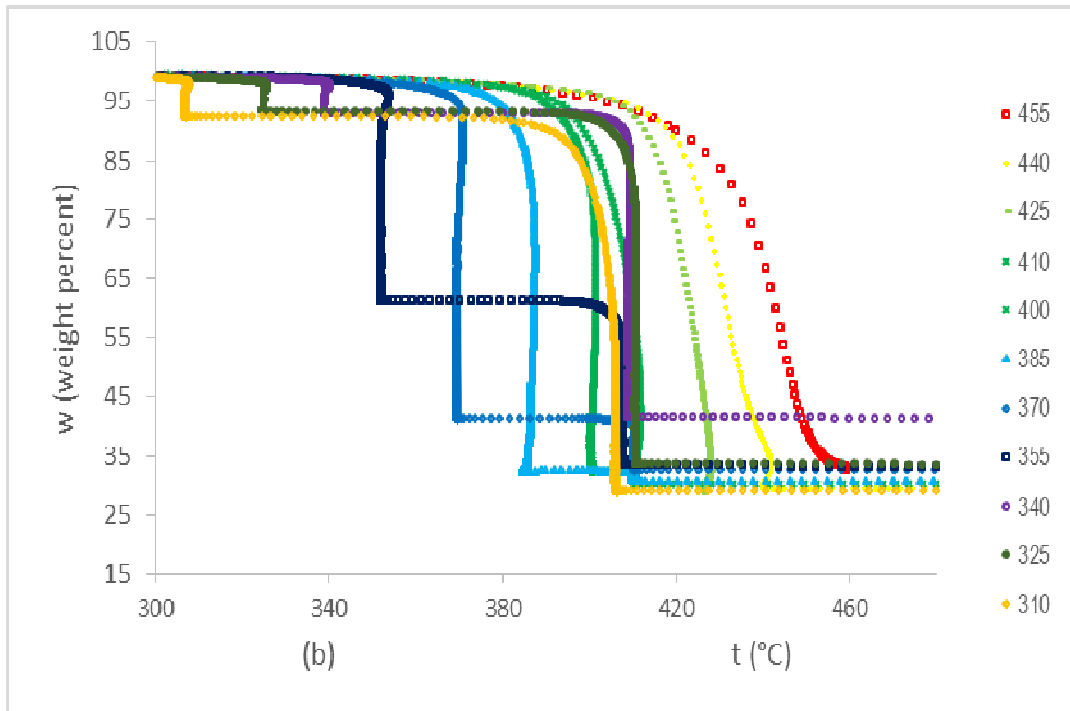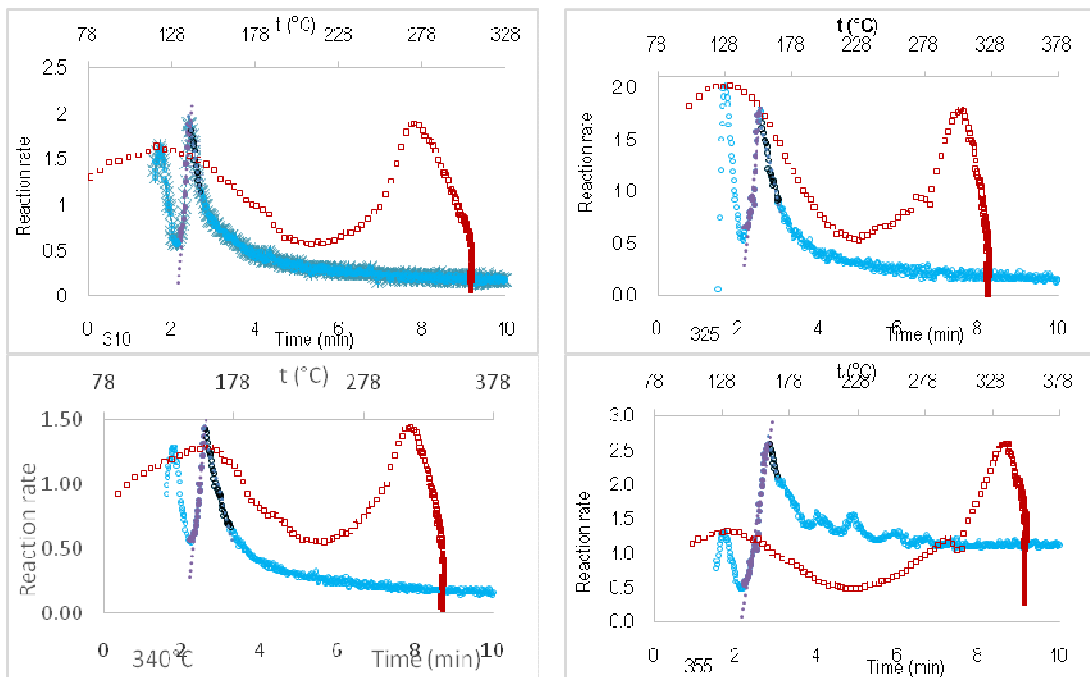
Fig. 2. Thermogravimetric analysis of PLEG: (a) weight-loss versus time for 11 samples of PLEG; (b) weight loss versus temperature for 11 samples of PLEG, and (c) expansion of (b) 300-480°C
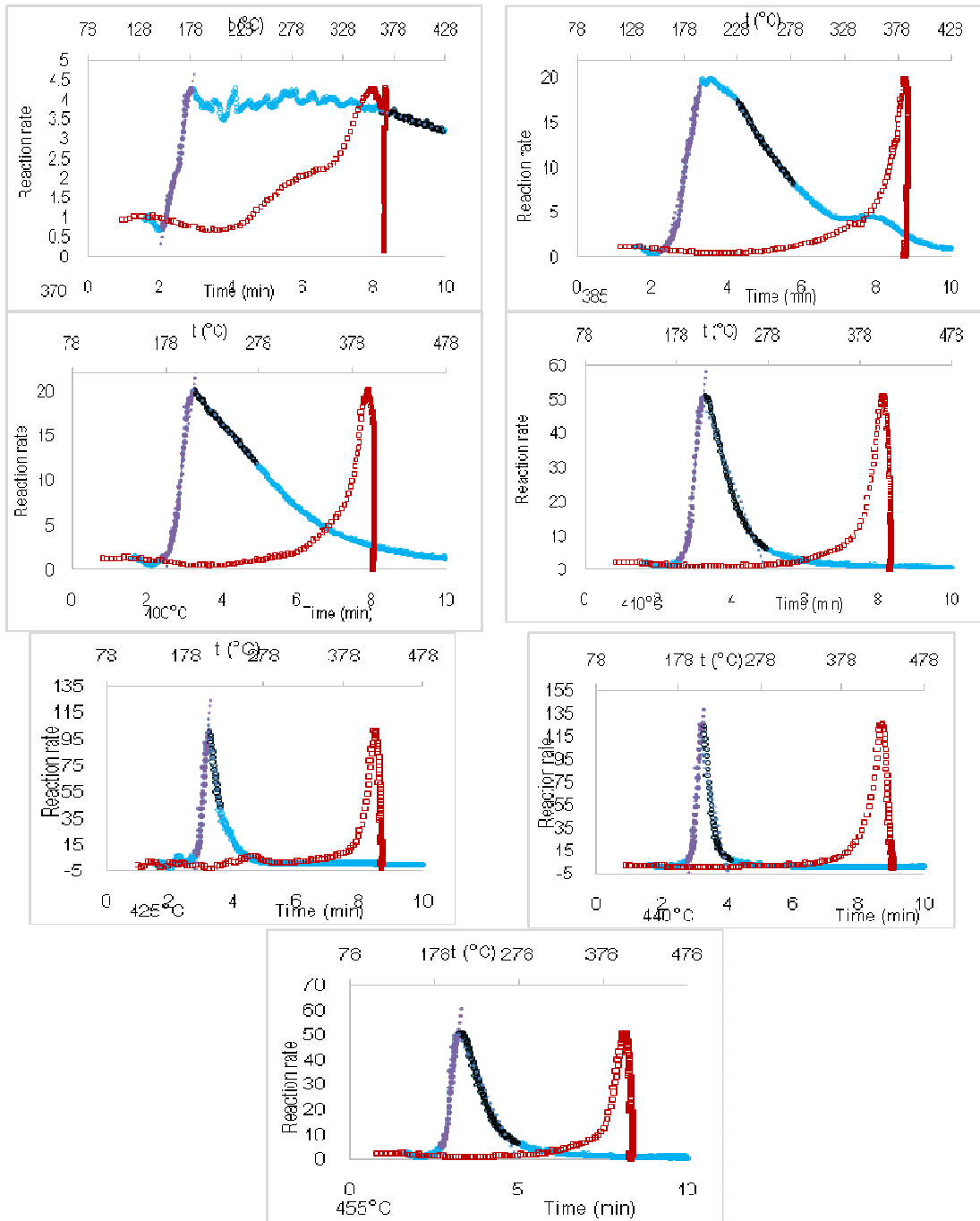
Fig. 3. Variation of the initial rate of weight loss for eleven samples of PLEG at eleven thermal scans, the red color related to rate versus temperature (upper horizontal ax.) The blue color represent the rate of weight loss versus time, other colors represent the traces that were used to evaluate the values of acceleration and deceleration process

From the graphs of Fig. 3, 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 due to isothermal process were estimated. These data were tabulated in Table 1.

3.2.1 Variation of acceleration of weight loss by temperature

TGA temperature and time are inter-related as T (K or °C) = αt(min) +ß, where α and ß and constants; α is the heating rate, and ß is the initial temperature either in K or °C. 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 increased the weight loss accelerated, and A also increased (the data in 4th column of Table 1). The best line that describes the variation of A values versus temperature was: A = 9.08E-4EXP(0.0289)t (Fig. 4). It had an exponential form similar to the Arrhenius relationship for the rate constant of a reaction, which was within expectations [eq (6)]. Substituting temperature in Eq (4) by time, T = α + ßt, then derivative of the resulting equation equation with respect to time (at z, w, n, and Ea constants), and d/dt[-Ea/R(α+βt) = F(t) gives accounts for the A function (eq (6)) which regains the exponential form again.

$$A = \frac{d}{dt}\left[zw^n e^{-\frac{E_a}{R(\alpha+\beta t)}}\right] = \left[e^{-\frac{E_a}{R(\alpha+\beta t)}}\right]\frac{d}{dt}\left[-\frac{E_a}{R(\alpha+\beta t)}\right]$$

$$A = E_a F(t) e^{-\frac{E_a}{R\beta t}}$$

(6)

Therefore, the calculated values of A and their variations were within expectations.
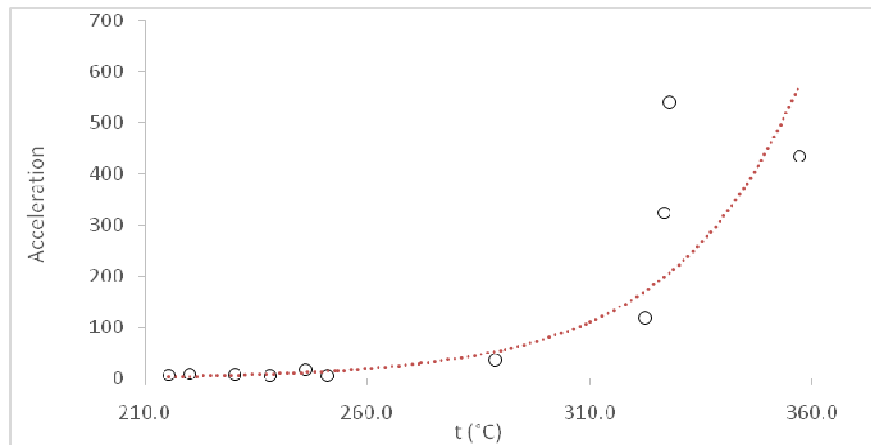

Fig. 4. Representation of acceleration of weight loss of PLEG versus temperature of isotherms

3.2.2 Variation of rate of weight loss by temperature

During the thermal scan, the rate of weight loss of PLEG increased by increasing the temperature (and therefore by time), which reached a maximum, then began to decrease; this decrease also continued in the isothermal process. The variation of maximum rate of weight loss versus temperature during the isothermal process (Fig. 5) followed the exponential form of Rate = 4.73E9 EXP(-12500/T). This equation has the same exponential form as the Arrhenius equation [eq (4)] which is within theoretical expectations.

Table 1. The results of the thermal scans of the pyrolysis process of LEGs at various temperatures

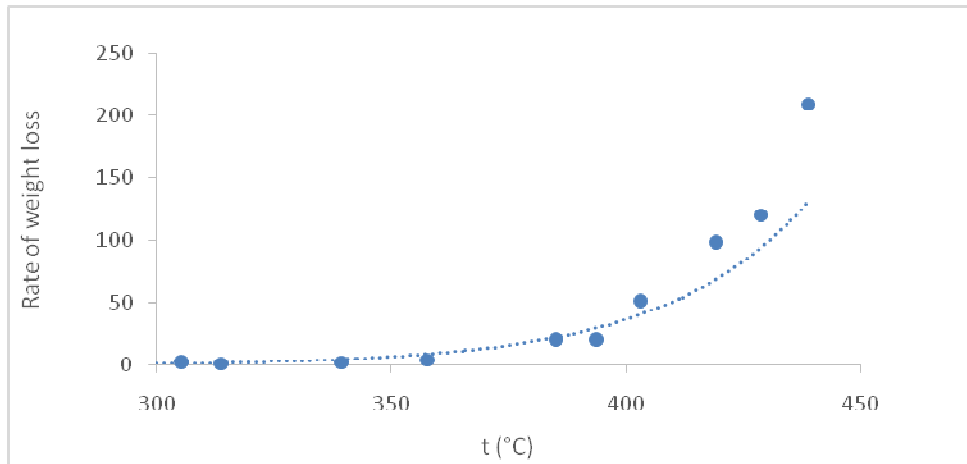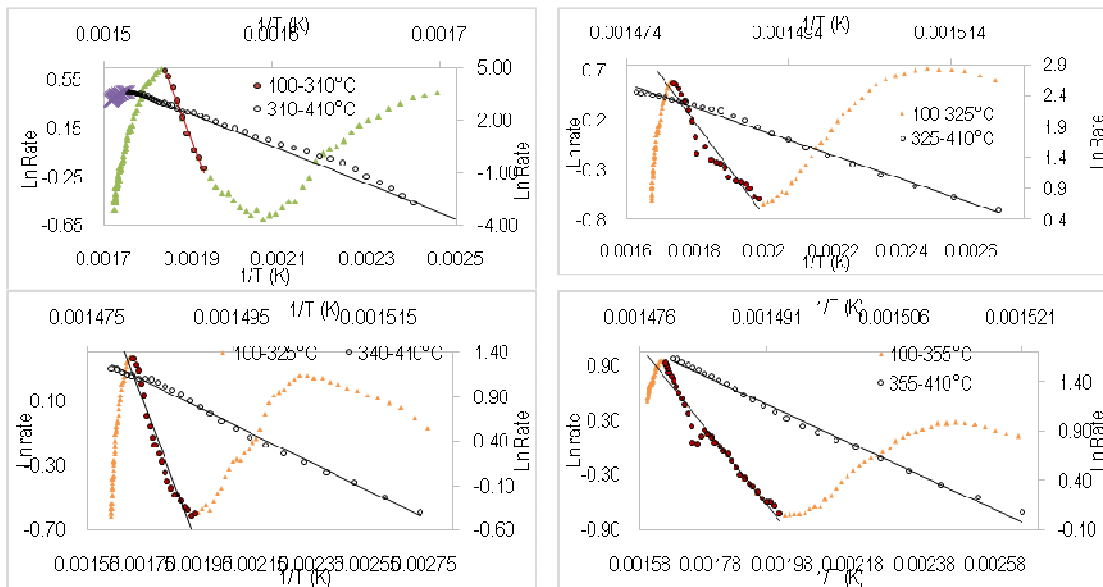|	First isotherm							At max		
	Start									
	t (mim)	T (K)	Accel-eration	Rate (max)	w%	k*	R. Ea(max)	T (min)	T (K)	Decel-eration
1	2.13	215	7.60	1.89	99.64	1.89	8,823	2.43	274	-3.10
2	2.17	238	3.71	1.79	99.24	1.80	5,449	2.55	306	-1.78
3	2.27	251	3.71	1.45	99.26	1.46	6,185	2.60	314	-1.28
4	2.17	230	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
10	2.52	579	0	120	80.23	1.50	-24,109	3.27	698	-248.54

* Assuming a first order reaction

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

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:

$$Ln\ Rate = -\frac{E_a}{RT} + Lnz + nLnw$$

(7)

The slope of the graph of "Ln rate" versus "1/T" results in the value of "–Ea/R" (Fig. 6).
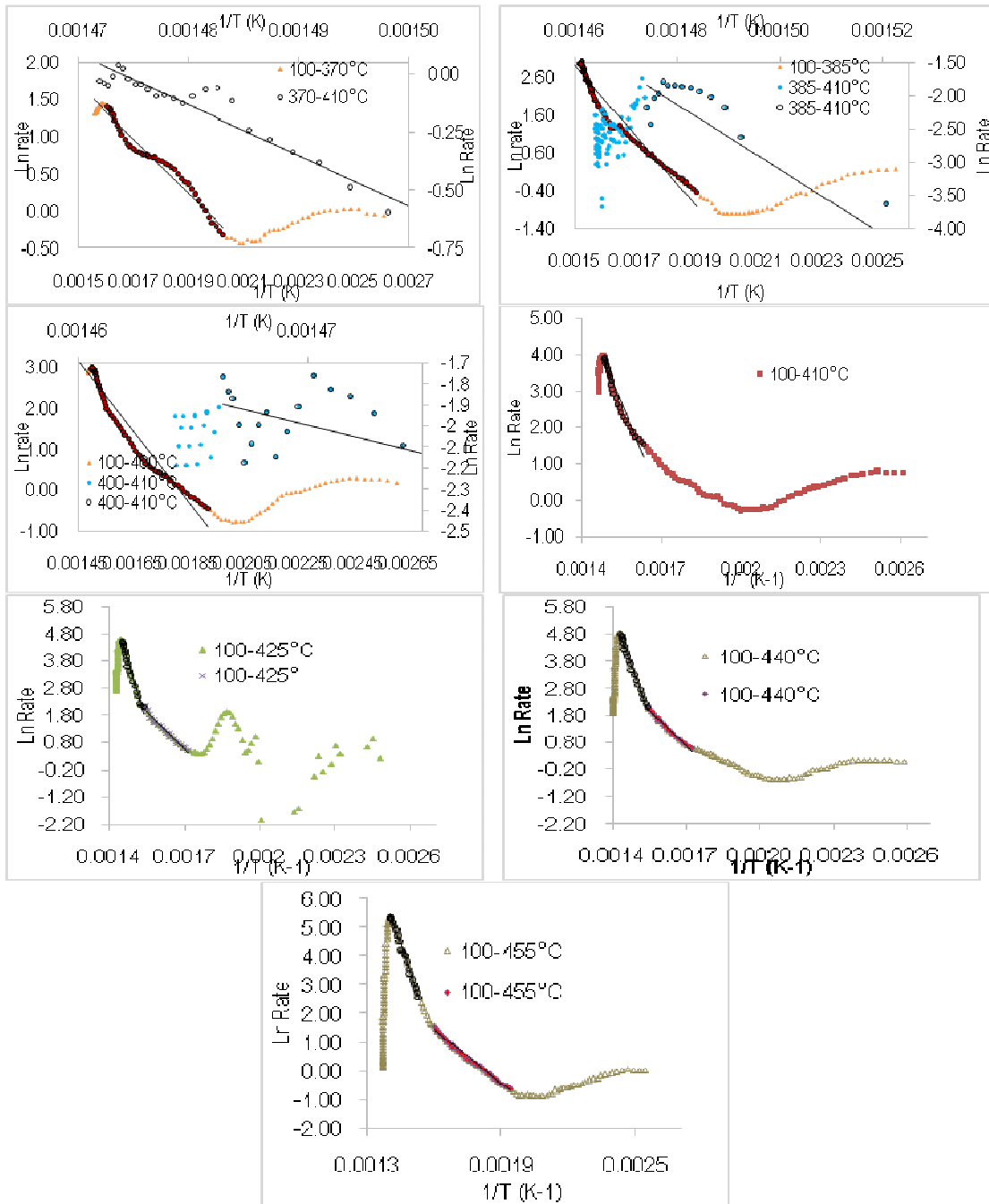
Fig. 6. Variation of "Ln rate" of weight loss versus "1/T (K)" for the18 thermal scans of the samples of PLEG from 308°C and 455°C

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 is expected to be positive) for a pure compound. (Fig. 6) represents plots of variations of "Ln rate" weight loss versus "1/T" for

samples of PLEG. The entire range of the thermal scan did not follow Eq (6). Several traces with different slopes were observed, as was expected, for a complex mixture of materials such as PLEG. Fora deeper study, let us analyze the scan of sample 1, covering ranges 100-310°C.Three traces with slopes positive, negative, positive, with minimum and maximum like an "N" shape were observed. The rate of weight loss decreased from 100-238°C, then 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 continued during the entire time of isotherm at 307°C. Then during the next thermal scan (307 - 406°C), the rate of weight-loss increased, reaching a maximum at 399°C (about 7°C before starting the second isotherm temperature.) This kind of behavior was observed for all 11 samples as can be observed in (Fig. 6). The data obtained from (Fig. 6) also are tabulated in (Table 1).

3.2.3 Variation of Ea by temperature

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 the 8th column of (Table 1). (Fig. 7) shows the variation of Ea versus temperature. As the temperature of the first isotherm process increased the value of the weight loss' Ea also increased. This was within expectation. If the weight loss' Ea was not an increasing function of temperature, a full weight loss must be observed during the first isotherm process. The increment of Ea versus T also had the exponential form (Fig. 7). The variation of Ea for the thermal scans below 425°C, though having the exponential form, also followed a third degree polynomial as well:
$Ea/R = 0.00740t^3 - 4.94t^2 + 820t + 5000$, where $300 < t\,(°C) < 425$.

It is noteworthy to mention that based on these experimental data the values of Ea of weight loss at temperatures over 435°C was less than the temperatures below 435°C (Fig. 7).
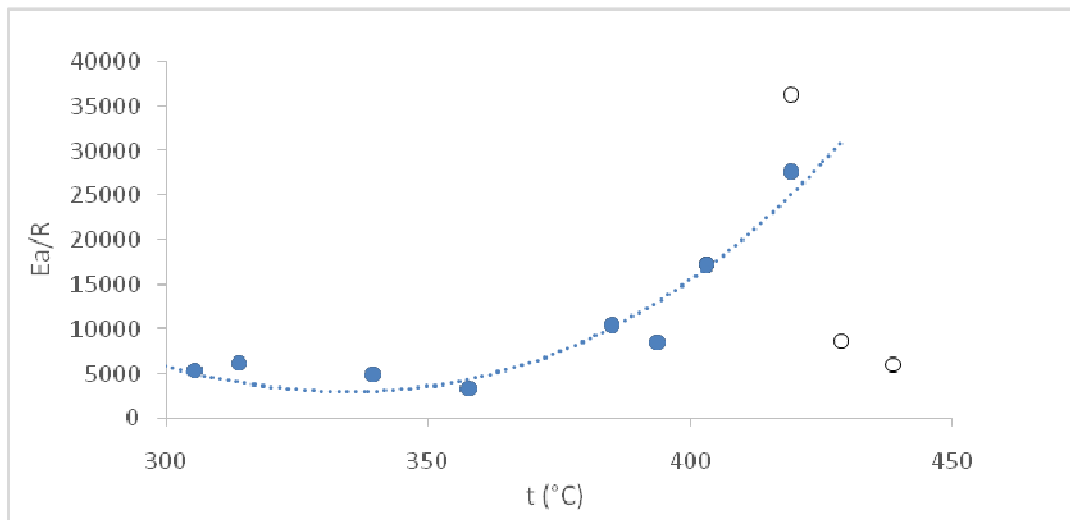

Fig. 7. Variation of Ea versus T for eleven isotherms of PLEG

The value of k obtained from the variation of weight loss rate versus temperature, assuming the reaction be first order, was tabulated in the 7th column of (Table 1). The values of k estimated in this manner were not accurate since the weight loss orders were not uniform

over all temperature ranges, and neither the reactions were first ordered reactions. The values of k also increased by temperature and they had the exponential form as was expected.
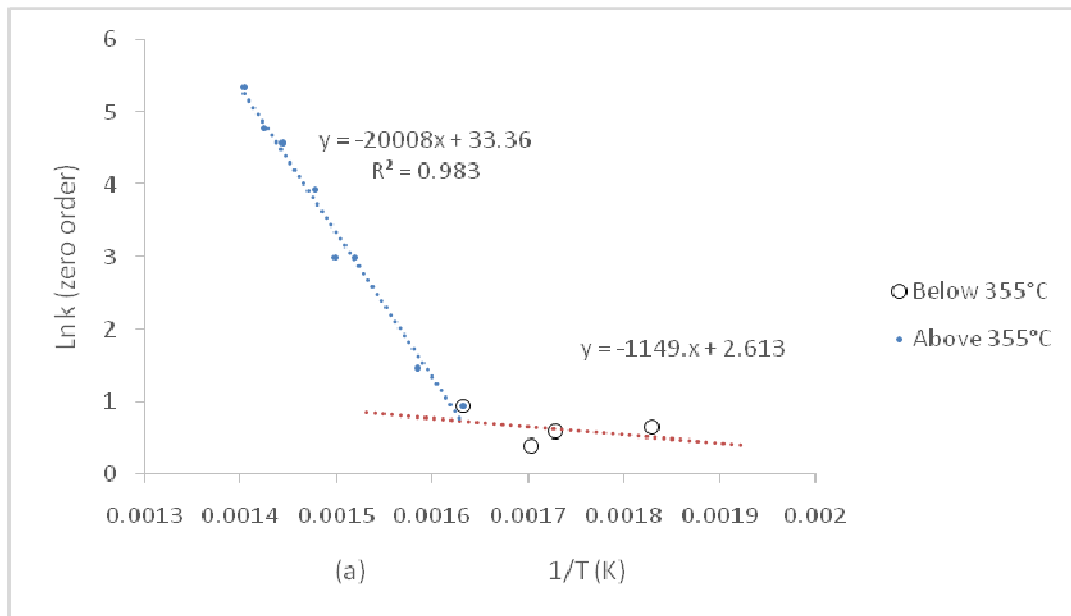
The rate of weight loss for the thermolysis process had an exponential form with a maximum. At the maximum rate of weight loss the order of reaction became zero; therefore, the maximum rate of weight loss, R_{max} =k for the zeroth order reactions. These values also are tabulated in the (Table 1).

3.2.4 The arrhenius equation

The logarithmic form of Eq (3) results:

$$Ln\ k = Ln\ z - Ea/RT \tag{8}$$

Application of Eq (8) to the 7th and 10thcolumns of data shown in (Table 1) resulted in evaluation of Ea for the pyrolysis of the PLEG samples. (Fig. 8) shows the variation of "Lnk" versus "T^{-1}" (K^{-1}) for eleven PLEG samples. The slope of the graph in (Fig. 8) is related to Ea of the weight loss process of the PLEG samples. There is a discontinuation of the experimental data around 355°C (Fig. 8). The Ea of weight loss at lower temperatures (below 355°C) was lower than the Ea of weight loss at temperatures above 355°C. Lower Ea results in higher reaction rate. However, the experimental rate of weight loss below 355°C was slower that above this temperature. This indicates that different types of chemical reactions were taking place at above and below 355°C. If the same chemical reactions at both temperatures were occurred, the rate of weight loss at lower Ea would be faster than at larger Ea value. As the temperature increased, the rate of weight loss also increased which was within expectation. At lower temperatures the main reaction was loss of HCl from the PLEG samples. Elimination of HCl (bp - 89°C) from the backbone of the chloroprene radical (328 kJ/mol) would consume less energy than the elimination of carbon chains (347–356 kJ/mol) by chain scissoring of neoprene segments at the same temperatures.
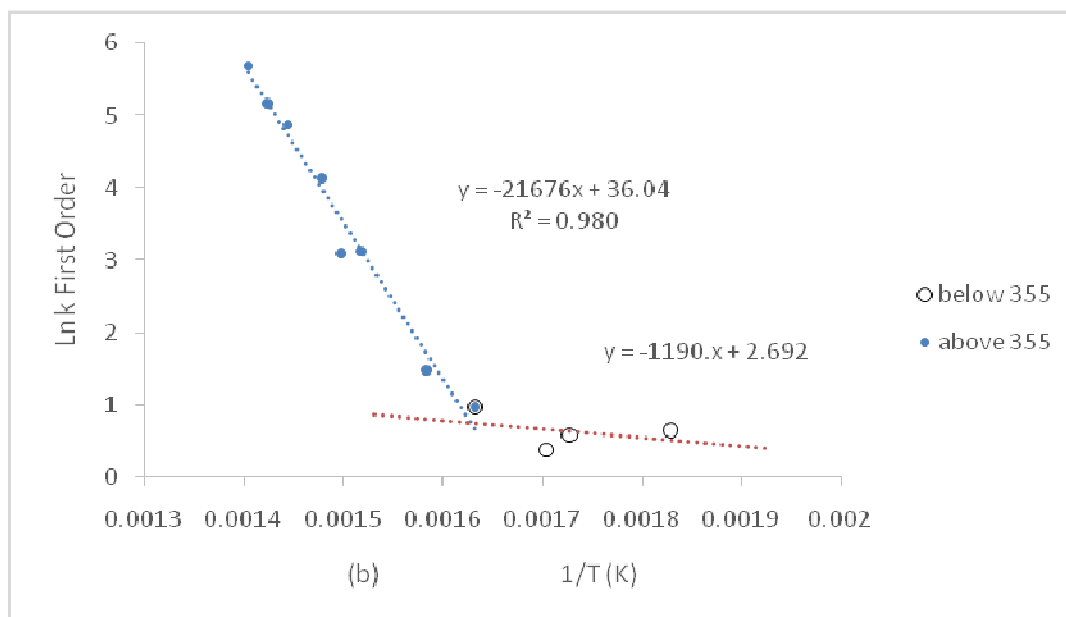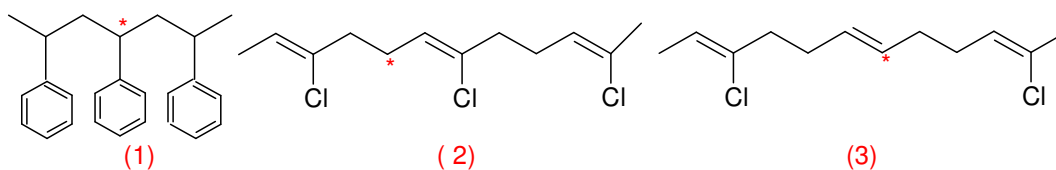
Fig. 8. Variation of Ln k versus 1/T for eleven samples of PLEG assuming: (a) a zeroth order reaction; (b) a first order reaction

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 temperatures confirmed that at temperatures above 435°C the Ea for pyrolysis is less than that of the temperatures below it. The experimental results showed part of the pyrolysis products of PLEG were reached in chlorinated compounds, particularly, HCl [42] which are potentially hazardous for environment and human health On the other hand, a large number of molecular and radical species are involved in the pyrolysis 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 compared with polyethylene chains, similar to PS decomposition; because of the allylic resonance of the resulting radical. The lower activation energy of PLEG is similar to PS due to the preferential formation of the long lived resonantly stabilized radicals,

Cl and H - abstraction reactions include both inter-and intramolecular or backbiting reactions. It also should be noted that the Cl⁻ and H-abstraction reactions is much faster than ß-decomposition reactions. In typical temperature conditions (310-450°C), the ß-decomposition reaction becomes the slowest step, the rate-determining step, and the smaller radicals formed generate the parent molecule before undergoing a new ß-scission.

However, the formation of large quantities of eight carbons compounds resulting from the pyrolysis of LEGs is an indication of ɣ-scissions of de-chlorinated neoprene.

The weight loss at 355°C and higher temperatures took a different course. Sixty percent or more of the materials were volatized during the first isotherm. Keeping in mind that around 30% of the mass of the PLEG are stable over 550°C; thus, 70% of the mass of PLEG are volatiles under 550°C. These volatiles could be low boiling inorganics, high boiling organics such as plasticizers, and materials that decomposed at high temperatures such as neoprene and high molecular mass plasticizers and additives. Chlorine contributes 40% of pure neoprene mass, when it is eliminated from neoprene in the form of HCl, 41.2% of weight loss can be attributed to release of HCl. Therefore, useful organic content of PLEG was less than 30% of its original weight. The isotherm at 355°C recorded (100-69 =) 31% weight loss in the first stage of heating. If all weight loss at this temperature be attributed to elimination of HCl, then, it will be a practical process to eliminated chlorinated compounds before complete degradation of PLEG to other chemicals.

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COMPETING INTERESTS

Authors declare that there are no competing interests.

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