PYROLYSIS KINETICS AND THERMAL DECOMPOSITION BEHAVIOR OF POLYCARBONATE – a TGA-FTIR study

by

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This study covers the thermal degradation of polycarbonate by means of Thermogravimetric Analyzer coupled with Fourier transform infrared spectrometer (TGA-FTIR). Thermogravimetric analysis of polycarbonate was carried out at four different heating rates of 5, 10, 15, and 20 °C per minute from 25 °C to 1000 °C under nitrogen atmosphere. The results indicated that polycarbonate was decomposed in the temperature range of 425-600 °C. The kinetic parameters, such as activation energy, pre-exponential factor and reaction order were determined using five different kinetic models; namely Coast-Redfern, Friedman, Kissinger, Flynn-Wall-Ozawa (FWO), and Kissinger-Akahira-Sunose (KAS). Overall decomposition reaction order was determined by Coats-Redfern method as 1.5. Average activation energy was calculated as 150.42, 230.76, 216.97, and 218.56 kJ/mol by using Kissinger, Friedman, FWO, and KAS models, respectively. Furthermore, the main gases released during the pyrolysis of polycarbonate were determined as CO_2, CH_4, CO, H_2O, and other lower molecular weight hydrocarbons such as aldehydes, ketones and carbonyls by using thermogravimetric analyzer coupled with Fourier transform infrared spectrometer.

Key words*: polycarbonate, thermal decomposition, pyrolysis kinetics, TGA-FTIR*

Introduction

Polycarbonate (PC) is a lightweight plastic that is widely used in many areas due to its high mechanical strength, thermal stability, excellent electrical resistance and high outstanding optical transparency. With a worldwide production rate of 2.7 million tons/year, PC is the second large consumed engineering polymer in the world. Main application areas for PC are electronic equipment, construction materials, compact discs (CD or DVD), automobile/aircraft industry, and medical devices. The properties of PC also make it an ideal choice for drinking bottles and high quality food containers. Disposal of PC, especially drinking water bottles and food containers, is a critical problem that attract attention for the last years. Recycling seems the best option for the disposal problem, however, it is not seriously carried out especially in developing countries. Direct combustion of PC is hazardous as it releases high amounts of carbon dioxide and smoke during the breakdown of PC resulting in air pollution. One of the thermochemical conversion methods, pyrolysis might be a promising and environmentally friendly conversion technique to overcome such disposal problems [1, 2].

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Pyrolysis is defined as the thermochemical degradation of organic materials in the absence of oxygen and it is used to convert polymers into valuable products such as synthetic fuels. Pyrolysis of polymers is based on a series of complex reactions including the decomposition of the polymer into lower molecular weight condensable and non-condensable volatiles, composition and yield of which are influenced by many factors, such as heating rate, temperature, pressure, residence time, moisture content, composition of biomass material and size of particles [3-5]. Therefore, it is necessary to clearly identify the pyrolysis process, and chemical kinetics. Thermogravimetric analysis is a useful tool to evaluate the thermal decomposition behavior and kinetics of pyrolysis process since it provides precise measurement depending on temperature and other experimental conditions that are well-known and well-controlled [6, 7]. Several studies were carried out about the decomposition behavior of PC using different analytical techniques such as TG-FTIR, TG-MS or Py-GC [1, 8-10]. However, detailed analysis of pyrolysis kinetics of PC is not found.

In this manner, the TGA of PC and simultaneous FTIR analysis of the evolved volatiles are involved in this report. Moreover, the effect of heating rate on PC pyrolysis process was studied, and activation energy and other kinetic parameters were determined using Coats-Redfern (CR) [11], Friedman [12], Kissinger [13], Flyn-Wall-Ozawa (FWO) [14, 15] and Kissinger-Akahira-Sonuse (KAS) [16] models.

Experimental

Thermal degradation of polycarbonate

Polycarbonate samples that are used for TGA experiments were obtained from a plastic packaging factory located in Kırklareli, Turkey. The samples (average particle size $5.00 > D_p > 1.8$ mm) were used directly without any pretreatments such as drying, grinding or screening.

Thermal analysis was carried out on Setaram Labsys Evo Thermal Analyzer and the sample weight losses were recorded as a function of temperature and time. 10 ± 0.5 mg of sample was used for each test and experiments were carried out at heating rates of 5, 10, 15, and 20 °C per minute under nitrogen atmosphere at a flow rate 20 mL per minute in the temperature range from 25 °C to 1000 °C.

Evolved gases were then passed through a transfer line that was kept at 250 °C to avoid condensation and simultaneous FT-IR spectra was recorded with a Thermo Nicolet IZ 10 FT-IR. IR spectra were recorded between 4,000-700 per centimeter at a resolution of 4 per centimeter with 32 scans.

Pyrolysis kinetic analysis

Pyrolysis of polymer is a solid phase degradation reaction that produces some condensable and non-condensable volatiles and negligible char. General expression for the reaction rate constant, k, is defined by the Arrhenius equation:

$$k = A\mathrm{e}^{(-E/RT)} \tag{1}$$

where E is the activation energy, T – the absolute temperature, R – the gas constant, and A – the pre-exponential factor or frequency factor [4]. The fundamental rate equation used in all kinetics studies is generally described as:

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$$\frac{dx}{dt} = kf(x) \qquad (2)$$

where $f(x)$ is the reaction model, a function depending on the actual reaction mechanism. Equation (2) expresses the rate of conversion, dx/dt at a constant temperature as a function of the reactant conversion loss and rate constant. The conversion (x) is defined as:

$$x = \frac{W_0 - W_t}{W_0 - W_f} \qquad (3)$$

where W_0, W_t, and W_f are the initial mass of the sample, mass of the sample at time t, and the final residual mass, respectively [17, 18]. By replacing the rate constant with equation (1), rate expression becomes:

$$\frac{dx}{dt} = Af(x)e^{-E/RT} \qquad (4)$$

The expression of the function $f(x)$ is used for describing first order reaction and it is proportional to the concentration of nondegraded material, thus many authors restrict the mathematical function $f(x)$ to following expression:

$$f(x) = (1-x)^n \qquad (5)$$

where n is the reaction order. Substituting eq. (5) into eq. (4) gives the expression of reaction rate in the form [4, 19]:

$$\frac{dx}{dt} = A(1-x)^n e^{-E/RT} \qquad (6)$$

Non-isothermal method employs a heating rate (β), usually linear, to raise the temperature. A linear heating program follows:

$$T = T_0 + \beta t \qquad (7)$$

$$dT = \beta dt \qquad (8)$$

where T_0 is the starting temperature, β – the constant heating rate and T – the temperature at time t. The following relationship can be defined for non-isothermal experiments:

$$\frac{dx}{dT} = \frac{dx}{dt}\frac{dt}{dT} \qquad (9)$$

where dt/dT describes the inverse of the heating rate, $1/\beta$ and dx/dt represents the isothermal reaction rate, and dx/dT denotes the non-isothermal reaction rate. An expression of the rate law for non-isothermal conditions can be obtained by substituting eq. (4) into eq. (9):

$$\frac{dx}{dT} = \frac{A}{\beta}f(x)e^{-E/RT} \qquad (10)$$

Equation (10) represents the differential form of the non-isothermal rate law [20, 21].
Model-fitting and model-free methods that are listed in tab. 1 are used to analyze either isothermal or non-isothermal solid-state kinetic data from TGA.

Table 1. Model-fitting and model free methods

Model-fitting		Model-free	
Isothermal	Non-isothermal	Isothermal	Non-isothermal
Conventional	Differential Freeman-Carroll Coats-Redfern	Standard Friedman AIC	Kissinger Flynn-Wall-Ozawa Vyazovkin and AIC Kissinger-Akahira-Sonuse

Model-fitting methods consist in different models to the data, so that a model is chosen when it gives the best statistical fit. From this, the activation energy and pre-exponential factor were calculated [4].

Model-free methods calculate the reaction activation energy without modelistic assumptions which is usually done by grouping the terms such as pre-exponential factor and model into the intercept of a linear equation and using the slope of that equation to calculate the activation energy. Pre-exponential factor can be calculated from the intercept of the linear equation but requires modelistic assumptions for such a determination. Therefore, model-free methods usually report only activation energies [20].

Coats-Redfern (CR) method is widely used for study on the analysis of pyrolysis kinetics and kinetic parameters, namely activation energy and pre-exponential factor [22].

Rearranging and integrating eq. (10), the following expression can be obtained:

$$\frac{1-(1-x)^{1-n}}{1-n} = \frac{A}{\beta} \int_0^T e^{-E/RT} dT \qquad (11)$$

Since has no exact integral, $e^{-E/RT}$ can be expressed as an asymptotic series and its integration with ignoring the higher-order terms gives:

$$\frac{1-(1-x)^{1-n}}{1-n} = \frac{ART^2}{\beta E}\left[1 - \frac{2RT}{E}e^{-E/RT}\right] \qquad (12)$$

Expressing eq. (12) in logarithmic form result in following equation for $n \neq 1$:

$$\ln\left[\frac{1-(1-x)^{1-n}}{T^2(1-n)}\right] = \ln\left[\frac{AR}{\beta E}\left[1 - \frac{2RT}{E}\right]\right] - \frac{E}{RT} \qquad (13)$$

In order to simplify the calculations, the order of the reaction, n is assumed to be unity, and hence eq. (12) can be presented as:

$$\ln\left[-\frac{\ln(1-x)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\right] - \frac{E}{RT} \qquad (14)$$

The slope of curve $\ln[(1-(1-x)^{1-n}/(1-n)T^2]$ or $\ln[-\ln(1-x)/T^2]$ *vs.* $1/T$ produce $-E/R$ and hence the activation energy can be determined. The expression $\ln[AR/\beta E(1 - 2RT/E)]$ in eq. (13) and eq. (1) is essentially constant, by taking temperature at which $W_t = (W_0 + W_f)/2$ in the place of T in the intercept term and hence pre-exponential factor A can also be determined [6, 23].

Friedman method is a differential isoconversional technique that can be expressed in general terms as written below:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \beta\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right) = A\mathrm{e}^{-E/\mathrm{R}T} f(x) \tag{15}$$

Taking natural logarithms of each side from eq. (15) yields:

$$\ln\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right) = \ln\left[\beta\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)\right] = \ln\left[Af(x)\right] - \frac{E}{\mathrm{R}T} \tag{16}$$

It is assumed that the conversion function $f(x)$ remains constant, which implies that degradation is independent of temperature and depends only on the rate of mass loss. A plot of $\ln(\mathrm{d}x/\mathrm{d}t)$ or $\ln(\beta(\mathrm{d}x/\mathrm{d}T)]$ *vs.* $1/T$ yields a straight line, the slope of which corresponds to $-E/\mathrm{R}$ [21].

Kissinger method uses the maximum decomposition temperature (T_m) at which the rate of weight loss is the highest. In this method activation energy can be determined from equation:

$$\ln\left(\frac{\beta}{T_\mathrm{m}^2}\right) = \ln\left(\frac{A\mathrm{R}}{E}\right) + \ln\left[n(1-x_\mathrm{m})^{n-1}\right] - \frac{E}{\mathrm{R}T_\mathrm{m}} \tag{17}$$

where x_m is the conversion corresponding to the maximum of a differential kinetic curve. The activation energy, E, can be calculated from a plotting $\ln(\beta/T^2\mathrm{m})$ *vs.* $1/T_\mathrm{m}$ [19].

FWO is one of the most commonly accepted methods for the computation of kinetic parameters. This method uses the correlation between different heating rates, activation energy and inverse temperature. In this method activation energy can be determined from equation:

$$\ln(\beta) = \ln\left(\frac{AE}{\mathrm{R}g(x)}\right) - 5.331 - 1.052\frac{E}{\mathrm{R}}\frac{1}{T} \tag{18}$$

Assuming x has a fixed value, E can be determined from the slope of the straight line obtained by plotting $\ln(\beta)$ *vs.* $1/T$ [5].

KAS is an integral iso-conversional technique. Equation (19) is the fundamental expression of analytical method to calculate activation energy for KAS model:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{A\mathrm{R}}{Eg(x)}\right) - \frac{E}{\mathrm{R}T} \tag{19}$$

Thus, for constant x, the plot of $\ln(\beta/T^2)$ *vs.* $1/T$ obtained from the thermo-grams recorded at several heating rates should be a straight line whose slope can be used to evaluate the activation energy [24].

Results and discussion

Thermogravimetric analysis

Figures 1(a) and (b) are TG and dTG curves, respectively, for the pyrolysis of polycarbonate at four heating rates 5, 10, 15, and 20 °C per minute. Similar plots are obtained at different rates, initial weight loss due to the presence of moisture in the samples, then somewhat indistinct rise in the TG between 120 and 440 °C, immediately followed by the main weight loss zone. The maximum rate of weight loss in this main decomposition stage occurred between 479.25 and 566.94 °C for 10 °C per minute heating rate. No further weight

loss was apparent beyond 627 °C. It is seen that temperature alteration of 85 °C is enough for the completion of decomposition for all heating rates.
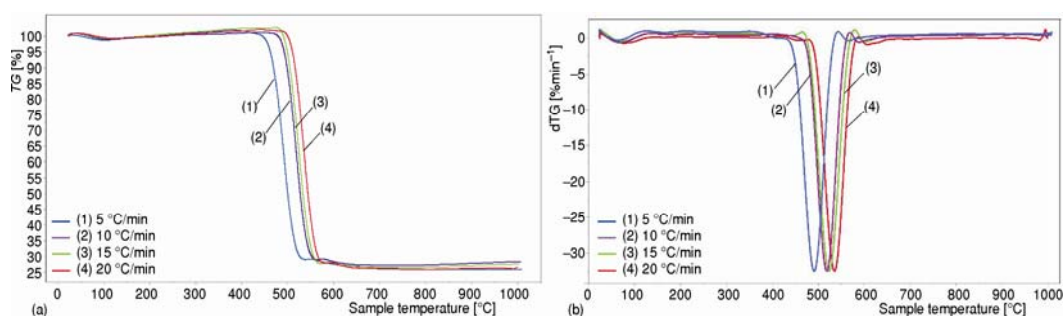
Figure 1. TG (a) and dTG (b) curves of polycarbonate at different heating rates (for color image see journal web site)

Table 2. Temperature and weight loss characteristics of PC at different heating rates
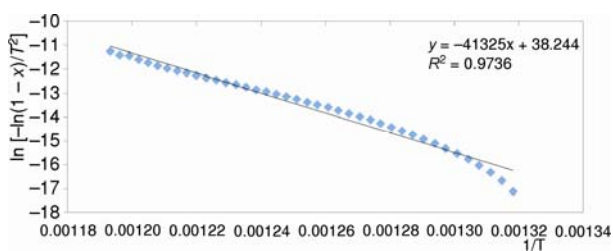
Heating rate [°Cmin^{-1}]	Temperature [°C]			Weight loss [%]
	Start	Maximum	End	
5	444.80	492.58	542.49	71.20
10	479.25	519.61	566.94	71.02
15	490.76	523.92	576.40	72.28
20	500.25	537.41	585.55	72.29

Figure 1 also denotes the effect of heating rate. It is seen that higher heating rates shifts TG curve positions and maximum peak temperature (T_m). When heating rate is increased from 5 to 20 °C per minute, maximum peak temperature is shifted from 492.58 to 537.41 (tab. 2). This significant change in the decomposition temperature is as a result of the delay in thermal degradation process and most probably due to the presence of increased thermal lag. The reason is that the sample reaches decomposition temperature in a shorter time when higher heating rates are considered [25].

Kinetic analysis

The thermal decomposition of polycarbonate occurs through a number of reactions in series and parallel, totally giving a weight loss data provided by TGA. This data, can be used to predict the kinetics of decomposition reactions and hence, may give an idea about the thermal behavior of polymeric substances during pyrolysis that may be a useful data for further reactor design operations [26].

In this study, kinetic parameters are determined by different models that were explained in previous sections.

Figure 2. Plot of ln[–ln(1 – x)/T^2] *vs.* 1/T for 10 °C per minute

Coats-Redfern method

The results obtained with Coats-Redfern method are presented below. Figure 2 shows the typical plot of ln[–(1 – x)/T^2] *vs.* 1/T for 10 °C per minute, indicating that pyrolysis of PC occurs in one step and it can be assumed that this overall decomposition is a first order reaction.

Coats-Redfern method is further used for the determination of the over-all reaction order to check the accuracy of first order. The order of decomposition is obtained by substituting different values of n into eq. (13) (or eq. (14) when $n = 1$) to obtain the appropriate plots which should give a straight line for the correct value of reaction order. Thus, several values of n are considered, and the related correlation coefficients (R^2) were calculated. According to correlation coeffi-

Figure 3. Plot of Y *vs.* 1/T for various reaction orders
(for color image see journal web site)

$$\left(Y = \ln\left[\frac{1-(1-x)^{1-n}}{(1-n)T^2} \right] n \neq 1 \quad \text{and} \quad Y = \ln(1-x)/T^2) n = 1 \right)$$

cients, the reaction order was determined as 1.5 since it gives the highest R^2 value for Coats-Redfern method for each heating rate. A typical figure of this method is given in fig. 3 for 10 °C per minute heating rate. It is observed from these curves that although $n = 1.5$ gives the best fit, first order reaction assumption still seems to be correct since it also gives very high R^2 values that are close to that of 1.5th order.

Table 3 shows the kinetic parameters that were determined at different heating rates. Activation energy, E, is dependent on heating rate and tends to increase as heating rate increases.
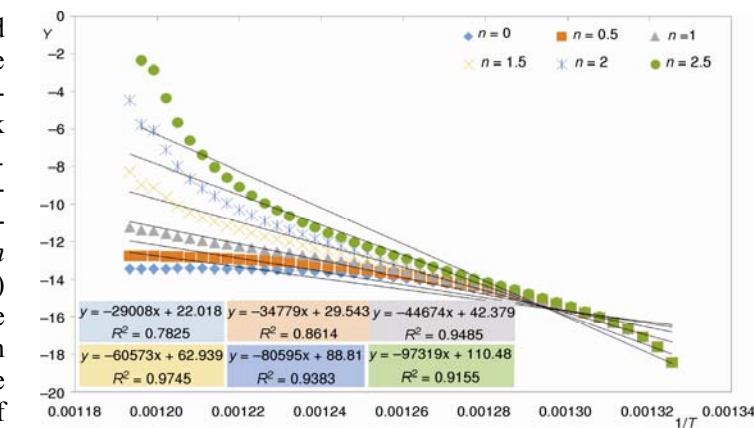
Table 3. Kinetic parameters at different heating rates (Coats-Redfern Method)

Heating rate [°Cmin⁻¹]	Temperature [°C]	E [kJmol⁻¹]	A [min⁻¹]	R^2
5	444.8-542.5	310.15	2.87E+20	0.972
10	479.25-566.94	343.58	1.75E+22	0.974
15	490.76-576.40	328.92	1.8E+21	0.966
20	500.25-585.55	347.19	1.93E+22	0.976

Kissinger method

For the Kissinger method, the activation energy was calculated by eq. (17) where T_m is the maximum peak temperature. The activation energy obtained from Kissinger method is 148.45 kJ/mol and its plot is shown in fig. 4.

Friedman, FWO, and KAS methods

Figure 5 gives the relationship of activation energies with conversion extent calculated by the Friedman, FWO and KAS respectively. It is seen that average activation energies are similar for KAS and FWO models
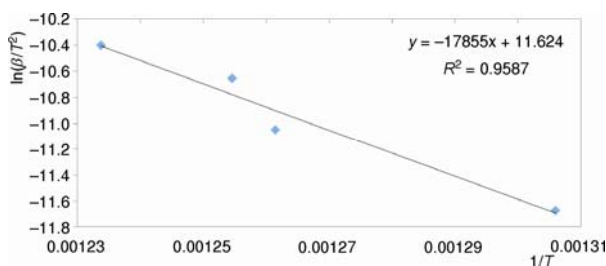
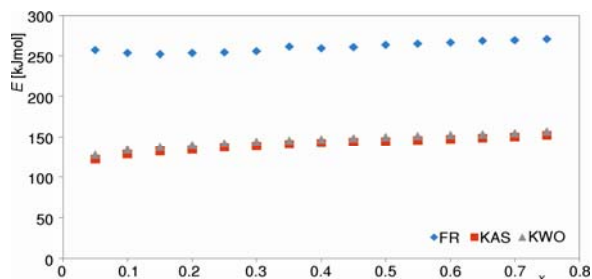

Figure 4. Kissinger plot of PC

Figure 5. Activation energies calculated by Friedman, KAS, and FWO models at different conversion degrees

whereas activation energies calculated by Friedman model matches with Kissinger model. Average values for activation energies are found as 260.93 kJ/mol, 140.20 kJ/mol and 145.57 kJ/mol for Friedman, KAS and FWO models, respectively.

TGA-FTIR analysis

During TGA, evolved gases were detected by FT-IR simultaneously. Figure 6 shows the Gram-Schmidt curve that is based on all the individual spectra. Gram-Schmidt curve is plotted by the calculated values of infrared extinction coefficient of the evolved gases and their corresponding concentrations over the entire wave number range [1]. One sharp peak at about 51 min that corresponds to the maximum weight loss in TGA is seen in fig. 6. 51 minutes corresponds to approximately 535 °C which is higher than the maximum weight loss temperature obtained from TGA for 10 °C per minute heating rate. This shift is as a result of the delay between TGA furnace and detector in the FT-IR. Evolved gases are swept through a transfer line which is kept at 250 °C to avoid condensation of relatively higher molecular weight product gases [1, 7, 27, 28].
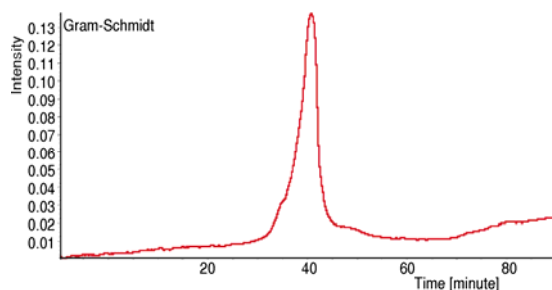

Figure 6. Gram-Schmidt curve of thermal degradation of PC
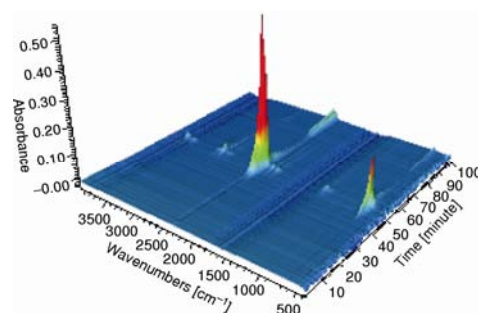

Figure 7. 3d FT-IR spectrum of gases evolved from thermal degradation of PC

3d FT-IR spectra of the evolved gases during thermal decomposition of PC is given in fig. 7. In this spectra, absorbance bands due to evolved gases can be observed between 41th and 56th min (corresponding temperatures are 435 and 585 °C, respectively) which is similar with Gram-Schmidt and TGA data. It is obvious from fig. 7 that when pyrolytic reactions start at about 435 °C, related products such as CO_2, CO, CH_4, and H_2O are formed. Assignments of some main absorbance bands related with main functional groups are summarized in tab. 4 [27]. The most intensive absorbance band observed between 2247 and 2396 per centimeter for PC pyrolysis is attributed to C = O stretching vibrations indicating the presence of CO_2 which is the main product. C-H stretching vibration band (2996-3024 per centimeter), assigned to the presence of hydrocarbon gases mainly CH_4, has its maximum absorbance at 525 °C. The peaks due to free alcohol or H_2O are observed between 3520 and 3756 per centimeter wavenumber and maximum release is obtained at 545 °C. Two typical absorption bands between 2145-2222 and 2058-2135 per centimeter are ascribed to the presence of CO in the evolved gases.

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Table 4. FT-IR results of the evolved gases during thermal decomposition of PC

Wave number (1/cm)	Chemical bond	Vibration	Evolved gaseous product	T_1 [°C]	T_m [°C]	T_2 [°C]
3.400-3.700	O-H	Streching	H_2O, phenol, alcohol	505	535	545
2.780-3.054	C-H	Streching	Aromatic, aliphatic and/or olephinic hydrocarbons	465	525	595
2.255-2.392	C = O	Asymmetric streching	CO_2	435	535	615
2.144-2.239 2.058-2.150	C-O	Streching	CO	505	535	555
1.278-1.326	C-H	Bending	Aromatic, aliphatic and/or olephinic hydrocarbons	485	525	595
584-741	C = O	Bending	CO_2	435	535	575

T_1: Temperature at which product gas starts to be formed; T_m: Temperature at which maximum product gas is obtained; T_2: Temperature at which product gas ends

Conclusions

In this study, thermal behavior of polycarbonate has been investigated using thermogravimetric analysis and simultaneous FT-IR for the detection of evolved gases. The kinetics of PC thermal degradation was determined at four different heating rates under nitrogen atmosphere. The pyrolysis process of PC occurred in a one-step decomposition between 480 and 570 °C temperature range loosing 71% of its initial mass. It was observed that higher heating rates resulted in a shift in the decomposition temperature.

The activation energy, pre-exponential factor and reaction order were obtained by Coats-Redfern method. Moreover, the activation energy was calculated using Kissinger, Friedman, Flynn-Wall-Ozawa and Kissinger-Akahira-Sunose as 150.42, 230.76, 216.97 and 218.56 kJ/mol respectively. Calculated Ea values for PC thermal degradation using various kinetic models does reveal that use of the Kissinger model results in lower apparent activation energy than those obtained using the other kinetic models. FWO and KAS models result in similar activation energies meaning that both methods can be used to obtain correct approach.

In situ FT-IR analysis of the evolved gases showed that CO_2 is the main product of pyrolysis, whereas little amounts of CH_4, CO and -OH containing compounds also exists. As a result, it can be concluded that pyrolysis seems to be an alternative method for the disposal of PC when appropriate conditions are chosen.

Acknowledgements

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