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# The Effects of Hydrothermal Aging Characterized by SEC on the Degradation Kinetic of Polycarbonate Calculated through TGA

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Bisphenol A (BPA) is the principal component of many polymers such polycarbonate (PC) and epoxy resins. These polymers are commonly used to make baby bottle, drinking water bottle, CDs, food containers, dental sealant, and so on. BPA can migrate from PC to foods and beverages. In order to establish the relationship between the migrant contaminant and its polymer, and explain the release mechanism of the BPA, the impact of different factors on PC aging was studied by measuring molecular masses using size exclusion chromatography (SEC). It has been found that the molecular weights of PC samples change as a function of treatment conditions. In general, the trend was to shift the Mn toward a lower average molecular weight with increasing treatment temperature, pH and treatment duration. The same PCs were explored by Thermogravimetric analysis (TGA), and its degradation kinetic was studied. The PC decomposition follows the Arrhenius law, which allows the determination of the activation energy (Ea) from thermal degradation curves with Friedman isoconversional method. The results show clearly that the activations energies which indicate the threshold of degradations reactions decrease with increasing temperature and pH.

## 1. Introduction

Bisphenol A polycarbonate (BPA-PC) is an engineering thermoplastic with high impact strength, heat resistance and high modulus of elasticity. BPA has been widely used in the plastic industry for the production of polycarbonate plastics and epoxy resin. The main consumer products developed from BPA are baby bottle, drinking water bottle, lining of food can, dental sealant, and so on (Vandenberg et al, 2007).Many studies have demonstrated the estrogenic disruption effect of BPA, especially in the early life stages of animals (Sun et al, 2014). Polymerization processes do not have a 100% yield, and the finished plastic material might contain trace residue levels of the monomer (Casson et al, 2014). It has been demonstrated that at higher temperatures, hydrolysis of PCs can occur, releasing traces of BPA monomer on its surface. Consequently, BPA migrates in food or beverages (Hoekstra and Simoneau, 2013)

The degradation of PC leads to BPA migration. Bisphenol A has become a controversial issue because it was detected in many environmental things; water and some bottled water were analyzed by GC-MS, and the results show that the concentration of BPA detected was 17.6 to 324 ng $L^{-1}$(Li et al, 2010). Nam et al (2010), observe that the levels of BPA migration were rapidly increase when the water temperature was over 80°C; in addition, the d-spacing of PC baby bottle increases with repeated use from 0.499 nm in brand-new bottles to 0.511 nm with bottles used for 6 months. The results obtained in another study revealed that the BPA migration varied from 228 to 521 μg $L^{-1}$ after being heated at 70 °C for 6 d (Cao and Corriveau, 2008). It is well known that degradation leads to changes in molecular weight, which subsequently causes changes in material characteristics (Soleimani et al, 2012). Size Exclusion Chromatography (SEC) and Gel permeation chromatography (GPC) techniques have been applied for the determination of BPA-PC characteristics (Liang Xu et al, 2004).

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Materials degradation has been carried out for many years using numerous techniques to analyze the data. Thermogravimetric analysis TGA is usually used as a means of determining polymers degradation and kinetic parameters (Ignazio et al, 2011). There are two approaches to obtain kinetic data: isothermal and nonisothermal methods. For isothermal methods, reactions are followed at several constant temperatures while nonisothermal methods involve heating samples at one or more constant heating rates and following the course of the reaction (Aik Chong Lua et al, 2006).

Since the overall thermal stability of polymers is connected with the degradation rate, the determination of the kinetic parameters of degradation, and in particular, of the apparent activation energy (Ea), is of great importance. The non-isothermal methods are the most commonly used for performing the kinetic analysis of polymers (Fuying et al, 2013). Various degradation models including the Kissinger, Friedman, Flynne-Walle-Ozawa, MacCallum-Tanner and van Krevelen methods widely used for estimating the kinetic parameters (Ea) (Aik et al, 2006) and (Fei et al, 2008).

The Friedman isoconversional method has been the most generally used for determining the activation energy at fixed conversions (Friedman, 1964). The slopes of the lines drawn through isoconversional points for certain reaction progress α at different heating rates allows the determination of the activation energy Ea. In the present work, the effects of hydrothermal aging of polycarbonate on the degradation kinetic and molecular masses were studied with varying temperature, pH, and contact time.

## 2. Experimental

### 2.1 Material

Baby bottles made of polycarbonate, bought from a local supermarket, are chosen to be the study samples. Citric acid, and NaOH from SIGMA ALDRICH Chemistry (France). THF unstabilized from BIOSOLVE (The Netherland) was adopted for SEC analysis, and water was distilled and then purified via a Millipore water purification system.

### 2.2 Hydrothermal treatments

The PC was prepared by cutting each baby bottle into several pieces; each one with an area of 3 cm$^2$. Pieces were immersed in a 25 mL of distilled water many times with varying, temperatures, and pH which was stabilized by buffers (Table 2). All PC samples and solutions were subjected to the following analyzes.

### 2.3 Polymer characterization

Thermogravimetric analysis TGA

TGA:Thermogravimetric analysis is the technique used to study the kinetic degradation and to calculate the activation energies. Thermogravimetric measurements were carried out with METTLER TOLEDO instrument connected to a gas flow system to work in inert atmosphere using nitrogen. Small samples (6-10 mg) were used with a different heating rate of 1, 2 and 5°C min$^{-1}$.

Size Exclusion Chromatography SEC

The technique used to determine molecular weights of PC samples before and after treatments.

Molecular weight distributions of polycarbonate were obtained using size exclusion chromatography (SEC). Multi-Detection measurements were carried with Viscotek system, GMHxl column at 40°C of Temperature, injection volume was 100 µL. All PC samples treated and listed in (Table 2) were dissolved in THF for 40 min, and analyzed three times.

## 3. Theoretical background(Kinetic model)

The change of the sample weight is registered as a function of time (t), and the conversion fraction (degree of degradation) is expressed as: $\alpha=\frac{Wi-Wt}{Wi}$

Where, $W_i$ is the initial sample weight, and $W_t$ is an actual weight at time t.

The fundamental rate equation used in all kinetic studies is generally described as

$$\frac{d\alpha}{dt} = k\, f(\alpha) \tag{1}$$

Where k is the rate constant, f (α) is the reaction model and α is the conversion fraction (degree of degradation).

The rate constant is usually described by the Arrhenius equation

$$k = A\, exp(-\frac{Ea}{RT}) \tag{2}$$

Where A is the pre-exponential factor, Ea the apparent activation energy, T the absolute temperature and R the gas constant.
Substituting Eq(2) in Eq(1) gives

$$\frac{d\alpha}{dt} = A\, exp(-\frac{Ea}{RT})\, f(\alpha) \tag{3}$$

In this work the activation energy was obtained from non-isothermal TGA. The methods used to calculate this kinetic parameter (Ea) is called model-free methods.

Friedman isoconversional method
The isoconversional method permits the estimation of apparent activation energy without the knowledge of reaction model. This procedure involves plotting ln (dα/dt) versus 1/T for fixed values of conversion (α) and at different heating rate, with the resulting line having slope proportional to Ea (Friedman, 1964).
Eq(3) can be written in logarithmic form:

$$ln(\frac{d\alpha}{dt}) = ln(A\, f(\alpha)) - \frac{Ea}{RT} \tag{4}$$

At a constant value of α, f(α) would be also constant and Eq(4) would be written in the form

$$ln(\frac{d\alpha}{dt}) = ln(const) - \frac{Ea}{RT} \tag{5}$$

The activation energy at a constant α value can be determined from the slope of the plot of the left hand side of Eq(5) against the inverse of the temperature, at constant values of α.

## 4. Results and discussion

### 4.1 TGA analysis

The experimentally obtained non-isothermal conversion (α−T) curves of non-used PC baby bottle (as example) for temperatures between under linear heating rate are presented in Figure 1.
It is seen that the conversion (α) increases with increasing temperature, and all polycarbonate samples curves have the same shape.

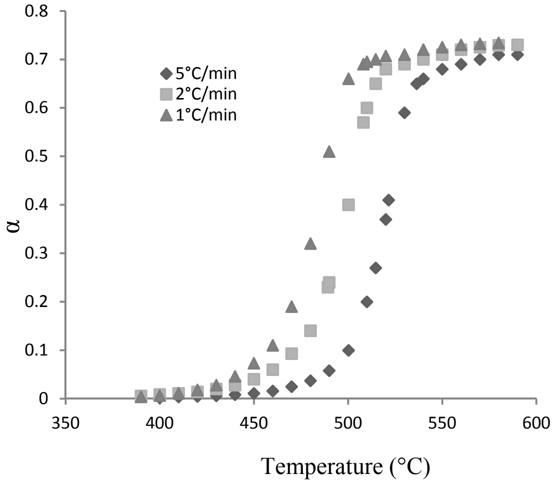

*Figure 1:Experimental curves obtained for the thermal decomposition of non-used polycarbonate baby bottle (PC19) under linear heating rate 1, 2 and 5°C min$^{-1}$.*

Polycarbonate activation energies
Figure 2 shows several of the isoconversional Friedman plots obtained from the simultaneous analysis, according with Eq(5) of the (α-T) curves shown in Figure.1 that were obtained under constant heating. The values of the activation energy calculated from the slope of the Friedman plots for different α values are included in Table 1 with their corresponding linear correlation coefficients. The results demonstrate that a constant activation energy Ea=172.46 kJmol$^{-1}$ has been obtained.
Activation energy, which is the energetic threshold for a chemical reaction, is commonly used to evaluate the thermal stability of polymer materials (Kitahara et al, 2010). From the values of Ea presented in Table.2 and shown in Figure.3, we can observe that Ea values changes as a function of temperature, pH, and contact time.

So, with regard to pH values, we conclude that the higher the temperature values are, the less Ea is obtained. The result allows us to conclude that the bonds between the polymer chains become weaker (aging and polymer fatigue) requires low energy to break them, the carbonate linkages are subjected to hydrolytic attack at high temperatures. This is more effective in used PCs than new ones.

The lowest Ea values are also obtained for samples treated in alkaline solutions. So, we concluded that in the case of pH, the polymer degradation rate in alkaline pH is fast and requires low energy.Although higher pH values should accelerate PC degradation and increase the BPA release (Krishnan et al, 1993).

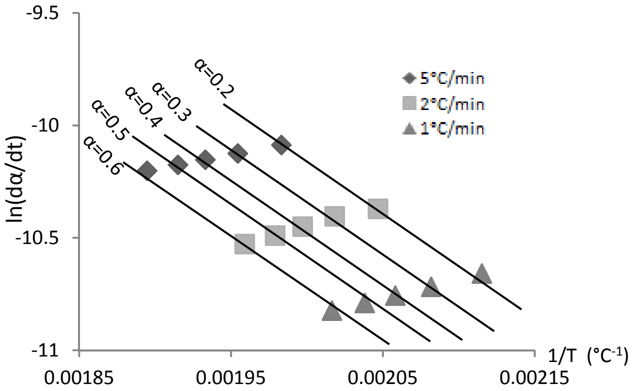

*Figure 2: Friedman plots of PC19 sample resulting for some selected* α values of the experimental curves presented in Figure.1.

*Table 1: Activation energy values for different values conversion and their correlation coefficients, obtained by Friedman isoconversional analysis for sample studied in Figure 1 (PC19).*

| α | Ea (kj mol$^{-1}$) | $r^2$ |
|---|---|---|
| 0.1 | 174.58 | 0.991 |
| 0.2 | 173.67 | 0.992 |
| 0.3 | 174.34 | 0.995 |
| 0.4 | 172.36 | 0.991 |
| 0.5 | 171.28 | 0.993 |
| 0.6 | 170.70 | 0.997 |
| 0.7 | 171.21 | 0.992 |
| 0.8 | 172.95 | 0.990 |
| 0.9 | 171.39 | 0.989 |

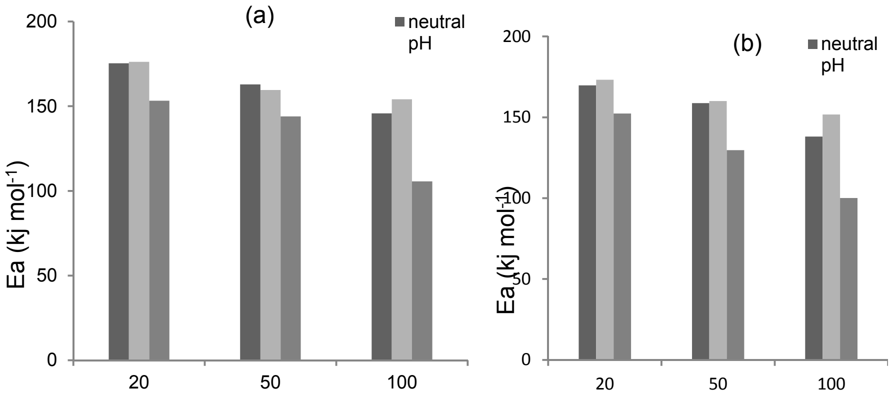

*Figure 3:Evolution of activation energy for all PC samples at different temperature:a) treated for 25h,b)50h.*

*Table 2: Activation energies and Molecular weights of PC samples after treatment conditions.*

| abbreviation | conditions | | | Ea (KJ mol$^{-1}$) | Mn (g mol$^{-1}$) | Mw (g mol$^{-1}$) |
|---|---|---|---|---|---|---|
| | T(°C) | pH | t (h) | | | |
| PC01 | 20 | 6.7 | 25 | 175.33 | 14,699 ± 105 | 35,277 ± 231 |
| PC02 | 20 | 1.8 | 25 | 176.25 | 14,442 ± 98 | 35,094 ± 286 |
| PC03 | 20 | 12.1 | 25 | 153.26 | 14,603 ± 80 | 35,047 ± 199 |
| PC04 | 50 | 6.7 | 25 | 162.89 | 12,781 ± 111 | 31,569 ± 301 |
| PC05 | 50 | 1.8 | 25 | 159.55 | 14,667 ± 113 | 35,787 ± 331 |
| PC06 | 50 | 12.1 | 25 | 143.98 | 11,406 ± 101 | 28,058 ± 308 |
| PC07 | 100 | 6.7 | 25 | 145.78 | 12,156 ± 97 | 29,903 ± 297 |
| PC08 | 100 | 1.8 | 25 | 154.12 | 14,819 ± 88 | 35,565 ± 343 |
| PC09 | 100 | 12.1 | 25 | 105.65 | 11,322 ± 74 | 28,305 ± 189 |
| PC10 | 20 | 6.7 | 50 | 169.78 | 14,743 ± 89 | 36,562 ± 332 |
| PC11 | 20 | 1.8 | 50 | 173.19 | 14,683 ± 91 | 35,532 ± 345 |
| PC12 | 20 | 12.1 | 50 | 152.32 | 13,408 ± 109 | 33,520 ± 264 |
| PC13 | 50 | 6.7 | 50 | 158.77 | 12,002 ± 71 | 29,404 ± 306 |
| PC14 | 50 | 1.8 | 50 | 160.02 | 13,945 ± 96 | 34,025 ± 357 |
| PC15 | 50 | 12.1 | 50 | 129.66 | 11,299 ± 83 | 28,021 ± 246 |
| PC16 | 100 | 6.7 | 50 | 138.11 | 11,978 ± 107 | 29,945 ± 209 |
| PC17 | 100 | 1.8 | 50 | 151.71 | 14,447 ± 121 | 35,395 ± 311 |
| PC18 | 100 | 12.1 | 50 | 100.13 | 10,541 ± 99 | 26,563 ± 251 |
| PC19 | without treatment | | | 172.46 | 12,099 ± 107 | 28,916 ± 207 |

## 4.2 SEC analysis

Changes in the molecular weight of the polycarbonate after different treatments and one sample undergone any treatment are shown in (Table 2).It is shown that the highest molecular weight of PC measured in all samples was 14,699 gmol$^{-1}$for sample treated in neutral pH at 20°C for 25h**.** The lowest was 10,541 g mol$^{-1}$ for samples treated in basic pH at 100°C for 50h. It is clear that the molecular weight of all PC samples decreases with increasing temperature, i.e. the molecular weight of samples treated in neutral pH for 25h was 14,699, 12781, and 12,156 g mol$^{-1}$ at 20, 50, and 100°C.

The influence of pH was also investigated. The molecular weight of PC samples reaches the highest value for PC samples treated in acid solution: 14,683, 13,945 and 14,447 g mol$^{-1}$ at 20, 50, and 100°C. The lowest values correspond to the samples treated in alkaline solution with 13,408, 11,299, and 10,541 g mol$^{-1}$ at 20, 50, and 100°C for the same duration of treatment (50h).

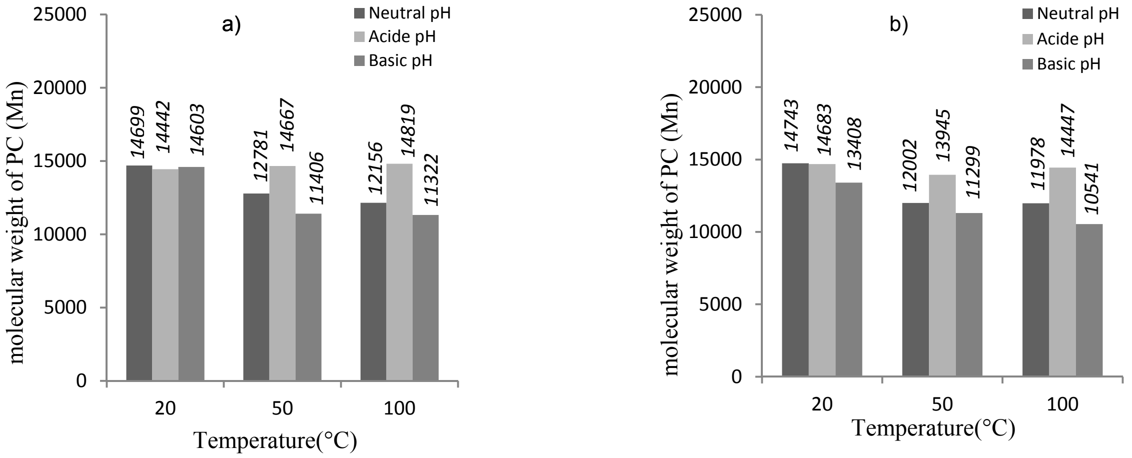

*Figure 4: Influence of treatment conditions on molecular weight for PC samples: a) treated for 25h, b) 50h*

The effect of usury time or treatment duration was demonstrated in (Figure 4). The molecular weight of all PC samples decrease with increasing duration treatment, i.e, the molecular weight for samples treated in neutral pH at 20°C for 25h and 50h was 14,699 and 14,743 g mol$^{-1}$.

These changes can be interpreted in molecular weight by the transfer reactions of the intermolecular chain derived from the degradation. The reaction at the end of the chains generates primary radicals. The trend for the weight average values is essentially as would be expected, with a decrease in Mn with increasing duration, temperature and pH.

Molecular masses of PC19 sample are strongly low; this case explains the phenomenon transport of non-polymerised monomer from polymer to solution. The presence of monomer and oligomer in the polymer decreases the average molecular weight, and treatments can be considered as washing/extracting operations before being degradation processes. It is worth mentioning that just after the first treatments, even the conditions are soft, and the masses decrease significantly.

## 5. Conclusion

The relationship between the changes in the molecular weights and the evolution of the activation energies of PC due to its aging was reported. The current work demonstrates that temperature, pH, and usury decrease the polymer molecular masses. We have also seen that the higher the temperature and pH values are, the less Ea is obtained, and a low pH appear to have a preservative effect on the polymer . The result allows us to conclude that the bonds between the polymer chains become weaker (aging and fatigue polymer) requires low energy to break them, the carbonate linkages are subjected to hydrolytic attack at high temperatures and pH,

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