Journal of Thermal Analysis and Calorimetry, Vol. 79 (2005) 383–387

APPLICATION OF MODEL-FREE KINETICS TO THE STUDY OF THERMAL DEGRADATION OF POLYCARBONATE

H. Polli[1], *L. A. M. Pontes*[1] *and A. S. Araujo*[2*]

[1]UNIFACS – Department of Chemical Engineering, Av. Cardeal da Silva, 132, 40.220-141, Salvador, BA, Brazil
[2]Federal University of Rio Grande do Norte, Department of Chemistry, CP 1662, 59078-970, Natal, RN, Brazil

The degradation kinetics of a linear (LPC) and a branched polycarbonate (BPC) was investigated by means of thermogravimetric analysis. The samples were heated from 30 to 900°C in nitrogen atmosphere, with three different heating rates: 5, 10 and 20°C min^{-1}. The Vyazovkin model-free kinetics method was applied to calculate the activation energy (E) of the degradation process as a function of conversion and temperature. The LPC shows that starts to loose mass slightly over 350°C and the BPC, slightly over 400°C. This shows that the BPC has more thermal resistance than LPC, and E for BPC was bigger than E for LPC.

Keywords: *model-free kinetics, polycarbonate, thermal degradation, thermogravimetry*

Introduction

Polycarbonate, mainly obtained from bisphenol-A (now referred as PC), is one of the most used engineering thermoplastics. The PC is a condensation polymer that forms a bulky stiff molecule, which promote rigidity, strength, creep resistance and high heat deflection temperature. The bulk crystallization chain is very difficult, so the PC is typically amorphous, exhibiting good transparency. The bulk amorphous chains produce considerable free volume, resulting in a polymer with high ductility and impact resistance [1].

The PC is applied in many areas such as: construction, electrical, automotive, aircraft, medical and packaging applications; recently in car lights and laser optical data storage (compact disks). The price of PC is between the commodity thermoplastics and special engineering thermoplastics, which makes this material one of the largest volume engineering thermoplastic, only after the polyamides [2, 3].

Since PC is normally processed in temperatures over 300°C (by injection molding process for example), causing degradation to some extent, several papers about the thermal decomposition in PC have been published [4–6], and many structures formed in PC chains during thermal degradation have been elucidated by means of various analytical techniques such as pyrolysis-mass spectroscopy, pyrolysis-gas chromatography and assisted laser desorption ionization. A serial of papers published by Montaudo *et al*. [7–11] and McNeill *et al*. [12, 13] are good examples of these works.

The PC samples used in this study were synthesized by continuous interfacial polycondensation. The disodium salt of bisphenol-A in aqueous alkaline solution reacts with phosgene in a tubular reactor in medium of an inert organic solvent; the organic solvent dissolves the phosgene in the beginning of the reaction, and acts as a medium for the arylchloro carbonates and oligocarbonates that are formed in solution. In the second step of the reaction the arylchlorocarbonates and oligocarbonates are condensed in a reactor under stirring to obtain the high molecular mass PC polymer over a catalyst. After the polycondensation reaction, the PC polymer is washed with an acid solution, and an alkaline solution, and again with an acid solution; the finishing operation includes drying and palletizing.

The molecular mass is controlled by addition of monofunctional compounds during the polycondensation reaction, permitting to obtain commercial PC grades with molecular mass from 15.000 to 30.000 g mol^{-1}. Figure 1 shows the schematic chemical reaction [1, 3, 14, 15].

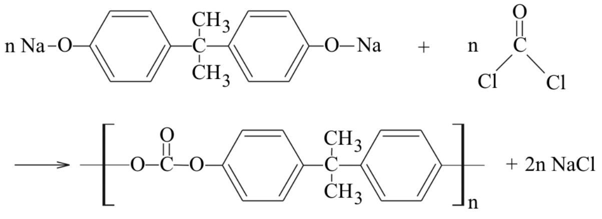

Fig. 1 Schematic chemical reaction for PC synthesis

---

[*] Author for correspondence: asa-ufrn@usa.net

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

The polymers are complex systems that becomes imprecise the determination of the kinetics parameters, for example activation energy, temperature where the degradation process starts and conversion rates. Many thermal analytical methods have been used to study the thermal degradation process in polymers (TG, DSC, DMA, TMA). In the last 10 years, some works have been published about kinetics of the thermal degradation process for polymers [16–19].

The model-free kinetics method proposed by Vyazovkin [20–23] to determine the kinetics parameters of a chemical reaction, has been applied recently to determine the thermal degradation process in many polymers with very good results [20–24].

However, no work was found in the literature about the kinetics parameters of the thermal degradation process in PC polymer using the model-free kinetics. In this work, we investigated the thermogravimetric kinetics for the degradation of two different PC: linear polycarbonate (LPC) and branched polycarbonate (BPC); the work was conducted under nitrogen atmosphere and different heating rates. By using integral curves and the Vyazovkin model-free kinetics, the activation energy (*E*), the conversion rates and polymer degradation time as a function of temperature were estimated.

Experimental

LPC and BPC were synthesized by continuous interfacial polycondensation. Prior the measurements, the samples were dried in a hot and forced air stove at 120°C by 4 h and kept in a desiccant flask. The samples were characterized with some ASTM methods, and the results are showed in the Table 1.

Table 1 Some results for characterization of LPC and BPC

Characteristic	Standard method	Results	
		LPC	BPC
$\overline{Mw}$/g mol^{-1}	ASTM-D-3536/91	21.90	22.50
$\overline{Mw}$/g mol^{-1}	ASTM-D-3536/91	6.60	8.10
PD	ASTM-D-3536/91	3.32	2.78
MFI-300°C/1.2 kg /g 10 min^{-1}	ASTM-D-1238	5.88	5.83
MFI-300°C/12 kg /g 10 min^{-1}	ASTM-D-1238	69.61	85.53
RMFI		11.83	14.67

The molecular mass measurements were conduced by Gel Permeation Chromatography (GPC). It must be noted that LPC and BPC presented values of molecular mass ($\overline{Mw}$) very closed one with another, with the purpose to avoid some influence of the molecular mass over the results.

The characteristic RMFI means Melt Flow Index Rate. The value is a relation between the MFI at 300°C/12 kg and the MFI at 300°C/1.2 kg. If the value was higher than 12.00 (even 20.00, at least), the polycarbonate is branched, if not, it is linear. This is a fast method to determine if an unknown polycarbonate is branched or not; however, this value does not inform the degree of branching in the polycarbonate.

The thermal degradation of LPC and BPC was carried out using a thermobalance Mettler-STGA 851, in the temperature range of 30–900°C, under nitrogen atmosphere (flow rate of 25 mL min^{-1}), using alumina crucible of 70 μL and heating rates of 5, 10 and 20°C min^{-1}. In each experiment, a mass of ca. 25 mg of sample mass was used. The Vyazovkin model-free kinetics method was applied to this process.

Model-free kinetics theory

The reaction rate of a thermal and catalytic reaction depends on conversion (α); temperature (T) and time (t). For each process, the reaction rate as a function of conversion, $f(\alpha)$, is different and must be determined from experimental data. For single reactions, the evaluation of $f(\alpha)$ with n^{th} order is possible. For complexes reactions, that occurs in polymer degradation for example, the evaluation of $f(\alpha)$ is complicated and, in general, unknown. In the last case, the n^{th} order algorithm causes unreasonable data.

Applying the model-free kinetics method, accurate evaluations of complexes reactions can be performed, in order to obtain reliable and consistent kinetic information about the overall process.

The model-free kinetics is a computer programmer basing on the Vyazovkin theory for the kinetics studies of complex reaction. In his approach no model is applied. The data in this approach is gathered during numerous experiments. The approach follows all points of conversion from multiple experiments instead of a single one.

Model-free kinetics method is based on an isoconversional computational technique that calculates the effective activation energy (E) as a function of the conversion (α) of a chemical reaction, $E=f(\alpha)$. A chemical reaction is measured at least in three different heating rates (β) and the respective conversion curves are calculated out of the TG measured curves. For each conversion (α), $\ln\beta/T^2$ is plotted *vs*. $1/T_\alpha$, giving rise to a straight line with slope $-E_\alpha/R$, therefore providing the activation energy as a function of conversion [24–28].

Results and discussion

The TG/DTG curves for LPC and BPC at different heating rates are shown in Figs 2 and 3, respectively. Both curves indicate that LPC and BPC show a thermal decomposition in one step, resulting in a residue of ca. 20% for LPC and 23% for BPC at 900°C. The curve in the Fig. 2 shows that LPC is stable until 380°C (with a heating rate of 5°C min^{-1}); in the curve in the Fig. 3 one can see that BPC is stable up to 430°C (with a heating rate of 5°C min^{-1}).

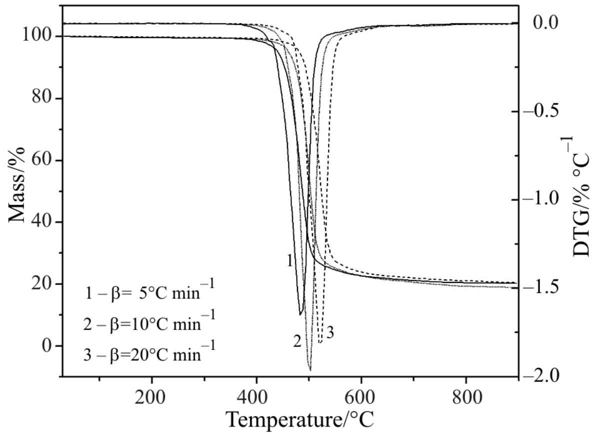

Fig. 2 TG and DTG curves for LPC at different heating rates

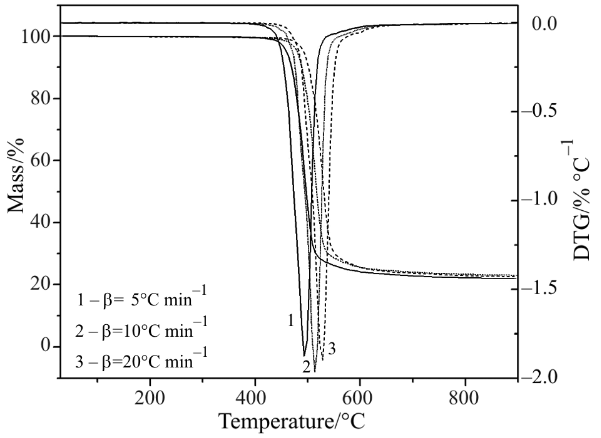

Fig. 3 TG and DTG curves for BPC at different heating rates

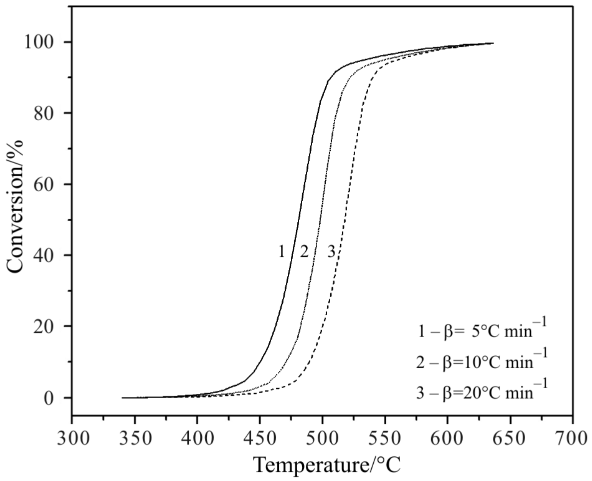

Fig. 4 Conversion of LPC as a function of temperature

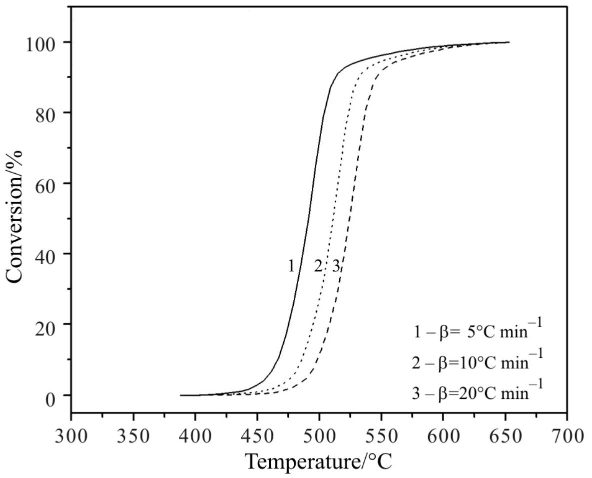

Fig. 5 Conversion of BPC as a function of temperature

It is observed that LPC exhibits a pronounced mass loss in the 350–620°C temperature range and, for BPC, the mass loss was observed in the range of 420–650°C. These ranges were selected for kinetics studies. Figures 4 and 5 show the degree of conversion as a function of temperature relative to the degradation of LPC and BPC, respectively. It is clearly noted that the degradation of LPC occurs with less energy when compared to BPC. This means that to produce some part for consumption in BPC (by injection molding for example) higher temperature is necessary to melt the polymers in order to avoid damages in the molecular structure and, consequently at the molded part; if the temperature was lower than the necessary, the molded part will exhibit a great residual tension or poor welding line, consequently the part will broken during its usage.

The observation made from curves in Figs 4 and 5 is more evident when examining the plots of degree of conversion *vs*. time, as it is shown in Fig. 6 for LPC and BPC, that were obtained from model-free data [23]. This graph shows comparative curves between LPC and BPC on four sets of temperature: 350, 400, 450 and 500°C.

One can see clearly that the time for the degradation of LPC and BPC decreases considerably as a function of temperature. At 350°C, only LPC exhibits some degradation as a function of time, for BPC one can see (Fig. 3) that the degradation starts slight over 400°C. At 400°C, LPC needs ca. 450 min to degrade 85% of the initial mass, and BPC needs the same time to reach 65% of degradation. However, at 450 and 500°C, practically both samples degraded with the same time and with the same conversion.

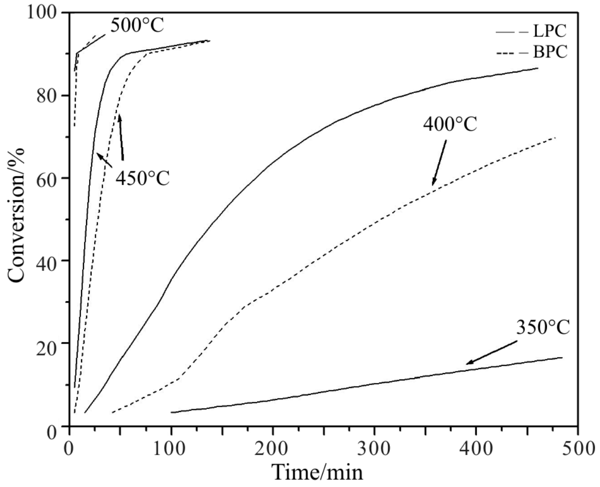

Fig. 6 Conversion of LPC and BPC as a function of time at different temperatures

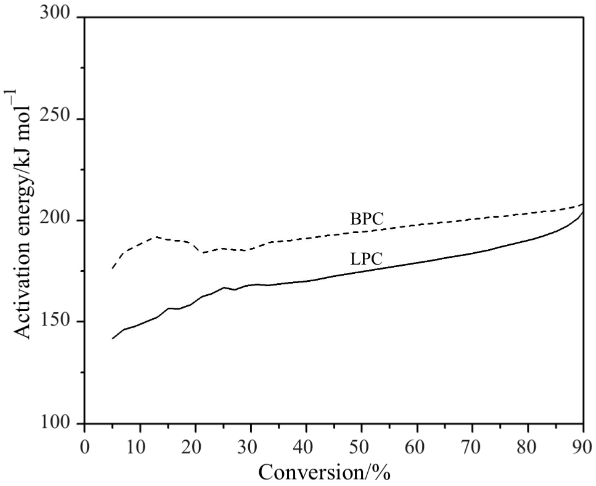

Fig. 7 Activation energy of LPC and BPC using the model-free kinetics

The activation energy (*E*) for the thermal degradation process of LPC and BPC, predicated by model-free kinetics theory is shown in Fig. 7; the values for *E* were obtained as a medium value between 20 and 90% of conversion, and a standard deviation was calculated. Note that the activation energy for BPC (193±7 kJ mol^{-1}) is 10% higher than for LPC (177±10 kJ mol^{-1}). This is in agreement with the fact that to mold some part in BPC, more temperature is required to melt it (consequently, more energy), than to LPC.

Also, it was possible to estimate the temperature of the degradation process for LPC and BPC, predicted by model-free data, providing an estimation of the time required to the degradation reaction, as summarized in Tables 2 and 3, respectively.

It was observed, for instance, for LPC to achieve 10% of degradation, is necessary to submit it at 433°C for a time of 10 min; whereas for BPC, to achieve the same degradation in the same time, 448°C temperature is necessary. Now, if one examines what happens in 90% of degradation, it is clear that for LPC, is necessary to submit it at 488°C for 10 min; and, for BPC at the same conversion, a temperature of 495°C necessary for the same period of time.

Considering the common process that are used to transform the PC polymer in parts for usage (by injection, extrusion and blow molding), one have to know the temperature of the molten phase that is purged by the machine (the temperature of the molten phase is the temperature set on the machine plus the temperature that result as a consequence of the mechanical work of the material inside of the machine).

Table 2 Isoconversion parameters for LPC

Time/min	Conversion/%										
	0	10	20	30	40	50	60	70	80	90	100
10	411.1	433.3	445.2	452.5	458.1	462.9	467.3	471.7	477.2	488.9	565.4
20	392.6	414.4	427.1	435.0	440.4	445.5	450.1	454.8	460.6	473.0	551.5
30	382.2	403.9	416.9	425.1	430.5	435.7	440.4	445.2	451.2	464.0	543.5
40	375.0	396.6	409.9	418.2	423.6	428.9	433.6	438.6	444.7	457.8	538.0
50	369.6	391.0	404.5	413.0	418.4	423.7	428.5	433.5	439.7	453.0	533.7
60	365.2	386.6	400.2	408.8	414.1	419.5	424.4	429.4	435.7	449.2	530.3
70	361.5	382.8	396.6	405.2	410.6	416.0	420.9	426.0	432.3	446.0	527.4
80	358.4	379.6	393.5	402.2	407.6	413.0	418.0	423.1	429.4	443.2	524.9
90	355.6	376.8	390.8	399.6	404.9	410.4	415.4	420.5	426.9	440.8	522.7
100	353.2	374.3	388.4	397.2	402.5	408.0	413.1	418.2	424.7	438.6	520.8
110	351.0	372.1	386.2	395.1	400.4	405.9	411.0	416.2	422.6	436.7	519.0
120	349.0	370.1	384.3	393.2	398.5	404.0	409.1	414.3	420.8	434.9	517.5

Table 3 Isoconversion parameters for BPC

Time/min	Conversion/%										
	0	10	20	30	40	50	60	70	80	90	100
10	–	448.7	457.2	464.0	469.4	473.7	477.7	481.7	486.4	495.9	559.3
20	–	433.2	441.0	447.6	453.2	457.5	461.6	465.7	470.4	479.9	543.9
30	–	424.4	431.8	438.2	444.0	448.4	452.5	456.6	461.4	470.8	535.2
40	–	418.3	425.5	431.8	437.6	442.0	446.2	450.3	455.1	464.5	529.1
50	–	413.7	420.6	426.8	432.7	437.2	441.4	445.5	450.3	459.7	524.4
60	–	409.9	416.7	422.9	428.8	433.3	437.5	441.6	446.4	455.8	520.6
70	–	406.8	413.4	419.5	425.5	430.0	434.2	438.4	443.2	452.6	517.5
80	–	404.1	410.6	416.7	422.7	427.2	431.4	435.6	440.4	449.8	514.8
90	–	401.7	408.2	414.2	420.2	424.7	429.0	433.2	437.9	447.3	512.4
100	–	399.6	406.0	412.0	418.0	422.5	426.8	431.0	435.8	445.1	510.3
110	–	397.7	404.0	410.0	416.1	420.6	424.8	429.0	433.8	443.2	508.4
120	–	396.0	402.2	408.1	414.3	418.8	423.1	427.3	432.0	441.4	506.6

Conclusions

The model-free kinetics applied in the research has proven to be comfortable evaluation tool in case of the study of degradation process of the PC. The thermogravimetric measurements provide an important link between the degradation temperature and thermal profiles of the PC samples. The results of activation energy show that the BPC has more thermal resistance than LPC, which means, BPC needs more temperature to process it to produce parts for usage.

Acknowledgements

The authors gratefully acknowledge FAPESB – Fundação de Apoio a Pesquisa do Estado da Bahia, for financial support, Policarbonatos do Brasil S/A for supply the samples, CNPq and FINEP/CTPetro.

References

1 D. G. Legrand and J. T. Bendler Eds, Handbook of Polycarbonate Science and Technology, Marcel Dekker Inc., USA 2000.
2 R. D. Deanin, Engineering Thermoplastics, Concise Polymeric Materials Encyclopedia, CRC Press, USA 1999.
3 L. Bottenbruch Ed., Engineering Thermoplastics, Hanser Publishers, USA 1996.
4 A. C. Hagenaars, W. J. Goddrie and Ch. Bailly, Polymer, 43 (2002) 5043.
5 S. Tsuge, K. Oba and H. Ohtani, Polym. Degrad. Stab., 74 (2001) 171.
6 S. Tsuge, K. Oba, Y. Ishida, Y. Ito and H. Ohtani, Macromolecules, 33 (2000) 8173.
7 G. Montaudo, S. Carroccio, C. Puglisi and F. Samperi, Macromolecules, 32 (1999) 8821.
8 G. Montaudo, C. Puglisi and L. Sturiale, Macromolecules, 32 (1999) 2194.
9 G. Montaudo, C. Puglisi and S. Carroccio, J. Anal. Appl. Pyrolysis, 64 (2002) 229.
10 G. Montaudo, C. Puglisi and S. Carroccio, Macromolecules, 35 (2002) 4297.
11 G. Montaudo, C. Puglisi and S. Carroccio, Polym. Degrad. Stab., 77 (2002) 137.
12 I. C. McNeill and A. Rincon, Polym. Degrad. Stab., 31 (1991) 163.
13 I. C. McNeill and A. Rincon, Polym. Degrad. Stab., 39 (1993) 13.
14 H. Schenell, Chemistry and Physics of Polycarbonates, John Wiley & Sons Inc., USA 1964.
15 J. Brydson, Plastics Materials, 7th Ed., Butterworth Heinemann, Great Britain 1999.
16 C. Roy, J. Yang and R. Miranda, Polym. Degrad. Stab., 73 (2001) 455.
17 F. M. B. Coutinho, M. C. Delpech and M. A. S. Habibe, Polym. Test., 21 (2002) 155.
18 A. Ksiazczak, H. Boniuk and S. Cudzilo, J. Therm. Anal. Cal., 74 (2003) 569.
19 S. M. Dakka, J. Therm. Anal. Cal., 74 (2003) 729.
20 A. S. Araújo, V. J. Fernandes Jr. and G. J. T. Fernandes, Thermochim. Acta, 392 (2002) 55.
21 S. Vyazovkin and V. Goriyachko, Thermochim. Acta, 194 (1992) 221.
22 S. Vyazovkin and N. Sbirrazzuoli, Anal. Chim. Acta, 355 (1997) 175.
23 S. Vyazovkin and C. A. Wight, Thermochim. Acta, 340 (1999) 53.
24 S. Vyazovkin, Int. J. Chem. Kinet., 28 (1996) 95.
25 V. J. Fernandes Jr., A. S. Araújo, V. M. Fonseca, N. S. Fernandes and D. R. Silva, Thermochim. Acta, 392 (2002) 71.
26 S. Vyazovkin, I. Dranca, X. Fan and R. Advincula, Macromol. Rapid Commun., 25 (2004) 498.
27 J. D. Peterson, S. Vyazovkin and C. A. Wight, Macromol. Chem. Phys., 202 (2001) 775.
28 J. D. Peterson, S. Vyazovkin and C. A. Wight, J. Phys. Chem. B, 103 (1999) 8087.