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THERMAL ANALYSIS KINETICS APPLIED TO FLAME RETARDANT POLYCARBONATE

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The degradation kinetics of polycarbonate with flame retardant additive 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_a) of the degradation process as a function of conversion and temperature. The results indicated that the polycarbonate without flame retardant additive starts to loose mass slightly over 380°C and the polycarbonate with flame retardant additive, slightly over 390°C (with heating rate of 5°C min^{-1}). The activation energy for flame retardant polycarbonate and normal polycarbonate were 190 and 165 kJ mol^{-1}, respectively.

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

Introduction

Flame resistance can be defined as a low speed of the burn process when in contact with hot sources, and the fast extinction of the flame when the source is removed [1]. Some polymers have this characteristic, or part of it; but, in many cases a flame retardant additive must be added to the polymer in order to obtain flame resistance characteristics.

A flame retardant additive act in the polymer at different ways: interfere chemically with the mechanism of flame propagation; can produce non combustibles gaseous minimizing the amount of air supplied to the flame; can react or change its state absorbing heat; and, can form a shell around the flame, avoiding the oxygen feeding to the flame.

The polycarbonate polymer has a good flame resistance in natural state. However, this characteristic can be further improved through the incorporation of appropriated flames retardant additives. Certain alkaline or alkaline earth sulfonates have proven to be particularly useful because they are added in such small amounts that most of the transparency of the polycarbonate is retain [2, 3]. Other groups of salts also have been reported, such as sulfonamide salts [4], perfluorborates [5], ether salts [6] and calcium titanates [7]. A further degree of flame resistance can be obtained through the combination of these salts with an antidrip compounds such as polytetrafluoroethylene [8, 9], that cause some compromising of the transparency, or hologenated compounds, like tetrachlorophthalimide [10] and tetrabromobisphenol-A oligocarbonate [11]. Halogen-free flames retardant also have been reported, such as polyphenylene sulfide [12] and polyphosphonate [13].

Many evaluation methods of tests can be applied to determine the efficiency of the flame resistance in polymers, such as UL-94 (serious of flammability tests developed by Underwriters Laboratory), ASTM-D-635-77 (measurements of time and extension of the combustion), ASTM-D-2863-77 (determination of the limited oxygen index), ASTM-D-1929 (determination of the self-ignition temperature), ASTM-D-2843 (determination of the smoke density), ASTM-E-662 (determination of the smoke emission), ISO-5657 (determination of the ignition time).

The combustion is a sequence of complexes physical and chemical process. The combustion of polymers is a kind of thermal degradation process. In this way, the determination of the kinetics parameters during this kind of thermal degradation, for example the activation energy, temperature where the degradation process starts and conversion reaction rates, will be helpful to determine the efficiency of the flame retardant additives added to the polymers. Many thermal analytical methods have been used to study the various degradation processes in polymers (TG, DSC, DMA, TMA); in the last years, some works have been published about kinetics of the degradation process for polymers [14, 15].

The model-free kinetics method proposed by Vyazovkin [16] to determine the kinetics parameters

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of a chemical reaction, has been applied to determine the thermal degradation process in many polymers with good results [17–20].

No work was found in the literature about the determination of the activation energy to estimate the efficiency of the flame retardant additive in the thermal degradation process in polycarbonate using the model-free kinetics. In this study, we investigated the kinetics of the thermodegradation process in two polycarbonates: VR-PC (no flame retardant type) and VRY-PC (flame retardant type), in order to define the activation energy required to the degradation process.

Experimental

The VR-PC and VRY-PC polycarbonates were synthesized by continuous interfacial polycondensation. Both types of polycarbonates were extruded in a double screw extrusion machine with a normal antioxidant and lubricant additives for this kind of polymer; in the VRY-PC type was added ca. 0.1% of an alkaline salt of a perfluorbutane sulfonic acid as a flame retardant additive. 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 thermal degradation of both grades was carried out using a thermobalance Mettler-TG/SDTA 851, at temperature range from 30 to 900°C, under nitrogen atmosphere (flow 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 was used. The Vyazovkin model-free kinetics method was applied to this process.

Results and discussion

TG curves for VR-PC and VRY-PC types at different heating rates are shown in the Figs 1 and 2, respectively. Both curves indicate that both types of PC show a thermal decomposition in one step, resulting in a residue of ca. 18% at 900°C. The curve in Fig. 1 shows that VR-PC type is stable until 380°C (with a heating rate of 5°C min^{-1}); in the curve in Fig. 2 we can see that VRY-PC is stable until 390°C (with a heating rate of 5°C min^{-1}).

It is observed that VR-PC type exhibit a pronounced mass loss in the range of 350–650°C and, the same is observed for VRY-PC type. This range was selected for kinetics studies by means of model-free. Figs 3 and 4 show the degree of conversion as a function of temperature relative to the degradation of both grades of polycarbonate. It is noted that the degradation of VR-PC type occurs with almost the same energy when compared with VRY-PC type.

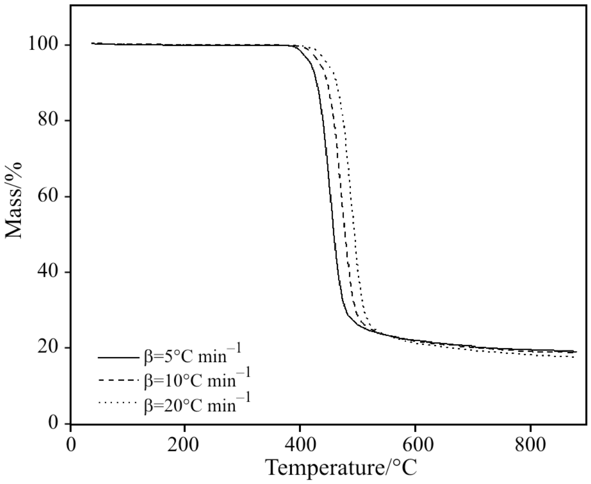

Fig. 1 TG curve for VR-PC type at different heating rates

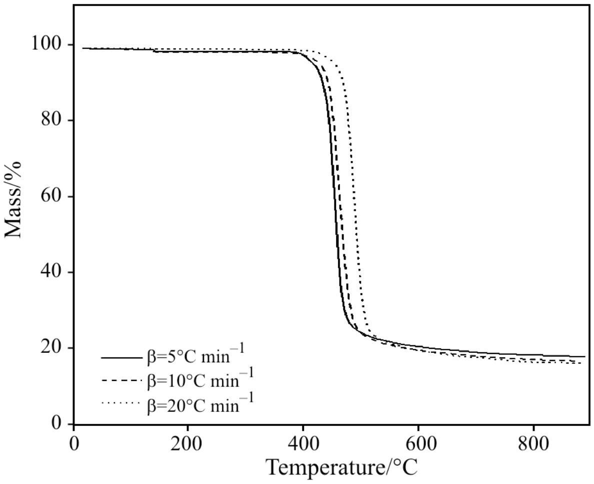

Fig. 2 TG curves for VRY-PC type at different heating rates

The observation made from curves in Figs 3 and 4 is more evident when is examined the plots of degree of conversion *vs*. time, as shown in Fig. 5 for VR-PC and VRY-PC types, which were obtained from model-free data. Those graphs show a comparative curves on four sets of temperature: 350, 400, 450 and 500°C.

We can see clearly that the time for the degradation of VR-PC and VRY-PC decrease considerably as a function of temperature. At 350°C, VR-PC degrade faster than VRY-PC; to degrade 10%, VR-PC needs ca. 150 min of exposure in this temperature and VRY-PC needs ca. 290 min. At 400°C, the same is observed; however, VR-PC needs ca. 10 min of exposure in this temperature and VRY-PC needs ca. 20 min to degrade. At 450 and 500°C, practically both PC types degrade in a few minutes when exposed in these temperatures.

Model-free kinetics method is based on an isoconversional computational technique that calculates the effective activation energy (E_a) as a function of the conversion (α) of a chemical reaction, $E=f(\alpha)$. A

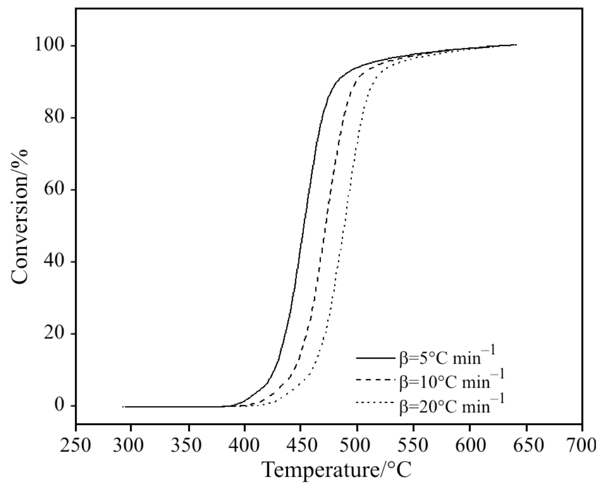

Fig. 3 Conversion of VR-PC type as a function of temperature

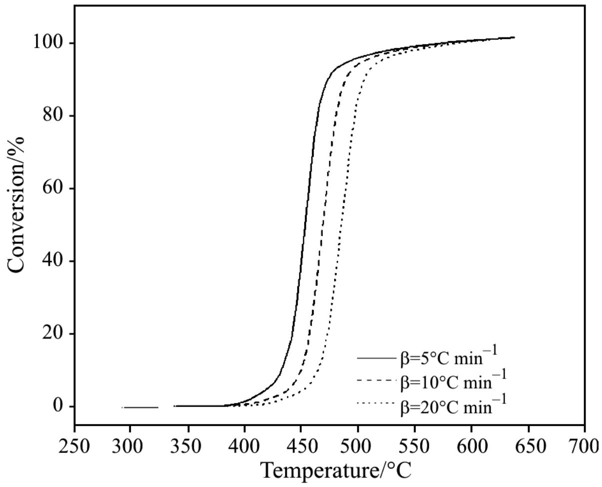

Fig. 4 Conversion of VRY-PC type as a function of temperature

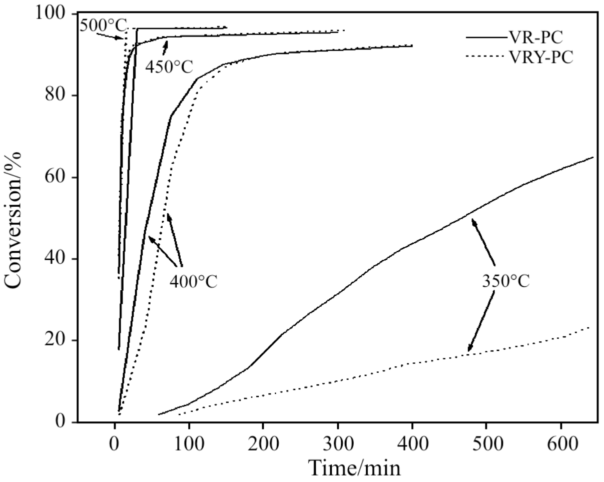

Fig. 5 Conversion of VR-PC and VRY-PC as function of time at different temperatures

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 $-E_a\alpha/R$, therefore providing the activation energy as a function of conversion.

The theory is based on the assumption that the reaction rate is:

$$\frac{d\alpha}{dt}=ke^{\frac{-E}{RT}}f(\alpha) \qquad (1)$$

and that the activation energy $E_a(\alpha)$ is constant for a certain value of conversion α (iso-conversional method). Taking the reaction rate Eq. (1), presented as $f(\alpha)$ and dividing by the heating rate $\beta=dT/dt$:

$$\frac{d\alpha}{dt}=kf(\alpha)\Rightarrow\frac{d\alpha}{dT}=\frac{k}{\beta}f(\alpha) \qquad (2)$$

where $d\alpha/dt$=reaction rate (s^{-1}); k=velocity constant (s^{-1}); α=conversion; β=heating rate ($K\ s^{-1}$).

Substituting k on Eq. (2) by the Arrhenius equation ($k=k_0e^{-E_a/RT}$) and rearranging gives:

$$\frac{1}{f(\alpha)}d\alpha=\frac{k_0}{\beta}e^{-E_a/RT}dT \qquad (3)$$

The integration of Eq. (3) up to conversion α (at the temperature T) gives:

$$\int_0^{\alpha}\frac{1}{f(\alpha)}d\alpha=\frac{k_0}{\beta}\int_{T_0}^{T}e^{-E_a/RT}dT \qquad (4)$$

where

$$\int_0^{\alpha}\frac{1}{f(\alpha)}=g\alpha$$

Since $E_a/2RT$ on Eq. (4) is much more bigger than 1, the temperature integral can be approximated by:

$$\int_{T_0}^{T}e^{-E_a/RT}dT\approx\frac{R}{E_a}T^2e^{-E_a/RT} \qquad (5)$$

Substituting the Eq. (5) on Eq. (4), rearranging and logarithmising, gives:

$$\ln\frac{\beta}{T^2\alpha}=\ln\left[\frac{Rk_0}{E_a\alpha g(\alpha)}\right]-\frac{E_a\alpha}{R}\frac{1}{T\alpha} \qquad (6)$$

Equation (6) is defined as a dynamic equation, which is used for the determination of the activation energy (E_a) for all conversion values (α).

The activation energy (E_a) for the thermal degradation process of VR-PC and VRY-PC grades, predicated by model-free kinetics theory is shown in Fig. 6; the values for E_a were obtained as a medium value between 10 and 80% of conversion, and a stan-

Table 1 Temperature of the degradation process for VR-PC type

Time/min	Conversion/%										
	10	20	30	40	50	60	70	80	90	95	99
10	407.9	417.9	424.9	429.7	434.9	439.6	444.7	451.1	464.0	495.0	548.9
20	392.3	401.2	408.0	412.7	417.9	422.5	427.6	434.2	448.6	483.5	541.6
30	383.5	391.8	398.5	403.1	408.4	412.9	417.9	424.8	439.9	476.9	537.4
40	377.4	385.3	391.9	396.5	401.8	406.2	411.3	418.2	433.8	472.3	534.5
50	372.7	380.4	386.9	391.4	396.7	401.1	406.2	413.2	429.2	468.8	532.2
60	368.9	376.4	382.8	387.3	392.6	397.0	402.1	409.1	425.5	466.0	530.4
70	365.8	373.0	379.4	383.9	389.2	393.6	398.7	405.8	422.3	463.6	528.8
80	363.1	370.2	376.5	381.0	386.3	390.6	395.7	402.9	419.7	461.5	527.5
90	360.7	367.7	374.0	378.4	383.8	388.1	393.1	400.3	417.3	459.7	526.3
100	358.6	365.4	371.7	376.2	381.5	385.8	390.9	398.1	415.2	458.1	525.2
110	356.7	363.4	369.7	374.1	379.5	383.7	388.8	396.0	413.3	456.6	524.3
120	355.0	361.6	367.9	372.3	377.6	381.8	386.9	394.2	411.6	455.3	523.4

Table 2 Temperature of the degradation process for VRY-PC type

Time/min	Conversion/%										
	10	20	30	40	50	60	70	80	90	95	99
10	418.4	427.5	431.8	435.3	439.0	442.1	445.5	450.2	460.9	492.1	554.9
20	403.2	412.9	417.1	420.5	424.0	426.9	430.2	434.8	446.2	480.7	546.7
30	394.6	404.7	408.8	412.0	415.5	418.3	421.6	426.1	437.9	474.2	541.9
40	388.7	399.0	403.0	406.2	409.7	412.3	415.5	420.0	432.1	469.6	538.6
50	384.1	394.6	398.6	401.7	405.2	407.8	410.9	415.4	427.6	466.1	536.1
60	380.4	391.1	395.1	398.1	401.5	404.1	407.2	411.7	424.1	463.3	534.0
70	377.4	388.1	392.1	395.1	398.5	401.0	404.1	408.6	421.1	460.9	532.2
80	374.7	385.6	389.5	392.5	395.9	398.4	401.5	405.9	418.5	458.8	530.7
90	372.4	383.4	387.3	390.2	393.6	396.0	399.1	403.5	416.2	457.1	529.4
100	370.4	381.4	385.3	388.2	391.6	394.0	397.0	401.4	414.2	455.5	528.2
110	368.5	379.6	383.5	386.4	389.8	392.1	395.2	399.6	412.4	454.0	527.1
120	366.8	378.0	381.8	384.7	388.1	390.5	393.5	397.9	410.8	452.7	526.1

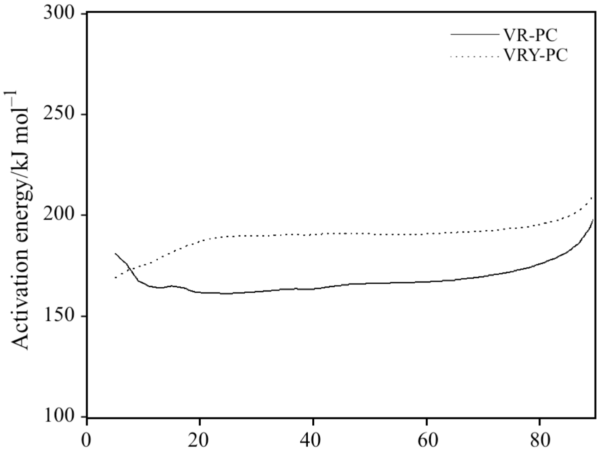

Fig. 6 Activation energy of VR-PC and VRY-PC grades using the model-free kinetics

dard deviation was calculated. Note that the activation energy for VRY-PC grade (190±4 kJ mol^{-1}) is higher than for VR-PC grade (165±3 kJ mol^{-1}). This means that the flame retardant additive is effective to retard the degradation process.

Also, it was possible to estimate the temperature of the degradation process for VR-PC and VR-PC types, predicted by model-free data, providing an estimation of the time required to the degradation reaction, as summarized in Tables 1 and 2, respectively.

It was observed, for instance, for VR-PC type to achieve 10% of degradation, is necessary to submit it at 408°C for a period of time of 10 min; whereas for VRY-PC type, to achieve the same degradation in the same time, is necessary a temperature of 418°C. These results come to show the potentialities of the isoconversion method in the estimate of time and temperatures necessary the degradation of polymers and other organic substances [21, 22].

Conclusions

The model-free kinetics applied in this study has proven to be an evaluation tool in case of the study of degradation process of the PC with and without flame retardant additive, even considering the small percentage added to the polymer. The thermogravimetric measurements provide an important link between the degradation temperature and thermal profiles of both PC samples. The results of activation energy shown that the VRY-PC polycarbonate type with flame retardant additive has more thermal resistance than VR-PC polycarbonate without flame retardant additive, which means, VRY-PC type is more resistant to burn than VR-PC type.

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