A KINETIC STUDY OF THE THERMAL AND OXIDATIVE DEGRADATIONS OF A NEW POLY(ARYLENE)ETHER COPOLYMER

L. Abate, I. Blanco, A. Pappalardo and A. Pollicino

Dipartimento di Metodologie Fisiche e Chimiche per l'Ingegneria, University of Catania, Viale A. Doria 6, 95125 Catania, Italy

Abstract

The degradation of a new thermoplastic poly(arylene)ether copolymer was carried out in both dynamic and isothermal heating conditions, under nitrogen flow and in a static air atmosphere. The measurements showed that the copolymer degraded through two stages in both investigated environments with the formation of a stable residue in N_2 and complete mass loss in air. The apparent activation energy values associated with the degradation processes were evaluated. The obtained results suggested different degradation mechanisms between N_2 and air. Results were discussed and compared with those obtained for several polymers previously investigated.

Keywords: kinetics, poly(arylene)ether, thermal degradation

Introduction

In the last decades the interest of many international polymers producers has been devoted to the research of new materials having favourable properties to be used as matrices for high performance composites. Thermosetting polymers have been largely used to this aim, but some aromatic thermoplastic polymers, and polyetherketones and polyethersulfones in particular, seem to be suitable for this application [1–5]. The most important advantage of thermoplastics over toughened thermosets is the lower cost manufacturing. Nevertheless, high thermal stability is requested for these polymers because of high temperatures which they can encounter during processing and in service or during repair. Moreover, the determination of kinetic parameters associated with their degradation processes is an interesting topic of research.

Our group has in progress a comparative kinetic study on the degradation of new aromatic thermoplastic polyethers containing carbonyl and sulfone linkages, which could be used as matrices for composites [6–10].

In this work we report our studies on the thermal and oxidative degradations of the following thermoplastic poly(arylene)ether copolymer

$$F-[-(Ar-CO-ArAr-CO-Ar-O-Ar-SO2-Ar-O-)_{0.6}$$
$$-(-Ar-CO-ArAr-CO-Ar-O-ArAr-O-)_{0.4}]_n$$
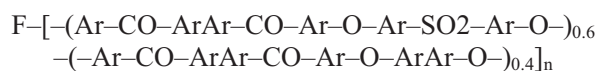
(where Ar=1,4-substituted phenylene) having a ratio between sulfone and ketone groups higher than those of the polymers previously studied. We determined the apparent activation energy values (E_a) associated with its degradation in various experimental conditions. Thermogravimetry (TG) and differential thermogravimetry (DTG) were used for measurements.

Experimental

Materials

The polymer was supplied by ICI (Wilton, Great Britain) in the form of powder and was used as received. Samples were dried at r.t. under vacuum and kept in a desiccator under vacuum until use.

TG and DTG measurements

A Mettler TA 3000 thermogravimetric analyser coupled with a Mettler TC 10 A processor was used for the degradation experiments. The temperature calibration of our equipment was performed according to the method suggested by the supplier [11] based on the change of the magnetic properties of three metal samples (Isatherm, Nickel and Trafoperm) at their Curie points (142.5, 357.0 and 749.0°C, respectively). The temperature calibration was repeated every month.

Degradations were performed in both dynamic and isothermal heating conditions, under a pure nitrogen flow (20 mL min^{-1}) and in a static air atmosphere.

Dynamic experiments were performed by heating samples from 35 up to 950°C at the various selected scanning rates (1, 2, 2.5, 5, 10, 15, 20 and 25°C min^{-1}). For isothermal degradations, samples were quickly heated (40°C min^{-1}) from 35°C to the selected temperature and then maintained at this temperature for 900 min (degradations under N_2 flow) or until total mass loss (degradations in air). The following set of temperatures (480, 490, 500, 510 and 520°C) was used for isothermal experiments in both investigated environments.

Samples of 6–10 mg, held in alumina crucibles, were used and their masses were measured as a function of temperature (dynamic heating conditions) or time (isothermal heating conditions).

Results

The mass losses observed in the complete used range of temperature (experiments in the scanning mode) and time (experiments in isothermal heating conditions) are reported in Table 1.

The temperatures at 5% mass loss were also determined by the experiments in dynamic heating conditions, with the aim of acquiring non-kinetic information about the thermal stability of our polymer (Table 2).

Table 1 Mass loss (%) recorded in dynamic and isothermal heating conditions

Dynamic heating conditions[a]			Isothermal heating conditions		
$\Phi^{b}/$ °C min^{-1}	Mass loss/ % (N_2)	$\theta/$°C^{c} (air)	$\theta/$°C	Mass loss/ %^{d} (N_2)	$t/$min^{e} (air)
1	42.3	571.9	480	27.0	538
2	42.1	610.4	490	33.1	355
2.5	41.6	643.7	500	29.3	243
5	42.6	727.7	510	46.1	166
10	44.1	793.0	520	58.9	109
15	43.6	902.0			
20	42.5	897.0			
25	43.5	940.0			

[a]Temperature range: 35–950°C; [b]Heating rate; [c]Temperature at which 100 mass% loss was observed
[d]Mass% loss after 900 min; [e]Time employed to reach the 100 mass% loss

Table 2 Temperatures at 5% mass loss in the experiments in the scanning mode

Φ /°C min^{-1}	$\theta/$°C (N_2)	$\theta/$°C (air)
1	517.3	457.8
2	522.0	482.7
2.5	534.2	494.0
5	546.2	535.0
10	552.0	552.0
15	566.5	554.0
20	571.0	566.5
25	572.5	567.2

Degradations in dynamic heating conditions

Degradations in the scanning mode were first performed in inert environment. The obtained TG and DTG curves evidenced, at all used heating rates, a very sharp degradation stage at lower temperature, followed by another broad and irregular stage at higher temperature associated with a little mass loss, with the formation of a residue stable up to 950°C.

Experiments in a static air atmosphere showed a complete mass loss at all used heating rates. The DTG curves evidenced that oxidative degradations proceeded through two partially superimposed stages.

The Kissinger method [12] was chosen among the several methods reported in literature [12–15] to draw kinetic parameters from measurements in the scanning mode. The equation obtained by Kissinger is:
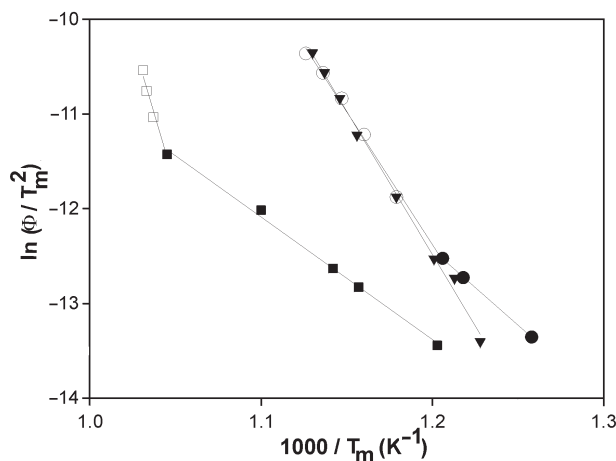
Fig. 1 Kissinger plot for the degradation stage under N_2 flow ($\blacktriangledown$) and for the first ($\bullet$) and the second ($\blacksquare$) degradation stage in static air atmosphere (o) for Φ=5, 10, 15, 20, 25°C min^{-1}; ($\square$) for Φ= 15, 20, 25°C min^{-1}

$$\ln(\Phi/T_m^2)=\ln(nRAW_m^{n-1}/E_a)-E_a/RT_m \qquad (1)$$

were Φ is the heating rate, T_m is the temperature at maximum rate of mass loss, n is the apparent reaction order, R is the universal gas constant, A is the pre-exponential factor, W_m is the mass of the sample at the maximum rate of mass loss and E_a is the apparent activation energy. According to this equation, the E_a values associated with a degradation process can be determined through the linear dependence of $\ln(\Phi/T_m^2)$ on $1/T_m$ at various heating rates. Reliable T_m values, which are the temperatures of the DTG peaks at various used heating rates, could be single out only for the first degradation stage under nitrogen and for both degradation stages in static air atmosphere (Table 3).

Table 3 Temperatures at maximum rate of mass loss (T_m) for the several used heating rates (Φ). The indexes 1 and 2 refer to the first and the second degradation stage

Φ/°C min^{-1}	T_m/K (N_2)	T_{m_1}/K (air)	T_{m_2}/K (air)
1	814.0	794.8	831.1
2	824.1	821.2	863.9
2.5	832.4	828.9	875.4
5	848.1	848.4	909.4
10	865.1	862.1	957.1
15	872.4	872.1	963.9
20	879.1	880.1	968.1
25	884.8	888.1	970.2

Table 4 Regression coefficients and apparent activation energies of the degradation stages calculated by Kissinger equation for different heating rates (Φ). The indexes 1 and 2 refer to the first and the second degradation stage

	Under N_2 flow				In static air atmosphere									
Φ/ °C min^{-1}	a^*	$b \cdot 10^{-3}$ **/ K	r***	E_a/ kJ mol^{-1}	Φ/ °C min^{-1}	a_1^*	$b_1 \cdot 10^{-3}$ **/ K	r***	E_a/ kJ mol^{-1}	Φ/ °C min^{-1}	a_2^*	$b_2 \cdot 10^{-3}$ **/ K	r***	E_a/ kJ mol^{-1}
1–25	23.7	−30.1	0.9980	251	1–2.5	6.7	−15.9	0.9996	132	1–10	2.1	−12.9	0.9984	107
	(±0.9)	(±0.8)		(±6)		(±0.6)	(±0.5)		(±4)		(±0.5)	(±0.4)		(±3)
					2.5–25	21.2	−27.9	0.9974	232	10–25	53	−61	0.9945	507
						(±1.2)	(±1)		(±8)		(±5)	(±5)		(±42)

*A=ln($nRAW_m^{n-1}/E_a$)
$^{**}b=E_a/R$
***Product moment correlation coefficient

Table 5 Regression coefficients and apparent activation energies by MacCallum equation for isothermal degradations at several degrees of conversion

	Under N_2 flow					In static air atmosphere				
D/%	n^*	a	$b \cdot 10^{-3}$/K	r**	E_a/kJ mol^{-1}	n^*	a	$b \cdot 10^{-3}$/K	r**	E_a/kJ mol^{-1}
2.5	5	−52.8(±1.8)	43.0(±1.4)	0.9983	358(±12)	5	−20(±3)	17(±2)	0.9756	146(±17)
5	5	−55.8(±1.2)	45.9(±0.9)	0.9994	381(±8)	5	−23(±2)	20.3(±1.9)	0.9872	168(±16)
7.5	5	−54(±2)	44.7(±1.7)	0.9978	372(±14)	5	−21.5(±1.2)	19.3(±1)	0.9963	161(±8)
10	5	−54.0(±1.8)	44.9(±1.4)	0.9984	373(±12)	5	−20.8(±0.9)	19.0(±0.7)	0.9977	158(±6)
12.5	5	−53.7(±1.6)	44.8(±1.2)	0.9989	373(±10)	5	−20.5(±0.5)	18.8(±0.4)	0.9993	156(±3)
15	5	−53.4(±1.0)	44.7(±1.1)	0.9991	372(±9)	5	−19.9(±0.8)	18.4(±0.7)	0.9981	153(±6)
17.5	5	−53.5(±1.6)	44.9(±1.3)	0.9987	373(±11)	5	−19.4(±0.7)	18.1(±0.6)	0.9986	151(±5)
20	5	−53.4(±1.7)	44.9(±1.3)	0.9987	374(±11)	5	−18.6(±0.8)	17.6(±0.6)	0.9979	146(±5)

*Number of points used for the linear regression
**Product moment correlation coefficient

The least squares treatment of the data of Table 3 according to the Kissinger equation gave rise to a single linear relationship for the degradations under nitrogen and to double linear relationships for those in air (Fig. 1). The corresponding Kissinger regression coefficients and the apparent activation energy values are reported in Table 4.

Degradations in isothermal heating conditions

Isothermal degradations under N_2 flow showed appreciable mass losses only starting from 480°C, because at lower temperatures degradations proceeded at very low and approximately constant rate. Moreover, isothermal experiments in both used environments were carried out at 480, 490, 500, 510 and 520°C.

Isothermal degradations in nitrogen atmosphere proceeded through a first high rate degradation stage, immediately followed by another one at low rate, with the formation of a stable residue at all used temperatures, while those in oxidative environment showed the complete degradation of polymer.

The MacCallum method [16], extensively reported by Hill *et al.* [17], was used to obtain kinetic parameters by isothermal measurements. This method is based on the following linear equation:

$$\ln t = a + b(1/T) \tag{2}$$

where t=time employed by sample to reach a fixed degree of degradation D, $a=\ln[F(1-D)]-\ln A$, $b=E_a/R$ and $F(1-D)$ is a function of the degree of degradation. Thus the apparent activation energy, E_a, could be obtained by the slope of the linear relationship $\ln t$ *vs.* $1/T$.

The apparent activation energy values were determined at several degrees of conversion (D=2.5, 5, 7.5, 10, 12.5, 15, 17.5 and 20%) for the experiments in both environments. The results are reported in Table 5.

Discussion

Dynamic experiments under nitrogen showed that, in these experimental conditions, the investigated polymer degraded in two stages. The first one could be attributed to random chain scission, in agreement with the large associated mass loss, while the second one was attributable to branching and crosslinking, according to the low mass loss and the irregular and broad shape of the DTG peak and the formation of a residue stable up to 950°C. The comprehensive mass loss in the complete temperature range was about the same in all experiments performed (Table 1), thus suggesting that the degradation processes were not affected by the heating rate.

A single Kissinger linear relationship was found for the first degradation stage and the associated apparent activation energy value was determined (Table 4); this value was similar to those found in the same experimental conditions for some aromatic thermoplastic polyethers containing both ketone and sulfone groups in their re-

peating units [7–9], but it was much lower than that found for the previously studied polyether in whose repeating unit only SO_2 groups were present [10].

The apparent activation energy values determined by isothermal experiments in inert atmosphere were not affected by the degree of conversion in the range $2.5\% \leq D \leq 20\%$. Nevertheless these values were quite higher than those from dynamic experiments, thus suggesting a more difficult initial degradation stage. This result could be depending on the temperatures used for the isothermal experiments, which were lower than those at which the 5% mass loss was observed.

The experiments performed in static air atmosphere showed that our polymer degraded through two stages also in both oxidative heating conditions, as supported by the DTG curves of dynamic experiments and the TG curves of the isothermal ones. Double Kissinger straight lines were obtained for both the degradation stages in the scanning mode (Fig. 1). The occurrence of double Kissinger relationships was reported in literature [17–19]. We observed this behaviour for some polymers previously studied and discussed it in some preceding papers on the basis of the slopes of the two straight lines obtained [6, 7, 9, 10]. In this case it is reasonable to suppose that at higher heating rates the degradation processes are under diffusive control, attributable to kinetically slow processes as the transport of O_2 or the degradation products in the melt. As a consequence the E_a values obtained at lower scanning rates must be considered the actual apparent activation energies associated with the two degradation stages of our polymer. The E_a value associated with the first degradation stage was much lower than that in inert environment, thus suggesting that the presence of oxygen largely affects the initial degradation process. This result was also in agreement with the low apparent activation energy value associated with the second degradation stage, where polymer degraded completely.

The E_a values from isothermal oxidative experiments determined at several degrees of conversion slightly decreased on increasing D, apart from at $D=2.5\%$, in agreement with the occurrence of an oxidative process involved in the second degradation stage and with the complete mass loss observed.

The average E_a value (156.2 kJ mol^{-1}) calculated for the range $5\% \leq D \leq 20\%$ was higher than the E_a value obtained for the first degradation stage by dynamic experiments, analogously to the measurements in inert atmosphere.

Some observations can be made on these results:

1. the temperatures at 5% mass loss (Table 2) were considerably higher than those found for the polyethersulfone [10], in the chain of which no ketone group was present. This finding suggested that the initial temperature of decomposition (which is difficult to single out exactly, but which can be considered roughly connected with the temperature at 5% mass loss) was higher for the copolymer here investigated, thus indicating a higher resistance to initial heat exposure;

2. the observed activation energy values of the first degradation stage in air atmosphere were much lower than those under N_2 flow, thus indicating different mechanisms of degradation in which oxidative processes were involved. It was also supported by the complete degradation observed in the oxidative experiments in both dy-

namic and isothermal heating conditions. This behaviour was different from that found for the polyethersulfone previously studied [10] which did not show any difference between oxidative and inert environments;

3. the E_a values of the first degradation stage in both nitrogen and air atmosphere were much lower than those of the overquoted polyethersulfone [10]. By contrast these values were practically the same as those found for the most part of the polyetherketones previously investigated, even if one SO_2 group was present in the repeating unit [7–9].

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