Thermochimica Acta 488 (2009) 43–48

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Thermo-oxidative degradation of MMA–St copolymer and EPS lost foams: Kinetics study

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ARTICLE INFO

Article history:
Received 20 December 2008
Received in revised form 24 January 2009
Accepted 27 January 2009
Available online 5 February 2009

Keywords:
Lost foam
MMA–St copolymer
EPS
Degradation
Thermo-oxidative

ABSTRACT

The thermal degradation of MMA–St random copolymer and EPS lost foams was studied by thermal gravimetric analysis (TGA) oxygen atmospheres and the results were compared with nitrogen one. The stabilizing effect of oxygen on thermal degradation of both foams and consequently possible mechanism was investigated. The activation energy was calculated under nitrogen and oxygen atmospheres by the Flynn–Wall–Ozawa method as a reliable way of determining the kinetic parameters. In this study the correlation method and isokinetic relationship (IKR) were used to estimate a model-independent pre-exponential factor ($\ln A$) corresponding to a given degree of conversion under both atmospheres.

1. Introduction

Lost foam casting (LFC) is an economic and new method to produce complex metal parts. Although this technology has several advantages compared to conventional casting methods, it still suffers from some inherent disadvantages, including surface carbon defects, melt penetration, surface and bulk pinholes [1]. This technology has different advantages compared to conventional casting methods in which the cast is made of expanded polystyrene (EPS) in aluminum casting or expanded methyl methacrylate–styrene (MMA–St) copolymer in iron casting [2]. LFC presents many advantages over other methods such as green sand or die castings. From the practical point of view, it simplifies the casting process and enables the manufacturing of complex shapes without the need for cores, which are useful in classical casting to produce holes or passages. LFC provides tight-dimensional tolerances, smooth surface finish and does not present parting lines (the lines which separate a mold into several parts). It therefore enables the reduction of the machining costs and the save on energy costs are higher than 30% with respect to standard castings.

Several techniques based on thermal gravimetric (TG) are commonly used in the study of pyrolysis kinetics. In polystyrene (PS) and EPS, the chain scission is the main thermal degradation mechanism which produces styrene monomer, dimer and trimer, through an intra-chain reaction [3]. The detectable product in poly-methyl methacrylate (PMMA) thermal degradation is monomer that strongly indicates a depropagation (unzipping) mechanism [4]. Furthermore the thermal degradation of PMMA has been studied under nitrogen and oxygen atmospheres in which the stabilizing effect of oxygen on the thermal degradation of PMMA has been reported [5]. In spite of various researches about thermal degradation of PS and PMMA, so far there is no particular study on thermal degradation of MMA–St copolymer foam except our previous work under nitrogen atmosphere [2].

The oxidative degradation of polymers is a free radical reaction. In this case, besides the usual degradation reactions, i.e., initiation, depropagation and termination, two additional important steps must be considered. These steps contain the main oxygen consuming reaction or conversion of formed hydrocarbon radicals to peroxy radicals and degenerate chain branching which are shown as follows [6]:

Radical conversion (stabilization):

$$R^\bullet + O_2 \Leftrightarrow RO_2{}^\bullet \tag{1}$$

Degeneration of chain branching:

$$RO_2H \rightarrow F(RO^\bullet + HO^\bullet) + (1-F)(RO + H_2O) \tag{2}$$

$$RO^\bullet + RH \rightarrow + R^\bullet + ROH \tag{3}$$

$$HO^\bullet + RH \rightarrow R^\bullet + H_2O \tag{4}$$

The initiation of thermo-oxidative degradation was conducted by direct reaction of the substrate and molecular oxygen and produced

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doi:10.1016/j.tca.2009.01.026

peroxy radicals. The very mobile products of the initiation step easily react with the active hydrogen of the polymer. The conversion of the hydrocarbon radical to a peroxy radical (Eq. (1)) in which is sometimes reversible, is an important step in degradation under oxygen atmosphere and in this step the majority of oxygen is absorbed by polymer. The alkyl radical that is generated in initiation reaction, react with oxygen, it means that a radical coupling reaction is occurred. The chain propagation reaction consists of the hydrogen abstraction reaction of the peroxy radicals. The decomposition of hydroperoxides to radicals is the most important step in polymer oxidation that is called “degeneration of chain branching” (Eq. (2)). The tertiary alkoxy radicals ($RO^{\bullet}$) and $HO^{\bullet}$ react with active hydrogen of the polymer and transforms to initial radical ($R^{\bullet}$), ROH in Eq. (3) and H_2O in Eq. (4). In these reactions, F denotes the efficiency of initiation in which after dissociation of the initiator molecule the paired radicals may either recombine (cage effect). This effect is more important especially when the media for polymer oxidation is viscous. Finally unimolecular or bimolecular termination of free radicals in polymer oxidation occurs almost exclusively by participation of peroxy radicals because the reaction of alkyl radicals with molecular oxygen (Eq. (1)), is very fast. At low oxygen pressures, termination reactions of the alkyl radicals are also important [6].

2. Theory

The kinetics analysis of non-isothermal data is generally performed by the following equation [7]:

$$\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT} = Af(\alpha)\,\exp\left(\frac{-E}{RT}\right) \tag{5}$$

where α is the degree of conversion and commonly defined as; $\alpha = (w_0 - w_t)/(w_0 - w_f)$ in which w_0, w_t and w_f are the initial, actual and final weight of the sample, respectively; t is the time, $f(\alpha)$ is the differential conversion function (kinetics model), E is the activation energy (J/mol), A is the pre-exponential factor (s^{-1}), R is the gas constant (8.314 J/(mol K)) and β ($\beta = dT/dt$) is the constant heating rate.

Rearrangement of Eq. (5) gives the following relationship for non-isothermal degradation corresponding to the given conversion:

$$g(\alpha) = \int_0^{T_\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A_\alpha}{\beta}\int_0^{T_\alpha} \exp\left(\frac{-E_\alpha}{RT}\right)dT \tag{6}$$

In which E_α and A_α are related to a given conversion. One of the iso-conversional methods is Flynn–Wall–Ozawa method in which the activation energy is estimated without the knowledge of reaction model. This method is useful for the kinetics interpretation of the TG data obtained from complex reactions. From Eq. (5) and Doyle approximation [8], the result of the integration is:

$$\ln\beta = \ln\left(\frac{AE}{R}\right) - \ln g(\alpha) - 5.3305 - 1.052\left(\frac{E}{RT}\right) \tag{7}$$

This equation generates a straight line when $\ln\beta$ is plotted against $1/T$ for iso-conversional fractions. The slope of the line will be equal to $-1.052E/R$ during a series of measurements with different heating rates at a fixed degree of conversion. If the determined activation energies change with conversion increment, the existence of a complex reaction mechanism can be concluded. Otherwise a single-step reaction may be occurred during pyrolysis.

To study the degradation mechanisms of the samples, in Eq. (6) various expression of differential, $f(\alpha)$, and integral, $g(\alpha)$, forms of the different solid state mechanisms (Table 1) have been proposed [9–11] and several analytical models have been used to estimate the Arrhenius parameters. One of such models is Coats–Redfern equation [12] in which with considering that $\ln(1-2RT/E)\to 0$ for Doyle approximation [8], the following equation will be written:

$$\ln\frac{g(\alpha)}{T^2} = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \tag{8}$$

The linear plot of $\ln[g(\alpha)/T^2]$ versus $1/T$ makes it possible to determine E and $\ln(A)$ from the slope and intercept of the graph, respectively. In some researches has been shown that these methods are unable to reveal the complexity of the process in which the obtained average value of parameters do not reflect changes in the mechanism and kinetics with the temperature and conversion [9,13,14], whilst the Flynn–Wall–Ozawa and Friedman iso-conversional methods are free model techniques which evaluate the dependence of the effective activation energy on conversion.

A model-independent estimate of the pre-exponential factor can be obtained through an artificial isokinetic relationship (IKR), in which in this method a common point of intersection of Arrhenius lines is defined as T_{iso} and k_{iso}. These values are isokinetic temperature and rate constant, respectively, in which the relationship between these parameters is written as:

$$\ln(k_\varepsilon) = \ln(k_{iso}) - \frac{E_\varepsilon}{R(T_{iso}^{-1} - T^{-1})} \tag{9}$$

where the subscript ε refers to a factor that produce a change in Arrhenius parameters. In a general case the actual value of $\ln A_\alpha$ can be determined by this method:

$$\ln A_\varepsilon = a + bE_\varepsilon \tag{10}$$

where $a = \ln(k_{iso})$ and $b = (RT_{iso})^{-1}$ are coordinates of the intersection point of Arrhenius lines. It is important that this approach is based on a completely artificial IKR derived from results of the model-fitting method [9,15].

Table 1
Reaction mechanisms to represent the solid-state process [9–11].

Model	Symbol	$f(\alpha)$	$g(\alpha)$
Nucleation and nuclear growth			
Mapel unimolecular law	A1	$1-\alpha$	$-\ln(1-\alpha)$
Avrami–Erofe’ev equation	A2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
Avrami–Erofe’ev equation	A3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
Avrami–Erofe’ev equation	A4	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
Diffusion			
Parabolic law	D1	$1/(2\alpha)$	α^2
Valenci equation	D2	$[-\ln(1-\alpha)]^{-1}$	$\alpha+(1-\alpha)\ln(1-\alpha)$
Jander equation	D3	$3(1-\alpha)^{1/3}/2[(1-\alpha)^{-1/3}-1]$	$[1-(1-\alpha)^{1/3}]^2$
Brounshtein–Ginstling equation	D4	$3/2[(1-\alpha)^{-1/3}-1]$	$1-2\alpha/3-(1-\alpha)^{2/3}$
Phase boundary controlled equation			
One-dimensional movement	R1	Constant	α
Contracting area	R2	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^2$
Contraction volume	R3	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$

Iso-conversional methods are reliable techniques which determine the activation energy at fixed conversions [9]. Different kinetics models with reaction mechanism fitting method have been used for estimating the kinetics parameters of different polymers and copolymers [10,11,16–21]. In some researches the effects of important parameters like oxidative environment and heating rate have been investigated [22,23].

In this work, the thermal degradation kinetics of MMA–St random copolymer and EPS lost foams are investigated under oxygen atmosphere and compared with nitrogen atmosphere [2]; the activation energies of lost foam copolymer have been calculated using Flynn–Wall–Ozawa [24] method and compared with those for EPS under both atmospheres. Furthermore the isokinetic relationship (IKR) were used to estimate a model-independent pre-exponential factor for each degree of conversion.

3. Experimental

3.1. Materials and methods

The materials and methods used in this study were the same materials, methods and characterization procedures which were conducted in our previous work. MMA–St random copolymer was synthesized by suspension copolymerization. The MMA–St molar ratio in all runs was kept constant at 70/30 [2]. MMA and styrene (St) (Merck, Germany) were washed twice with 5 wt% aqueous solution of sodium hydroxide followed by washing twice with distilled water to eliminate the inhibitors. The monomers then were dried over anhydrous calcium sulfate. *n*-Pentane (Merck, Germany) was used as blowing agent.

Average molecular weights (M_n, M_w) and polydispersity index (PDI) for copolymer were, 4.9×10^4, 1.18×10^5 and 2.38, respectively. Copolymer foam density was at the range of 19–22 g/l.

Commercially available expandable polystyrene (EPS) with a foam density of 18–21 g/l and average molecular weights (M_n, M_w) and polydispersity index (PDI) of 8.25×10^4, 1.75×10^5 and 2.12, respectively, was supplied by Tabriz petrochemical company (Tabriz, Iran).

3.2. Thermogravimetric analysis

Thermal gravimetric analyses were carried out for MMA–St and EPS foams by a thermogravimetric analyzer (TGA). The experiments were carried out on a PerkinElmer Pyris Diamond TG/DTA analyzer to study the non-isothermal degradation kinetics. 5 mg of fully expanded lost foam (MMA–St copolymer or EPS) was placed in an aluminum crucible and heated from room temperature to about 600 °C under nitrogen and oxygen atmospheres with a flow rate of 100 ml/min at different heating rates of 10, 15, 20 and 25 °C/min and weight loss versus temperature was recorded.

4. Results and discussion

4.1. Thermal degradation behavior

The weight loss versus temperature curves of dynamic thermal degradation of MMA–St copolymer and EPS foams obtained at different heating rates and under both nitrogen and oxygen atmospheres. In both foams, delay in degradation and shift of the curves to the higher temperatures with increasing of the heating rate is observed. It was evident that the thermal decomposition of MMA–St copolymer foam proceeds uniformly in the temperature range of 150–500 °C.

Under oxygen atmosphere after $T = 400$ °C a small amount of ash contents remained for EPS foam whilst for MMA–St foam after this temperature there was no observable char residue. The residue for EPS foam may be is due to some secondary reactions in high temperatures.

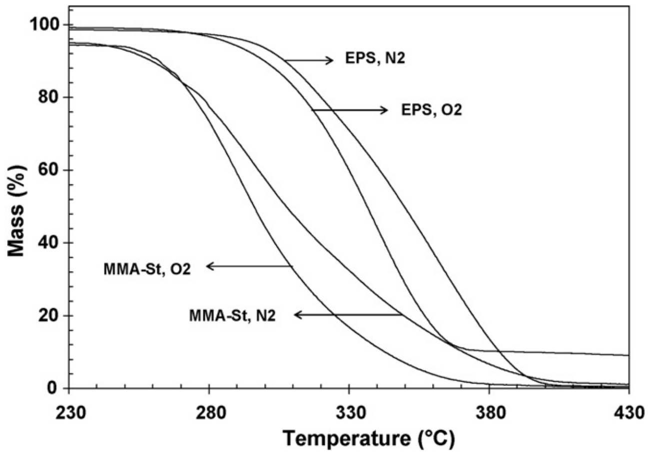

Fig. 1. Mass (%) versus temperature at $\beta = 10$ °C/min under different atmospheres for MMA–St copolymer and EPS foams.

The decomposition initiation temperature and the rate of weight loss for copolymer foam under both atmospheres are lower than that for EPS in all heating rates. Clearly, EPS foam is thermally more stable than copolymer foam, because the thermal decomposition of EPS foam initiates at higher temperatures compared to copolymer foam. This may be ascribed to the incorporation of MMA into St in copolymer that interfere with the degradation mechanisms of MMA and St and affect the degradation pathway of copolymer foam [2,25]. This phenomenon occurs due to special unknown mechanism in this random copolymer foam degradation process.

To investigate the effect of oxygen on thermal degradation, the weight loss versus temperature curves at $\beta = 10$ °C/min are plotted in Fig. 1, for both foams under two different atmospheres. As it is shown in this figurer, the initiation degradation temperature is delayed under oxygen atmosphere for MMA–St foam compared to nitrogen atmosphere in which after this small temperature delay interval, the rate of degradation under oxygen is higher than that the corresponding nitrogen atmosphere. This stabilizing effect of oxygen on the initiation of thermal degradation was observed as well as in thermal degradation of PMMA [5], in which the produced polymer alkyl radical under oxygen-containing atmosphere, is likely to react with oxygen to form a new stable polymer radical that is called peroxy radical. The initiation at both the vinylidene end group and the head-to-head linkage results in formation of the polymer radical. In an oxygen-containing atmosphere, this radical is likely to react with oxygen to form a new polymer peroxy radical which is more thermally stable than polymer radical about 100 kJ/mol and thus inhibits unzipping of the polymer chain. If unzipping is suppressed, degradation occurs through random scission that produces only a small amount of low molecular weight species capable of vaporizing [5]. Formation of the peroxy radical is reversible. In all experiments performed under oxygen-containing atmospheres, the reversible process is shifted toward formation of peroxy radical. Because this reaction is exothermic, an increase in temperature should favor the reverse reaction. Therefore, further heating should cause peroxy radical to ultimately decompose to oxygen and an original polymer radical. The onset of the depolymerization reaction is thereby shifted to higher temperatures [5]. The presence of –($COOCH_3$) groups in MMA structure of copolymer cause this stabilizing effect on the initiation of MMA–St foam degradation, whilst there is no oxygen containing group inside of EPS structure so this effect is not observed and the thermal degradation of EPS foam is occurred earlier and the rate of decomposition is higher

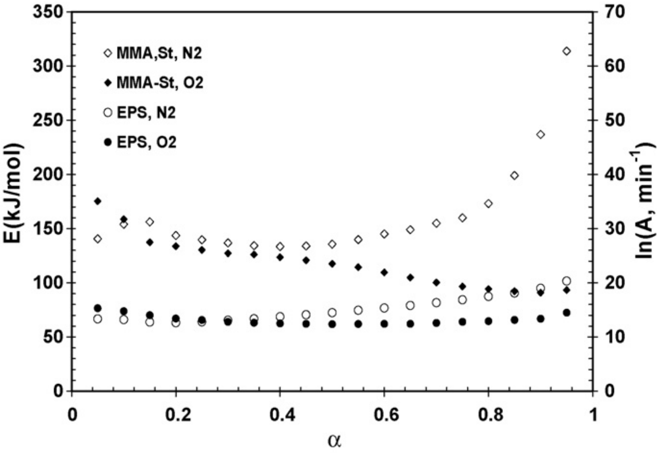

Fig. 2. Variation of activation energy (E) and pre-exponential factor ($\ln A$) versus conversion for both foams under nitrogen [2] and oxygen atmospheres.

under oxygen atmosphere compared to nitrogen atmosphere. Any other group with a low electron affinity should also demonstrate a stabilizing effect [6].

The probable mechanism for thermal degradation of copolymer foam under oxygen atmosphere is that formation of peroxy radical, which is exothermic and reversible. The initiation degradation temperature for copolymer under nitrogen atmosphere is about $T = 242\,^{\circ}\mathrm{C}$. The new radical is more thermally stable than the first polymer radical in which up to nearly $T = 255\,^{\circ}\mathrm{C}$, oxygen delays degradation by preserving the reaction centers in copolymer foam. At this temperature the accumulation of peroxy radicals or reaction centers are high in which after this with increasing of temperature, the reverse reaction is favored and caused the peroxy radical decompose to oxygen and radical. Produced peroxy radicals decompose fast and release highly reactive reaction centers, which consequently, this quick releasing of a great number of original radicals over a short period of time accelerate the degradation rate under oxygen atmosphere [5].

4.2. Degradation kinetics

TG curves (Fig. 1) show that up to $T = 230\,^{\circ}\mathrm{C}$, the weight loss becomes stable for copolymer and EPS lost foams. To eliminate the effect of pentane and water release on the degradation kinetics, the weight loss before $T = 230\,^{\circ}\mathrm{C}$ was ignored and the degree of conversion was modified for kinetics calculations in all heating rates.

The Flynn–Wall–Ozawa analysis under both atmospheres ($\ln\beta$ versus $1/T$ curves) for the conversion values in the range of 5–95% were conducted on both MMA–St and EPS foams. These results showed that the best fitting straight lines are nearly parallel for various heating rates and in various extent of conversion. Activation energies, E, corresponding to the different conversions and under nitrogen and oxygen atmospheres, determined from the slope of these lines, are shown in Fig. 2 for MMA–St as well as EPS lost foams.

In our previous work [2] it was evident that under nitrogen atmosphere and in the case of MMA–St foam, the activation energy, E, increases in the range of $0.05 \le \alpha \le 0.15$ then decreases in the range of $0.15 \le \alpha \le 0.70$ and finally reaches to 313.74 kJ/mol in $\alpha = 0.95$. The variation of activation energy versus conversion is an evidence of the complex degradation mechanism (probably parallel or consecutive reactions [6,7,26]) of MMA–St copolymer foam. This behavior was observed in the range of $0.05 \le \alpha \le 0.15$, $0.40 \le \alpha \le 0.70$ and so distinctly in the range of $0.70 \le \alpha \le 0.95$ [2].

For EPS foam under nitrogen atmosphere, the values of E decrease to 63.24 kJ/mol at $\alpha = 0.20$ and then increase regularly in the conversion range of 20–95% to 105 kJ/mol. This behavior is an evidence of multi-steps degradation reactions and consequently changing of the reaction mechanisms at the selected conversion range [2].

According to Fig. 2, for MMA–St foam under oxygen atmosphere, it is evident that the activation energy decreases over the whole conversion range. This behavior may indicate the changing of the mechanism to some endothermic reversible reactions [7]. As it is clear, nearly after $\alpha = 0.20$ the values of E decrease. As it was mentioned before the formation of peroxy radical is exothermic and reversible. With temperature increment, the reverse reaction is favored and heating of the samples cause the peroxy radicals to release highly reactive reaction centers (original alkyl radical) and oxygen (after $\alpha = 0.25$) consequently accelerates the degradation rate and decreases activation energy.

In the case of EPS foam under oxygen purge (Fig. 2), the variation of activation energy (E) with conversion is small in the range of 72–76.5 kJ/mol over the whole conversion range of 5–95%. There are no significance differences between the activation energy values in degradation of EPS foam under both atmospheres. The small difference between activation energy values is due to the oxygen atmosphere outside of the EPS foam in which the alkyl radicals react with oxygen to produce peroxy radicals and accelerate the degradation rate.

Furthermore the values of E for MMA–St copolymer foam in most conversion ranges are higher than EPS foam under both atmospheres. Due to unknown mechanism in this random copolymer foam degradation process, there is no explanation for this behavior.

An increasing dependence of E on α is found for competing reactions, some independent and consecutive reactions or the decreasing dependence of E on α corresponds to the kinetic scheme of an endothermic reversible reaction followed by an irreversible one [15]. The concave shape of decreasing of E on α may correspond to changing the mechanism from kinetic to a diffusion regime [6,24]. In this work according to Fig. 2 and the shape of E versus α, under both atmospheres, the diffusion degradation mechanisms (Table 1) were ignored in the following calculations for degradation of MMA–St copolymer and EPS foams.

Based on the various reaction mechanisms given in Table 1, the kinetics parameters obtained from the non-isothermal TG data for MMA–St copolymer and EPS foams, using Coats–Redfern equation under different atmospheres, are given in Table 2. These data are used in isokinetic calculations. As it was investigated in our previous work [2], the model-fitting method results in only one single pair of Arrhenius parameters in which the most solid state reactions are not simple one-step processes and consist of multiple steps during pyrolysis process, so the obtained kinetic parameters from the models in Table 1 are just used for simulating of experimental date and are not reliable [9].

The results of Table 2 obviously indicate the strong dependence of the kinetics parameters on the selected reaction mechanism. The values of correlation factors under nitrogen purge for the whole models in Table 2 are between 0.83 and 0.95 [2], whilst the correlation factors for these models under oxygen purge, are between 0.809 and 0.999. It is difficult to make a decision about exact thermal degradation mechanism.

In the case of EPS foam, the correlation factors for A_n type models are in acceptable ranges. From the calculated kinetic parameters under oxygen atmosphere, it is clear that the whole of kinetic data and correlation factors are higher than the corresponding data determined under nitrogen atmosphere. As it is clear from the results of Table 2, the values of Arrhenius parameters corresponding to those models that have high correlation

Table 2
Arrhenius parameters for non-isothermal pyrolysis of MMA–St copolymer and EPS foams at 10 °C/min under nitrogen [2] and oxygen atmospheres.

Foam samples	Mechanism	E (kJ/mol)	$\ln A$ (min^{-1})	Correlation factor
Nitrogen atmosphere				
MMA–St copolymer	A1	73.35	13.1340	0.9498
	A2	31.75	4.0384	0.9322
	A3	17.89	0.7119	0.9050
	A4	10.96	−1.1543	0.8605
	R1	48.00	7.1021	0.8317
	R2	59.19	9.1020	0.8983
	R3	63.56	9.7342	0.9176
EPS	A1	116.37	21.05887	0.9920
	A2	53.08	8.2476	0.9901
	A3	31.98	3.7322	0.9876
	A4	21.43	1.3275	0.9840
	R1	83.49	13.9655	0.9444
	R2	98.25	16.4607	0.9747
	R3	103.9	17.2771	0.9821
Oxygen atmosphere				
MMA–St copolymer	A1	97.93	18.9355	0.9332
	A2	44.14	7.1439	0.9180
	A3	26.21	2.9580	0.8973
	A4	17.24	0.7067	0.8690
	R1	63.62	10.9052	0.8093
	R2	78.67	13.7666	0.8772
	R3	84.59	14.7451	0.8977
EPS	A1	138.59	26.2509	0.9994
	A2	64.31	10.9721	0.9943
	A3	39.55	5.6491	0.9990
	A4	27.17	2.8551	0.9988
	R1	98.89	17.5797	0.9658
	R2	116.52	20.7577	0.9758
	R3	123.35	21.8433	0.9836

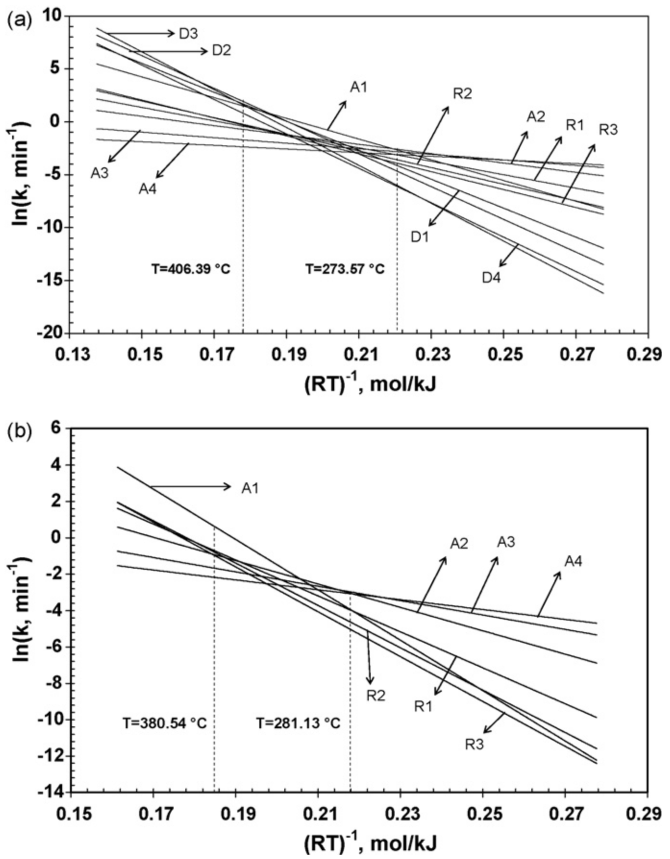

Fig. 3. Arrhenius lines plotted by data given in Table 2 under oxygen atmosphere to calculate isokinetic parameters: (a) MMA–St and (b) EPS foams.

factors vary significantly. Such an uncertainty in the kinetic parameters cannot lead to suitable kinetic predictions and reasonable mechanism.

The model-independent estimate of the pre-exponential factor obtained through an artificial isokinetic relationship (IKR), in which in this method a common point of intersection of Arrhenius lines was defined as T_{iso} and k_{iso}. These values were isokinetic temperature and rate constant, respectively, in which the relationship between these parameters and the calculation procedure has been discussed in theoretical section (Eqs. (9) and (10)).

The Arrhenius lines using IKR method are plotted in Fig. 3(a) and (b) by the parameters of Table 2 under oxygen atmosphere, for both MMA–St and EPS foams, respectively. As it is shown in these figures, like nitrogen atmosphere [2], there is an intersection interval in both foams, therefore an average intersection point corresponds to the isokinetic parameters (a and b) were used in which nearly all the plotted lines converge. These temperature intervals are indicated in Fig. 3 and corresponding to these temperatures, the values of a and b (isokinetic constants) can be determined. According to Eq. (10), the preexponentioal factors, $\ln A_\alpha$, corresponds to E_α for each degree of conversion were calculated for copolymer and EPS foam (Fig. 2).

5. Conclusion

The thermal decomposition of MMA–St copolymer and EPS foams under oxygen atmospheres at different heating rates has been studied by TGA in non-isothermal condition and compared with nitrogen atmosphere. The initiation decomposition temperature and rate of weight loss for copolymer foam is lower than EPS at all heating rates. The main reason for this behavior was the interference of degradation mechanisms of MMA and St in copolymer which affects the pathway of degradation process for copolymer foam.

The stabilizing effect of oxygen was observed in thermal degradation of MMA–St foam in which the produced alkyl radical under oxygen atmosphere, react with oxygen to form a stable polymer radical which is called peroxy radical. In initial stages of thermal degradation of MMA/St copolymer, the activation energy in oxygen atmosphere is higher than nitrogen atmosphere. Up to 50% conversion there is no significant difference at both atmospheres, after this conversion with increasing of temperature, peroxy radicals quickly release high reactive centers and oxygen which accelerates the degradation rate of copolymer and decreases the thermal degradation activation energy. Any other group with a low electron affinity should also demonstrate a stabilizing effect. This effect was not observed in thermal degradation of EPS foam because there is no oxygen-containing group inside of EPS structure.

The complexity of the pyrolysis reaction was shown by Flynn–Wall–Ozawa method in which the activation energy was changed with degree of conversion for both foams under different atmospheres. The values of activation energy decreases under oxygen atmosphere for copolymer whilst under nitrogen atmosphere, nearly the opposite behavior was observed. Furthermore in the case of EPS there was not any significant difference between activation energy values under both atmospheres. It was concluded that the activation energy calculated by Flynn–Wall–Ozawa method in whole rang of degree of conversion, for MMA–St copolymer foam was higher than EPS foam. The values of $\ln A_\alpha$ were determined using correction method and iso-kinetic relationships (IKR) under both atmospheres. Consequently, the model-free methods can be suggested as a suitable way of determining consistent kinetic parameters.

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