Thermal and Thermooxidative Degradation of Engineering Thermoplastics and Life Estimation

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ABSTRACT: This investigation deals with the thermal or thermooxidative degradation behavior of three engineering polymers [e.g., poly(ethylene terephthalate) (PET), poly(ether sulfone) (PES), and poly(ether ether ketone) (PEEK)] by using thermogravimetry-coupled mass spectrometry (TG-MS) analysis. The experiments were conducted both in argon and in air separately to study the changes in the degradation pattern of the polymers under varied sample environments. The samples were subjected to a programmed heating rate of 10°C/min and a temperature range from ambient to 800°C. For all these polymers, the decomposition rate, percentage weight loss, and the nature of the evolved gases were found to vary while changing the environment from argon to air. Methods of nonisothermal kinetic analysis, proposed by Flynn and Wall, and the shelf life estimation, proposed by Toop, have been described. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1737–1748, 2004

Key words: thermal degradation; thermooxidative degradation; lifetime estimation; mass spectrometry; engineering polymers; thermogravimetric analysis (TGA); activation energy; thermoplastics

INTRODUCTION

Thermal decomposition of polymeric materials exhibits complex thermogram. A controlled atmosphere applied for any thermal analysis of polymers also affects the decomposition process. The traditional thermal techniques can only provide the thermophysical information but seldom identify the effluents. Most effective means of getting such information is a simultaneous evolved gas analysis (EGA). The use of mass spectrometry for this purpose has been particularly rewarding because of its high sensitivity and ability to directly identify the vapor species when materials are subjected to a programmed heating.[1,2] The use of thermogravimetry-coupled mass spectrometry (TG-MS) was proposed by many authors for the study of the decomposition of polymers and EGA, structural characterization, and chemical modifications.[3–5] Materazzi[6] and Jansen[7] reviewed the EGA process for several polymers.

Another aspect of thermal analysis is the durability assessment or the lifetime prediction of the products.[8] The study has paramount importance for guaranteed service performance especially for critical application of products for defense and aerospace and also to build up user confidence in other potential applications. Lifetime prediction is done on the basis of identification of the critical reaction which limits the life of a material and is evaluated from the measurement of the reaction kinetics at elevated temperatures. By using proper kinetic expressions and through extrapolation of the results, one can estimate fairly accurately the service life of a material.[9] For kinetic analysis, traditionally both isothermal and nonisothermal methods are applied. However, the isothermal measurements suffer from the drawback of being rather time consuming. There is another difficulty of bringing the sample and the sample compartment to the required temperature without any decomposition of the sample. The nonisothermal or the dynamic method developed by Flynn and Wall[10] is, therefore, preferred, as it requires less experimental time and also overcomes the shortcoming of an isothermal method.[11] The dynamic method assumes a first-order kinetics, which is generally true for most of the polymers. While they are not, their earlier stages of decomposition are considered, which closely resemble the first-order kinetics.[12]

Studies on unsaturated polyester resin, ethylene vinyl acetate (EVA), and nitrile rubber (NBR) have shown the dependence of the rate of thermooxidative degradation on sample environment.[13,14] Wu et al.[15] studied the thermooxidative degradation of phosphorus containing poly(ethylene terephthalate) (PET). However, a detailed study of polymeric materials undergoing thermal (i.e., exposure to an inert medium, e.g., argon) or thermooxidative (i.e., exposure to air) degradation as well as estimation of their lifetime are lacking. Thermal degradation of PES and kinetics of

TABLE I
TGA Results

Sample	Argon medium		Air medium	
	OT[1] (°C)	Wt. loss (%)	OT (°C)	Wt. loss (%)
First step of decomposition				
PET[2]	407.42	88.93	392.13	90.57
PES[3]	538.65	57.39	522.81	50.29
PEEK[4]	564.97	44.64	558.22	39.47
Second step of decomposition				
PET	—	—	517.66	10.41
PES	700.57	2.80	614.97	51.59
PEEK	692.82	4.77	617.66	63.98
Residue at 800°C (%)				
PET	9.073		0.016	
PES	38.89		0.54	
PEEK	50.40		0.48	

[1] Onset temperature.
[2] Relpet 65801, Reliance Industries Ltd. (Mumbai, India).
[3] A-300, AMOCO Polymers Alpharetta (GA, USA).
[4] Victrex 450G, ICI Chemicals & Polymers Ltd. (Cleveland, UK).

SO_2 formation have been studied by Almen and Ericsson.[16] The pyrolysis of PEEK to estimate the functional group stability and the identification of the evolved gases was studied by Perng et al.[17] The present article describes the study of the effluent analysis and the effect of environment on the thermal degradation pattern, kinetic parameters, and lifetime estimation of PET, poly(ether sulfone) (PES), and poly(ether ether ketone) (PEEK).

EXPERIMENTAL

Materials

Samples of PET, PES, and PEEK were obtained from Reliance Industries Ltd. (Mumbai, India), AMOCO Polymers (Alpharetta, GA), and ICI Chemicals & Polymers Ltd. (Wilton, UK), respectively. The details of the samples are given in the Table I. The granular samples were dried in a vacuum oven at 70°C up to constant weight.

Method of TG-MS analysis

The combined TG-MS system used in the present study is shown schematically in Figure 1. The Hi-Resolution TGA 2950 (TA Instruments Inc., New Castle, NJ, USA) was coupled with a quadruple Thermo Star MS (Balzers Instruments Inc., Liechtenstein, Germany). The purge gas was introduced horizontally in the vertical TGA furnace through a small inlet that allows the decomposition products to exit through a port immediately adjacent to the sample. The MS interface tube is made of fused silica-lined stainless steel capillary, which was heated at 120°C to minimize the condensation of the effluents.[18] One end of the interface was connected to the TGA furnace exit port and the other end was attached to the MS inlet.

In TGA, samples (~ 5–10 mg in size) were put in a platinum pan and temperature was elevated from ambient to 800°C at a constant heating rate of 10°C/min in the controlled environment (viz., argon or air).

The effluents were first scanned in MS at a speed of 0.2 s/amu over the mass range of 1–300 amu in a scan analog (SA) mode. Each cycle of the SA mode took 01 min and the experiment was completed in a total no. of 77 cycles. The effluents were thus identified and thereafter the scanning was done in multiple ion detection (MID) mode at a speed of 0.5 s/amu to obtain the exact temperature profile. The residual gases were also measured and a zero gas subtraction was done to get the exact nature of the gases coming out of the sample.

Kinetic analysis

TGA experiments were done at different heating rates of 5, 10, and 15°C/min in both the media. The thermal degradation kinetics, based on Flynn and Wall method, require three or more different heating rates.[10] The approach assumes the basic Arrhenius equation

$$(d\alpha/dt) = A\exp(-E_a/RT)(1-\alpha)^n \qquad (1)$$

where α is the fractional decomposition of the sample; t is the time (s); A is the preexponential factor (1/s); E_a

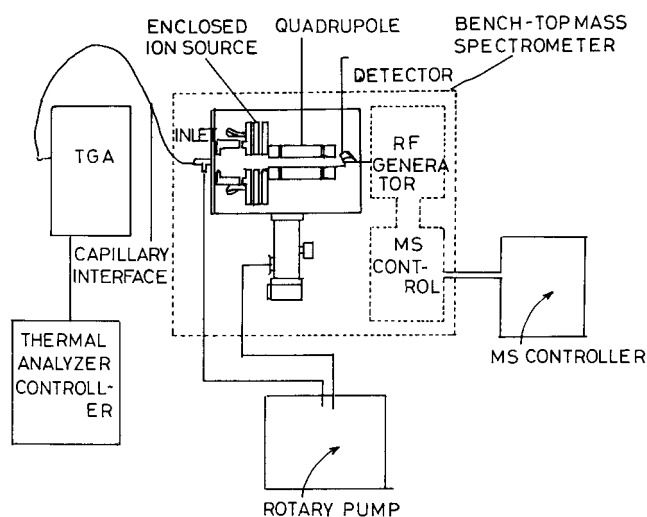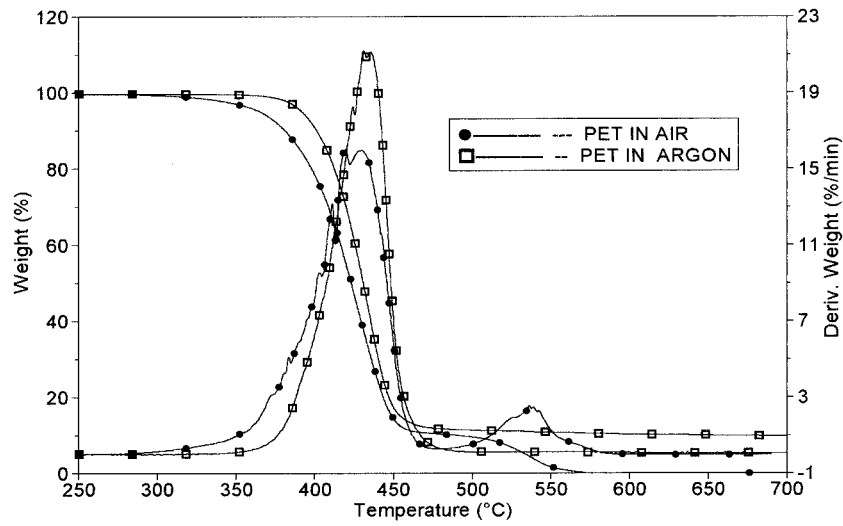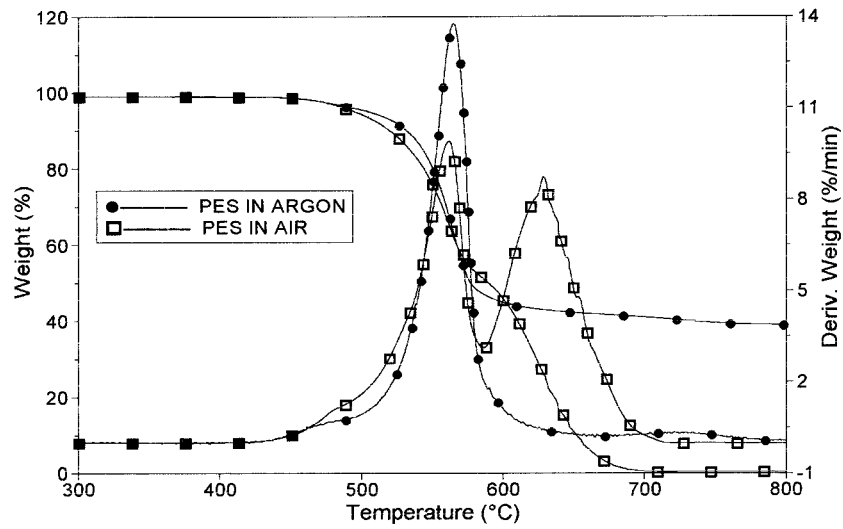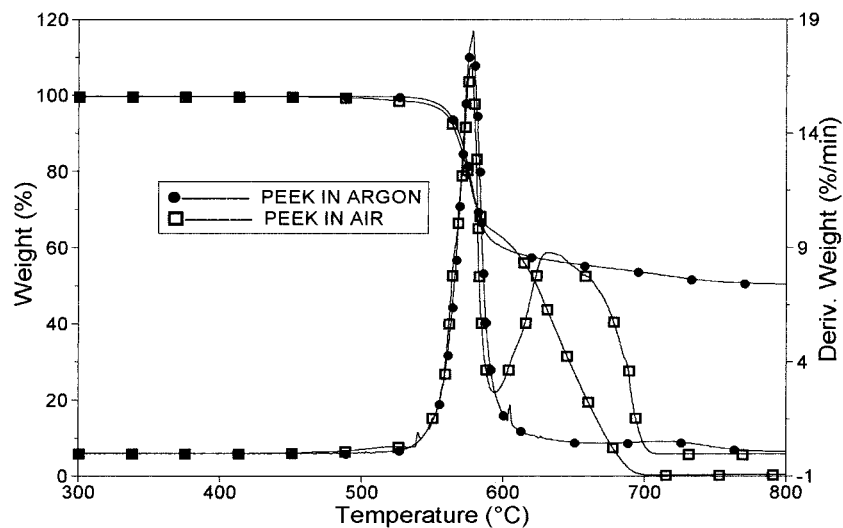**Figure 1** Schematic diagram of TG-MS coupled system.

Figure 2 (a) Comparison of TG and DTG thermograms of PET in argon and air; (b) comparison of TG and DTG thermograms of PES in argon and air; (c) comparison of TG and DTG thermograms of PEEK in argon and air.

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TABLE II
DTG Results

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Sample	Argon medium		Air medium	
	Peak temp. (°C)	MRD (%/min)	Peak temp. (°C)	MRD (%/min)
	First step of decomposition			
PET	434.14	20.98	419.45	16.00
PES	563.67	13.65	559.80	10.00
PEEK	578.50	18.48	577.43	16.96
	Second step of decomposition			
PET	—	—	537.24	2.43
PES	723.76	0.32	631.19	9.81
PEEK	711.49	0.53	631.52	8.77
	RT (min)	TWL (%)	RAWL (%/min)	RT (min)	TWL (%)	RAWL (%/min)
	Complete decomposition			
PET	12.26	87.74	7.15	28.46	99.42	3.49
PES	36.38	60.00	1.64	28.35	98.58	3.47
PEEK	29.48	49.37	1.67	16.86	97.99	5.81

MRD, maximum decomposition rate; RT, reaction time; TWL, total weight loss; RAWL, rate of average weight loss.

is the activation energy (J/mol); R is the gas constant; and n is the reaction order.

The equation can be rearranged to the form

$$E_a = -(R/b)(d\ln\beta)/[d(1/T)] \qquad (2)$$

where b is the constant (0.457), assuming reaction order $n = 1$; and β is the heating rate (°C/min).

By using a point of equivalent weight loss, a plot of $\ln \beta$ versus $1/T$ was constructed. The slope of the straight-line plot is then used to calculate the E_a for different conversion levels ranging from 5 to 25%.

Lifetime estimation procedure

The lifetime of the samples was calculated by using the following equation after Toop[19]

$$\ln t_f = \{E_a/RT_f\} + \ln[(E_a/\beta R) \cdot P(X_f)] \qquad (3)$$

where t_f is the estimated time to failure (min); T_f is the failure temperature (K); R is the gas constant; β is the heating rate (°C/min); and $P(X_f)$ is a function whose values depend on E_a at the failure temperature T_f.

RESULTS AND DISCUSSION

Thermogravimetry results

Both thermogravimetry (TG) and derivative thermogravimetry (DTG) plots of PET, PES, and PEEK have been shown in Figure 2(a-c), respectively, and the

results are summarized in Tables I and II. Table I shows that PET experienced a single-step decomposition in argon while it undergoes decomposition in two separate steps in air. As expected, the presence of oxygen in air caused a faster degradation of the sample and the onset temperature (OT), for the first step, was lowered by 15.29°C compared to that of argon. The corresponding weight loss in air was also increased by 1.64%. A negligible amount of residual weight at 800°C after the second step of decomposition in air signifies a complete combustion of the material compared to 9.073% residue in the case of argon. PES and PEEK, however, undergo two steps of decomposition in both argon and air. For PES, it can be seen that the OT values in the case of air was decreased by 15.84 and 85.60°C for the first and the second steps, respectively, compared to argon. The percentage weight loss also varied with the decomposition steps considered and nature of exposure medium. It has also been observed that 38.89% residual weight exits in the case of sample heated in argon, which is comparatively 38.35% higher than a negligible 0.54% weight loss in the case of air environment. Likewise, PES and PEEK also showed similar types of OT shift. From the above results, it is apparent that, for all the samples studied, the air medium resulted in a higher extent of decomposition.

Derivative thermogravimetry results

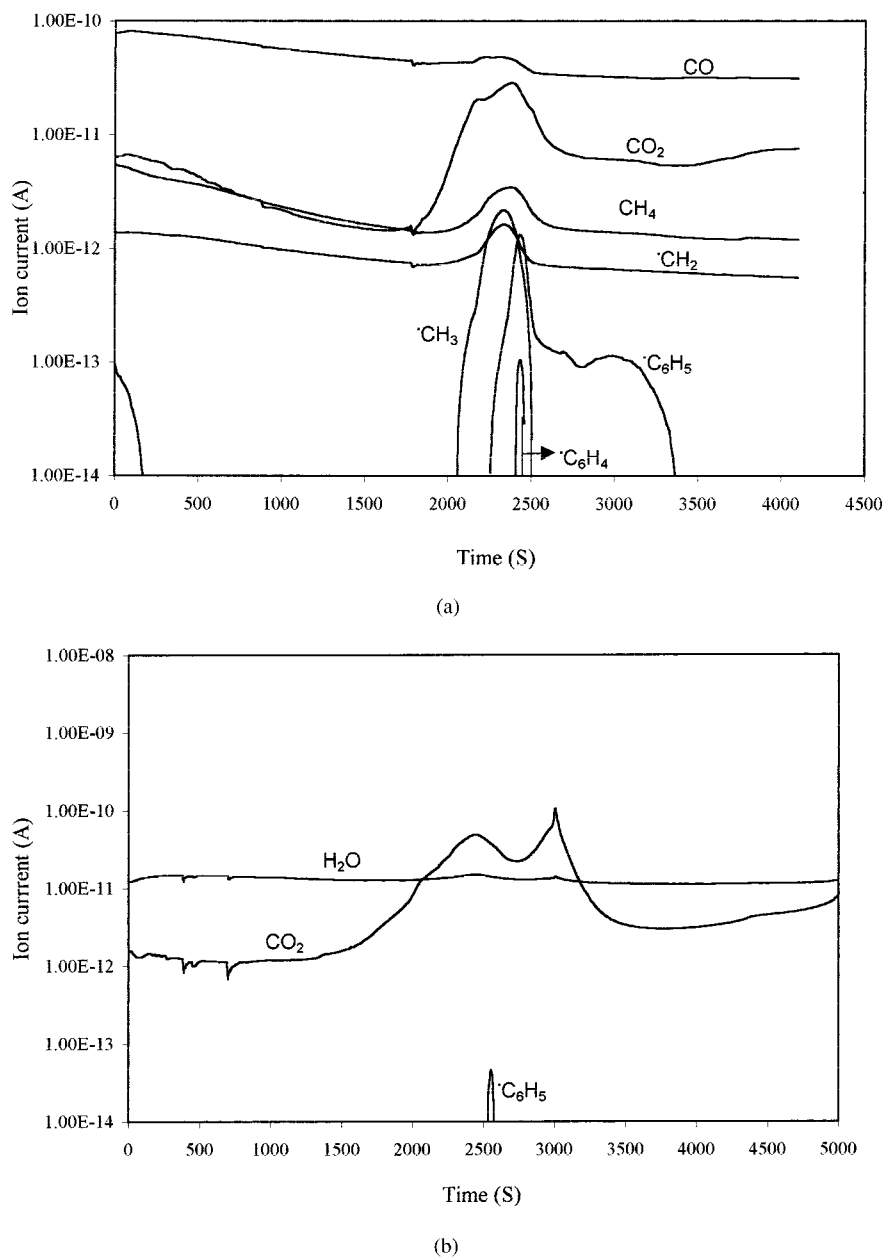Table II shows that, for the first step decomposition, the presence of air atmosphere caused a lowering of the

(a)

(b)

Figure 3 (a) Mass spectrograph of PET in argon; (b) mass spectrograph of PET in air.

peak temperature by 14.69, 3.87, and 1.07°C for PET, PES, and PEEK, respectively, compared to argon. For the second step, however, the respective values are 92.57°C (PES) and 79.97°C (PEEK). The maximum rate of decomposition (MRD) in the first step in air was decreased more than in argon in all cases and those for the second step were increased by 9.49%/min for PES and 8.24%/min for PEEK. Thus, the presence of air atmosphere caused a decrease of MRD for the first step but for the second step, the values were increased.

From Table II, it can further be seen that the total time elapsed for the completion of the degradation process is more in the case of argon than in air for all the polymers. However, for the PET alone, the introduction of air caused the decomposition in two separate steps and thereby the average weight loss value in air is lower than argon.

Mass spectrometry

The mass spectrographs of PET in argon and air media are shown in Figure 3(a, b). Fragments such as CO, CO_2, CH_4, $\cdot CH_3$, $\cdot CH_2$, $\cdot C_6H_5$, and $\cdot C_6H_4$ were identified in argon in Figure 3(a). Formation of CO_2 at the beginning of decomposition and fragments such as $\cdot C_6H_4$ at the end were due to the thermal energy transfer to polymer
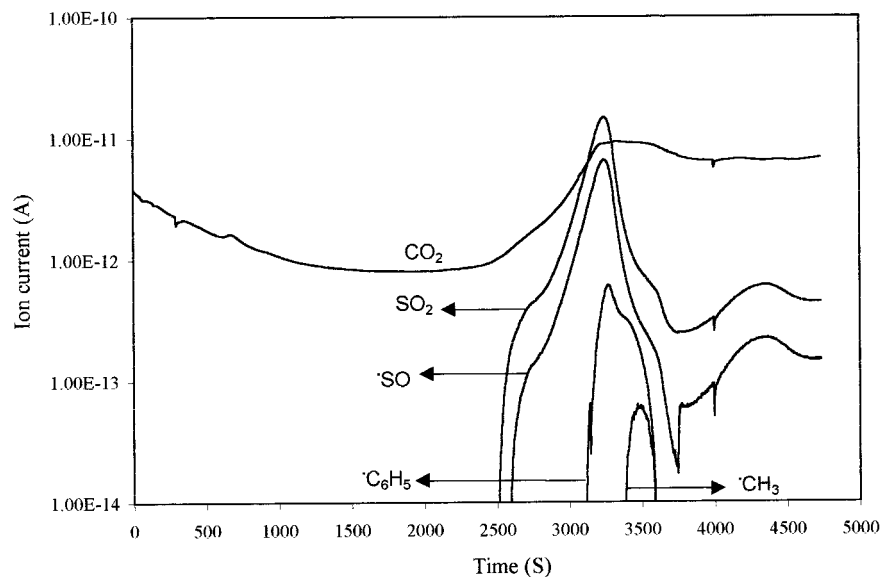
(a)
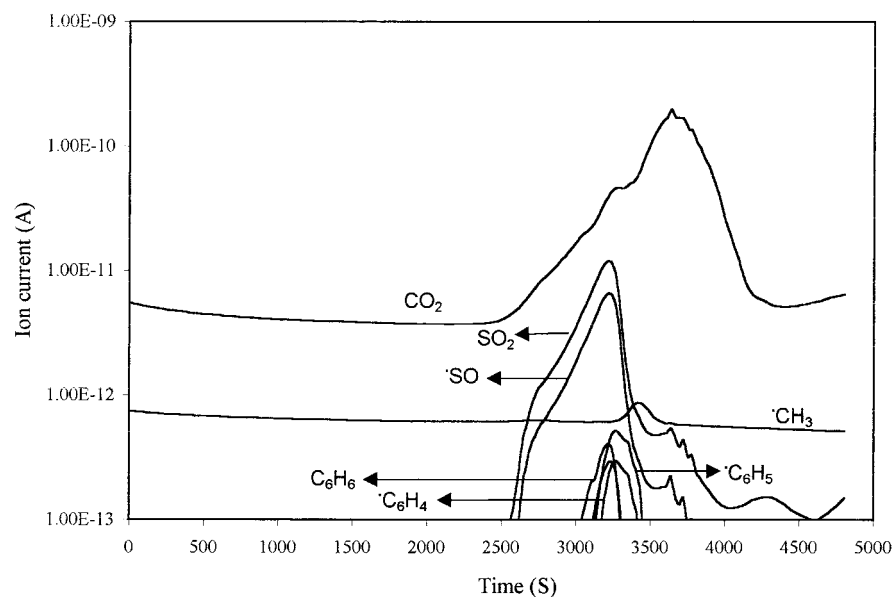
(b)

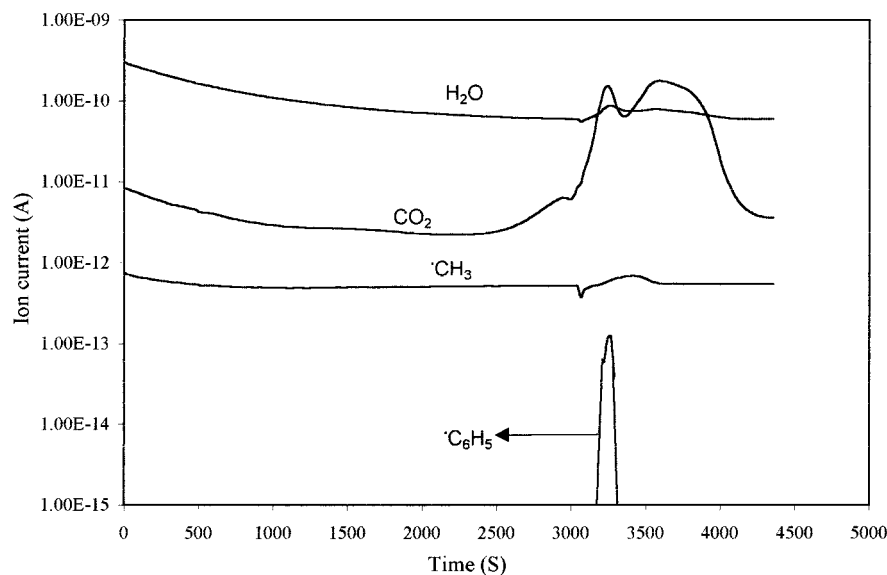**Figure 4**   (a) Mass spectrograph of PES in argon; (b) mass spectrograph of PES in air.

which first caused the chain scission of the weaker bond. However, the ion intensity observed for carbon dioxide was higher than that of carbon monoxide. This can be interpreted by the formation of the fragment such as $\cdot CH_2CH_2O$, which converts itself to acetaldehyde by re- arrangement process and enhances the peak intensity corresponding to carbon dioxide.[20] It can further be seen from Figure 3(b) that there was an absence of CO and the fragments because the CO_2 and H_2O appeared. This is because of the fact that in the presence of air, the inter- mediates react with oxygen and form the final species. The absence of fragment $\cdot C_6H_4$ in air may be attributed to its reaction with hydrogen from air to form $\cdot C_6H_5$.

The mass spectrographs of PES in argon and air media are presented in Figure 4(a, b). It can be seen from Figure 4(a) that the observed fragments in argon medium are CO_2, SO_2, $\cdot SO$, $\cdot C_6H_5$, and $\cdot CH_3$. However, the results shown in Figure 4(b) indicate the formation of fragments such as CO_2, SO_2, $\cdot SO$, C_6H_6, $\cdot C_6H_5$, $\cdot C_6H_4$, and $\cdot CH_3$. The peak intensity corresponding to CO_2 in air is much higher than in argon and, in addition, two new frag- ments (e.g., C_6H_6 and $\cdot C_6H_4$) appeared. These factors could be responsible for extra weight loss of 38.35% (Table I) in air medium compared to that of argon.

Figure 5 (a, b) represents the mass spectrograph of the PEEK in argon and air media, respectively. In
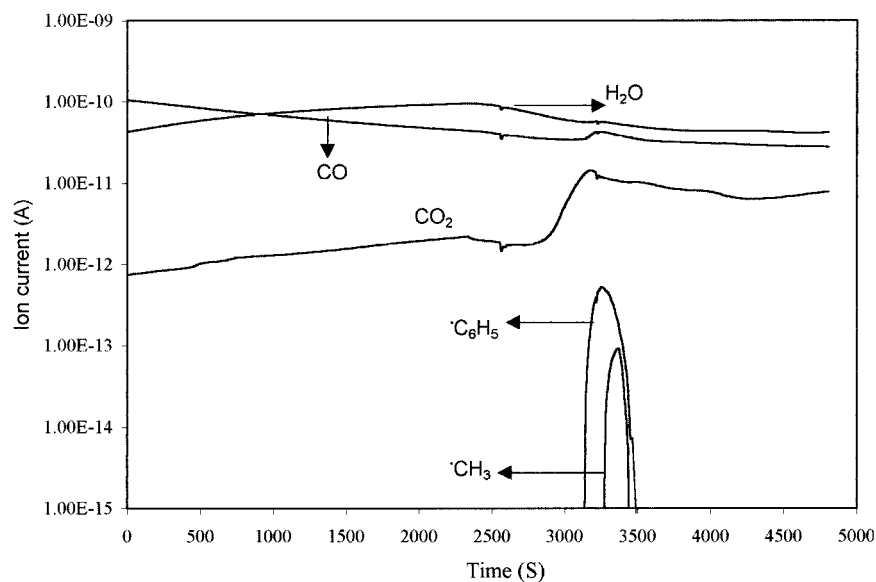
(a)

(b)

Figure 5 (a) Mass spectrograph of PEEK in argon; (b) mass spectrograph of PEEK in air.

argon, the observed fragments are H_2O, CO, CO_2, $\cdot CH_3$, and $\cdot C_6H_5$. In contrast, the CO is not observed in air because of the abundance of oxygen. The extra weight loss of 49.92% is mainly due to the formation of CO_2.

Kinetic analysis

The E_a at different conversion levels from 5 to 25% in steps of 5% for PET, PES, and PEEK are given in Figure 6(a, b) for argon and air, respectively. The plots of PET indicate that up to 10% conversion E_a increases

in argon while it remains almost constant in air. In the case of PEEK, E_a increases rapidly with the increase in the conversion level up to 10% in both media but remains almost constant for the rest of the conversion levels. It appears, therefore, for both PET and PEEK single-step degradation mechanism is operative, which is also supported by Flynn.[21,22] However, for PES, E_a in argon is increased up to 10% conversion level but decreased in the case of air. Although the percentage conversion in air hardly had any effect on E_a, in argon the PES shows an increasing trend of E_a value beyond 20% conversion. Variation of E_a values
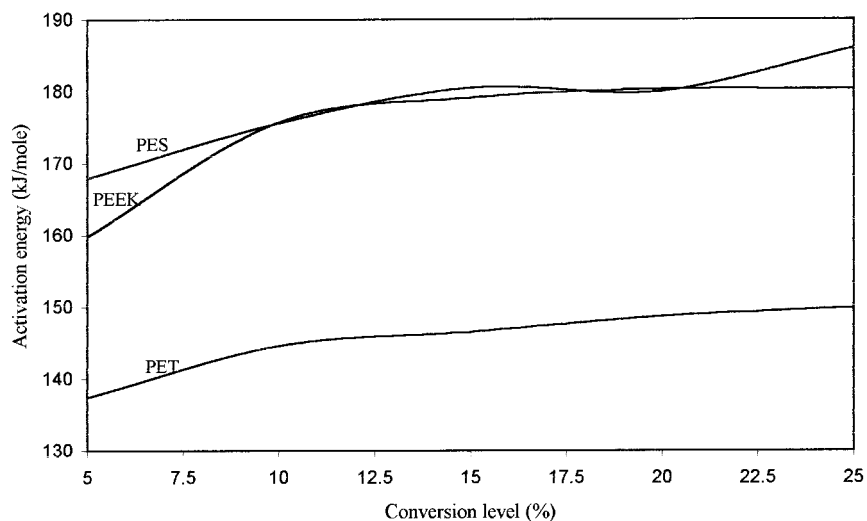
(a)
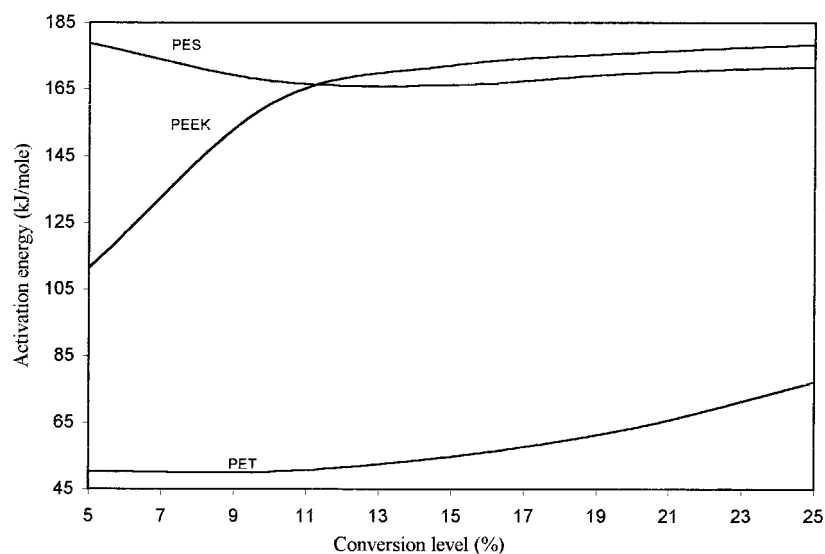
(b)

Figure 6 (a) Variation of activation energy with conversion level in argon; (b) variation of activation energy with conversion level in air.

TABLE III
Activation Energy *Ea* and Preexponential Factor *A*

|	Argon medium						Air medium					
	PET		PES		PEEK		PET		PES		PEEK	
Conversion level (%)	Ea (kJ/mol)	Log A (1/min)	Ea (kJ/mol)	Log A (1/min)	Ea (kJ/mol)	Log A (1/min)	Ea (kJ/mol)	Log A (1/min)	Ea (kJ/mol)	Log A (1/min)	Ea (kJ/mol)	Log A (1/min)
5	137.4	9.19	167.9	9.81	159.8	8.33	50.3	2.16	178.8	10.67	111.4	5.27
10	144.6	9.93	175.6	10.25	175.7	9.58	50.2	2.34	167.5	9.87	160.6	8.70
15	146.5	10.16	180.5	10.57	179.1	9.94	54.8	2.86	166.3	9.79	172.1	9.57
20	148.7	10.40	180.0	10.82	180.3	10.11	63.3	3.66	169.7	10.03	175.9	9.91
25	149.9	10.53	186.0	10.01	180.3	10.19	77.1	4.86	171.6	10.17	178.3	10.14

(a)

(b)
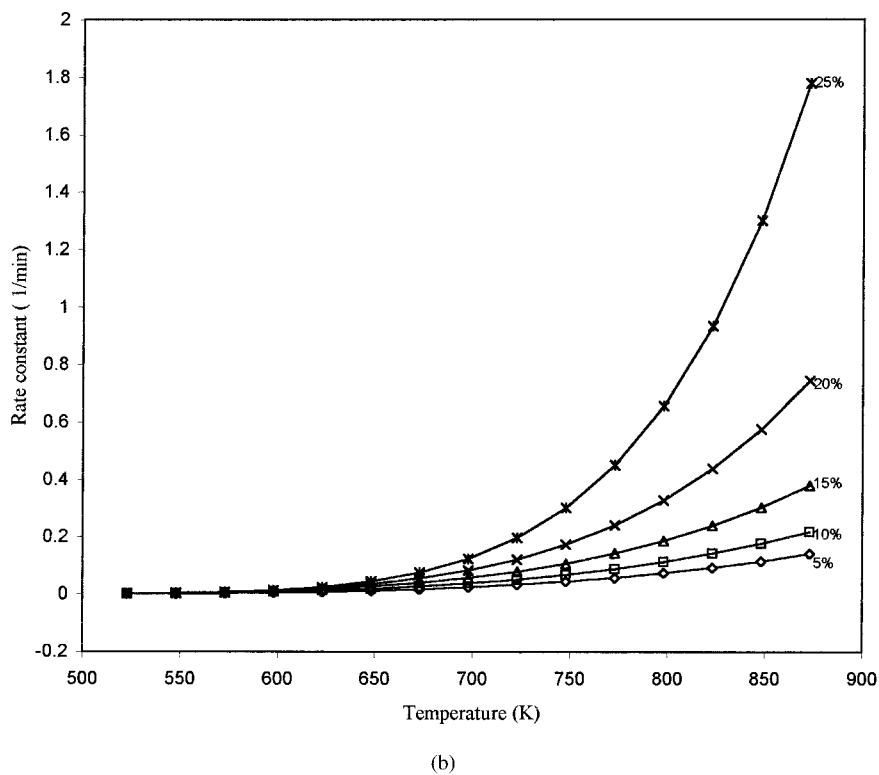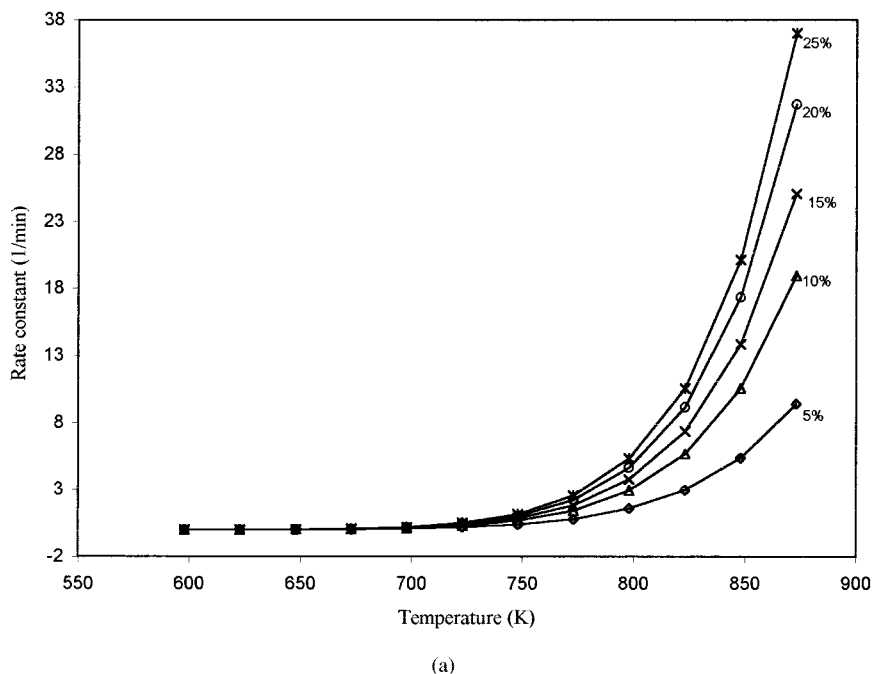
Figure 7 (a) Variation of rate constant with temperature for PET in argon; (b) variation of rate constant with temperature for PET in air.

in the case of PES, therefore, suggests a multistep reaction mechanism. A similar observation has also been reported earlier.[23,24] The absolute values of E_a and preexponential factor A for different samples are given in Table III.

The variation of rate constants with temperature has been plotted in Figure 7(a, b) at different conversion levels for PET in argon and air, respectively. The rate constant is almost parallel to the temperature axis up to 700 K in argon and 650 K in air and is followed by
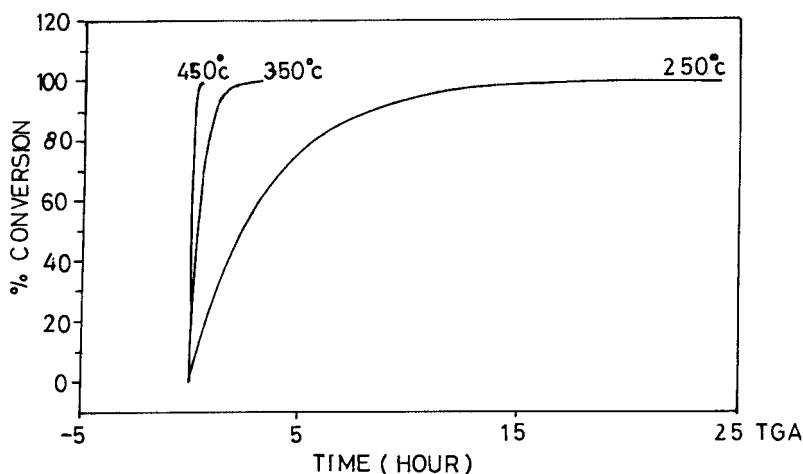
(a)
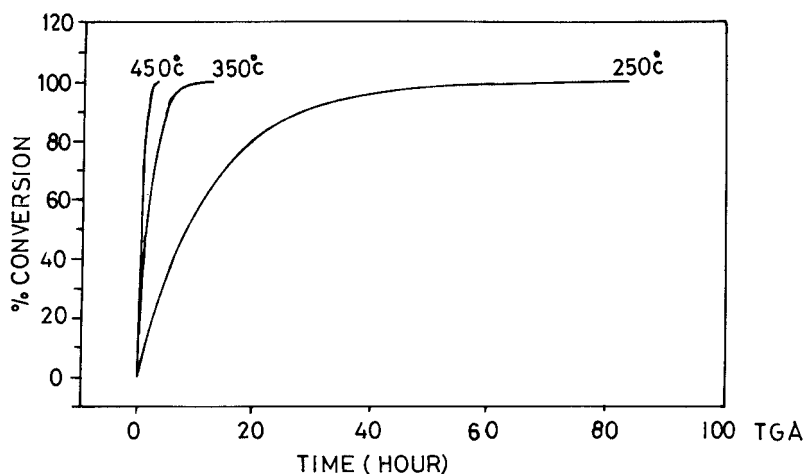
(b)

Figure 8 (a) Conversion versus time plot at different temperatures for PEEK in argon; (b) conversion versus time plot at different temperatures for PEEK in air.

the exponential trend for all conversion levels. A similar trend has also been found in the case of PES and PEEK (figures not shown). The correlation coefficient is found to be 0.980. Figure 8(a, b) is the conversion level versus time plot at temperatures of 250, 350, and 450°C in the main degradation region for PEEK in argon and air media, respectively. These figures indicate that the degree of conversion sharply increases at high temperatures. The nature of the plots is almost the same in argon and air. Similar results have also been found for the PES as well as for PET (figures not shown).

Lifetime estimation

The ability to predict lifetime is valuable so as to prevent an accident because of the premature failure

of the material. In the present case, the lifetime has been considered when the sample has experienced a 5% weight loss or is at its 5% conversion level in the thermogravimetry experiments.[25,26] By using the kinetics data, the lifetime for temperature range between 0 and 500°C has been calculated in both media and have been plotted in Figure 9(a–c) for PET, PEEK, and PES, respectively. The logarithm scale for the lifetime has been chosen for better comparison. In both media, a sharp fall of lifetime with increasing temperature, for all samples, can be easily seen from these figures. From Figure 9(a), it is apparent that lifetime is reduced originally in air medium for PET, whereas the rate of fall of lifetime with temperature is rapid in argon but gradual in air. The PEEK also shows a similar trend of lifetime variation with temperature [Fig. 9(b)] except for the fact that the rate of
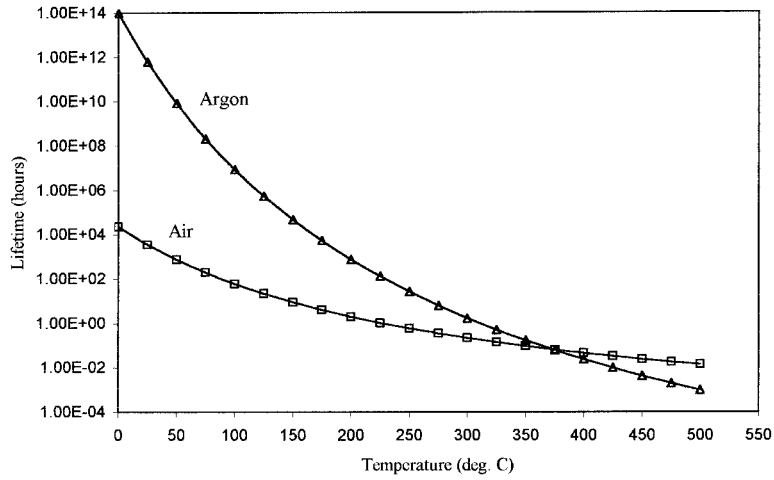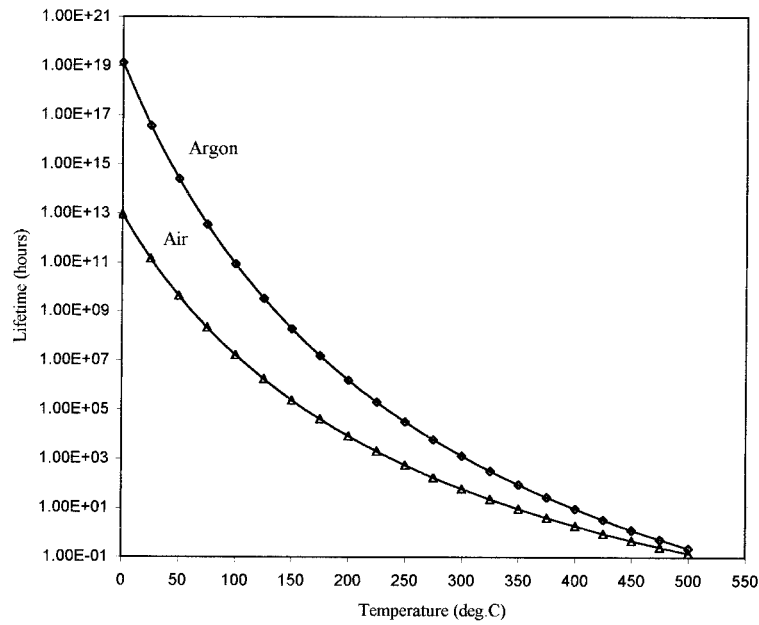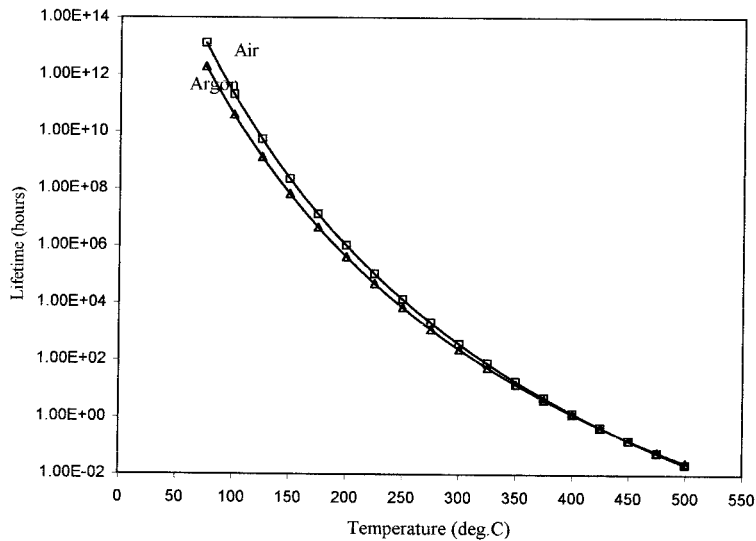
Figure 9 (a) Variation of lifetime with temperature for PET in argon and air; (b) variation of lifetime with temperature for PEEK in argon and air; (c) variation of lifetime with temperature for PES in argon and air.

variation of lifetime is similar irrespective of the choice of the media. Contrary to PET and PEEK, PES shows higher lifetime values for air than argon [Fig. 9(c)]. This can be also explained on the examination of Table III that reveals the higher value of preexponential factor at 5% conversion in air. This means that volatilization of gases is faster at initial stage of decomposition in argon and thus results in lower lifetime than air. However, beyond about 350°C, the plots of air and argon merge together supporting our earlier observation of the multistep reaction process for PES.

CONCLUSION

TG-MS technique was found to be effective in the elucidation of the degradation behavior of the engineering polymers (viz., PET, PES, and PEEK). The controlled environment subjected to the sample was found to produce a profound effect on the degradation profile.

The extent of decomposition of the polymers in air versus argon has been correlated quantitatively with the percentage weight loss, rate of decomposition, and mass spectrometer results (e.g., increase in the relative abundance of particular species or formation of new peaks during the heating process).

A detailed study on the lifetime and stability of the above engineering polymers has been undertaken and the results are expected to be important from an application point of view.

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