Macromolecules

Thermo gravimetric analysis on the effect of dimethyl terephthalate plasticizer on thermal degradation of polystyrene

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ABSTRACT

The thermal degradation behaviours of polystyrene plasticized with dimethyl terephthalate was studied by thermogravimetric (TG) analysis. The effect of added plasticizers on thermal degradation was also investigated under dynamic conditions (30-550°C) in pure nitrogen gas, at the heating rates 5,10,15, and 20°Cmin^{-1}. The characteristic of the TG curves were determined. These can be used to indicate the thermal stability of polystyrene films. Kinetic parameters, such as the activation energy (E), and the pre-exponential factor, (A) were calculated using the Flynn-Wall-Ozawa and Kissinger methods. The thermogravimetric (TG) curves of dynamic degradation of PS and PS doped with dimethyl terephthalate plasticizer were, obtained in the temperature range 30-550°C at the heating rates 5,10,15, and 20°Cmin^{-1}. PS doped with dimethyl terephthalate plasticizer showed an acceleration of photodegradation at higher temperatures in comparison with the non-plasticized PS films. It is evident that the thermal degradation of pure PS proceeds by one-step process between 400 and 550°C, which represent by a single peak in the corresponding DTG curves. The thermograms of PS/DMT blends show two unresolved degradation steps, the first corresponds to the thermal degradation of DMT and the second to the thermal degradation of PS.   © 2008 Trade Science Inc. - INDIA

INTRODUCTION

Polymer degradation is an important aspect of environmental and industrial research, because of its applicability in polymer recycling and in stability towards thermal heating and irradiation. The photo and thermal degradation kinetics of polymers is complex due to the polydispersity of polymeric chains. Thermal energy and exposure to UV- radiation can break polymer chains though chain scission[1-8]. The presence of air can also accelerate degradation through the thermal oxidation and thermal degradation processes in polymers[9, 10]. Thermal degradation of polystyrene has been investigated by many workers, McNeil et al. has investigated by pyrolysis, the degradation kinetics of polystyrene[2]. Polystyrene thermal degradation was reviewed by Cameron and MacCallum[11], and Cameron and Kerr reported a weak links in polystyrene chains[12]. The existence of weak links in polystyrene was used to explain the rapid drop in molecular weight at low reaction times. Chiantore et al. provided further evidence of weak link scission by degrading polystyrene at 200-

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300°C by pyrolysis and measuring the molecular weight distribution by gel permeation chromatography[13]. They also measured the rate coefficient and the activation energy for the degradation at longer irradiation times. Thermal degradation of polystyrene was investigated at 240-300°C, and found a dependence of the molecular weight distribution on reaction time[14]. Experimental data indicated that polystyrene degrades by both, random chain scission, and specific chain-end scission. The existence of weak links was evident, as indicated by rapid chain scission during an initial time period[14].

The mechanism of thermal degradation of polystyrene at higher temperatures was found to be more complicated. Though thermal degradation has been extensively investigated by pyrolysis experiments, the degradation kinetics and mechanism remains the subject of inquiry and discussion. A fairly complete and unified elucidation of the mechanism of thermal degradation of polystyrene has not yet achieved because of a detailed comparison between theoretical results for a given model mechanism and experiment. A chain depolymerization mechanism with transfer and assuming random initiation has been previously treated in this manner[15].

It is a common fact that the thermal stability of polymers in air is some how is lower than that in N_2. The aim of this work is to study thermal degradation of blended polystyrene with dimethyl terephthalate, under N_2 atmosphere by means of thermal gravimetrical analyzer (TG). Also compare the obtained results with that for thermal degradation of pure polystyrene. The thermal stability of plasticized polystyrene was found to be affected by the amount of plasticizer present in the polymer backbone.

EXPERIMENTAL

Materials

The sample of polystyrene(PS), was standard with narrow molecular weight distribution and was supplied by Across-Organics with high purity polystyrene, (Mw = 200 000, Mn=110000). Spectroscopic-quality, dichloromethane (DCM), was found to give no detectable absorption in range 250-400nm. It was purchased from Fluka GMBH and used as received. The used plasticize is dimethyl terephthalate (DMT), and was of

high purity of (99.8%), purchased from Across-Organics and were found to give no detectable absorption in rang 265-400nm.

Plasticized PS films used in this study were prepared by dissolving certain weight of the polymer in DCM solvent, then we add a known weight of the plasticizer dimethyl terephthalate (DMT) in order to obtain 20wt% solution. Then they were mixed in to determine the mass ratio (100/0, 95/5, 90/10, 85/15, 80/20, 70/30, 0/100) and stirred well. Finally, films of PS/DMT blends were obtained by evaporating the solvent followed by drying in vacuum at 30°C for 48h.

Thermogravimetric analysis

The thermal degradation of the synthesized samples was determined by non-isothermal thermogravimetric analysis in the temperature range from 30-550°C using NETZSCH STA 409 PG/PC thermoanalyzer in N_2 atmosphere flow. Thermal degradation experiments were carried out at nitrogen flow rate of 30ml/min⁻¹ and at various heating rates of 5,10,15,20°C min⁻¹. Before operating, the system was stabilized for one hour with nitrogen flow rate of 30ml/min⁻¹.

RESULTS AND DISCUSSION

Dynamic thermal degradation of plasticized polystyrene under inert nitrogen atmosphere
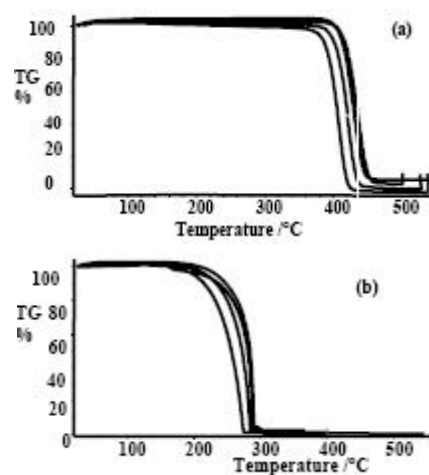
The thermogravimetric (TG) curves of dynamic ther-

Figure 1: TG curves of dynamic thermal degradation of PS (a) and DMT (b) at heating rate of 5, 10, 15, 20°C/ min, under N_2 flow (from left to right)

mal degradation of PS and DMT plasticizer obtained in the temperature range of 30-550⁰C at the heating rates 5,10,15,20⁰Cmin⁻¹ are shown in figure 1(a and b) abov.

As seen in figure 1(a), it is evident that the thermal degradation of pure PS proceeds by one-step process between 300 and 450⁰C, which represent by a single peak in the corresponding DTG curves. This agrees with the data published by Grassie et al.[16], and Chen et al.[17], where proposed degradation mechanism included depolymerization and intermolecular transfer. From the mass lose and residual yield, the mechanism of thermal degradation of PS films can be deduced to be the result of competition between a random chain scission which includes monomer volatilization[17], and an intermolecular mass sustained.

The temperature at the minimum rate of DTG curve corresponds PS degradation corresponds to the temperature at the maximum rate of PS degradation. With increasing heating rate the degradation starts at higher temperature, the temperature at the maximum rate of PS degradation increases and the maximum rate of PS degradation increases. This means that the rate of PS degradation depends on the heating rate. During this degradation step the weight loss is complete with only traces of residues.

Thermal degradation of pure PS and DMT occurs through one step between 200 and 500⁰C, depending on the heating rate, which characterized by a single peak
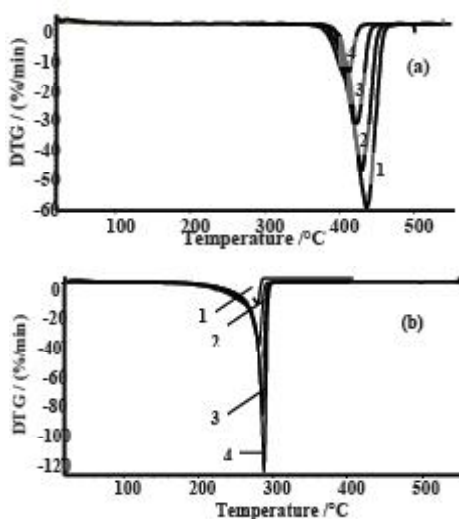

Figure 2: DTG curves of dynamic thermal degradation of PS (a) and DMT (b) at different heating rates. (1; 5ᵒC/min, 2; 10ᵒC/min, 3; 15ᵒC/min, 4; 20ᵒC/min)
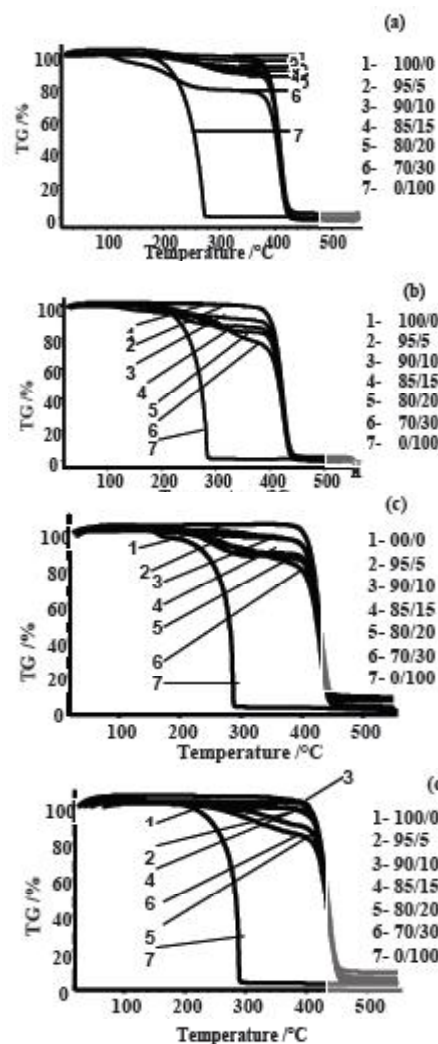

Figure 3: TG curves of dynamic thermal degradation of PS/DMT blends at different heating rates (a) 5ᵒC min⁻¹, (b) 10ᵒC min⁻¹,(c) 15ᵒC min⁻¹, (d) 20ᵒC min⁻¹

on DTG curves as shown in figure 2, (a) and (b) respectively.

In TG curves, a second degradation step is observed at heating rate above 15⁰C min⁻¹ and it appears below 200⁰C. It is also evident that PS is thermally more stable than DMT because thermal degradation of DMT starts earlier and goes on in a narrower temperature interval. With increasing heating rate, the degradation of DMT starts at higher temperature, the temperature at the maximum rate of degradation increases slightly, but the maximum rate of degradation increases sharply. This means that the rate of degradation of DMT is dependent very well on the heating rate.

Thermal degradation of pure PS occurs with one step, while thermal degradation of plasticized PS oc-
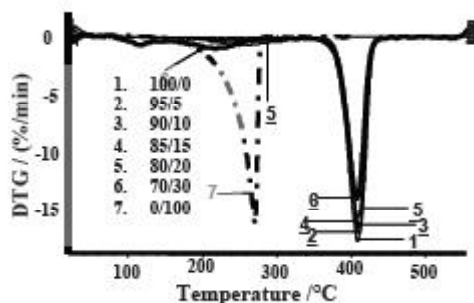
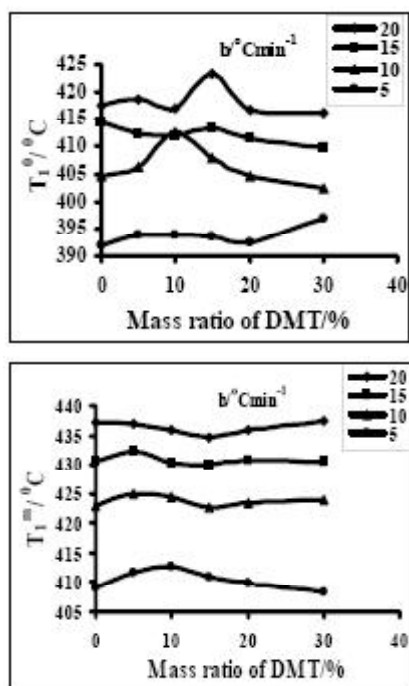**Figure 4: DTG curves of dynamic thermal degradation of PS/DMT blends at a heating rate of 10°C/min**

Figure 5: Effect of PS/DMT blend composition and heating rates on the onset temperatures (a), and on the temperatures at the maximum rates of degradation (b)

curs through two steps as shown by the thermogravi metric(TG) curves of dynamic thermal degradation, obtained in the temperature range of 30-550°C at the heating rates 5,10,15,and 20°Cmin⁻¹ are shown in figure 3(a-d), respectively.

The effects addition of DMT on TG curves is to decrease the temperature at which PS films start mass loses. For pure PS, the measurable mass lose starting between (400-460°C) is detected. This means that in these samples below 400°C very small degradation is present. It can be seen from the TG curves that the thermal degradation of plasticized PS films is higher than pure PS of similar molar mass.

The corresponding derivative thermogravimetric (DTG) curves, only for the heating rate 5°Cmin⁻¹, are shown in figure 4.

The thermograms of PS/DMT blends contain two unresolved degradation steps the first corresponds to the thermal degradation of DMT and the second to the thermal degradation of PS. The highest rate of PS degradation is achieved in the pure PS and the slowest rate of PS degradation is achieved in the blend PS/DMT 70/30. This means that the rate of PS degradation decreases by increasing the content of DMT in the blend. The temperatures at the maximum rate of degradation (represented by peaks on DTG curves) in PS/DMT blends are almost remain constant compared with pure PS. Furthermore, the widths are almost the same.

The characteristics of the TG and DTG curves: the onset temperatures of the start of degradation (T_1^0) (the intersections of the extrapolated base line with the tangents drawn in the inflection points of the TG curve), the temperature at the maximum rate of degradation step (T_1^m), the degree of conversion α is defined as:

$$\alpha = (m_0 - m)/)(m - m_f) \tag{1}$$

Where m_0, m and m_f refer to the initial, actual and residual mass of the sample. These are calculated by using NETZSH system software. Furthermore, the dependencies of onset temperatures (T_1^0) and the temperatures at the maximum rate of degradation in the first degradation step (T_1^m) on DMT ratio in the blends for different heating rates are shown in figure 5 (a and b), respectively. It is noticed that these characteristics depend on the composition on of PS/DMT blends. Within the same rate, it is clear that there is no obvious correlation between both T_1^0 and T_1^m with DMT composition, which means that DMT neither affect the beginning of thermal degradation nor the temperature of maximum degradation rate.

Furthermore, the dependence of the degree of conversion at the corresponding maximum rates of degradation (α_1^m) and the mass percent lose (Δm_1), at the end of the second degradation step on the PS/DMT blend ratios for different heating rates is shown in figure 6 (a and b) respectively.

With the addition of DMT to PS, (α_1^m) shows lower values than that for pure PS at the following heating rates (5°C min⁻¹, 10°C min⁻¹ and 15°C min⁻¹), while at
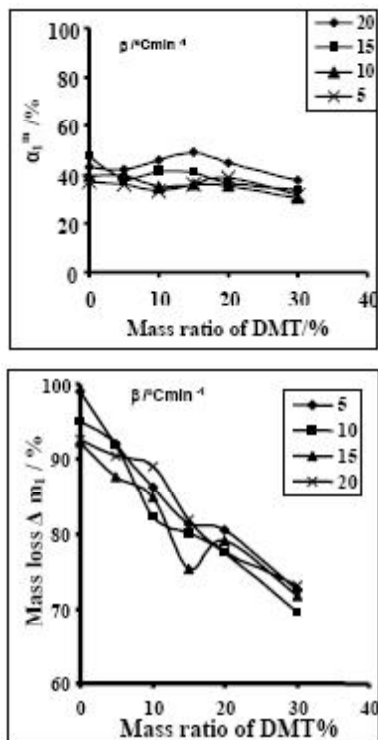
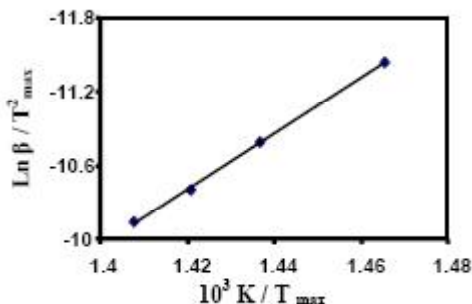**Figure 6: Effect of PS/DMT blend composition and heating rates on the α_1^m (a) and on the Δm_1 (b)**

Figure 7: Kissinger method plot of $\ln(\beta/T^2_{max})$ against $\ln(1000/T_{max})$ for PS/DMT blend

20^0C min^{-1} heating rate, the addition of DMT to PS, shows higher or the same values as for pure PS. At the same time, Δm_1 decreases with the increase in the added PS/DMT ratio in the blend, and found to depend on the heating rate.

Influence of heating rate on kinetic parameters of the thermal degradation

The application of dynamic TG methods can be used for unravelling the mechanism of physical and chemical processes that occur during polymer degradation. Thermal degradation of PS and PS/DMT blends

can be explained by evaluating some kinetic parameters such as, activation energy (E), Arrhenius factor (A), and conversion function (α).

The rate of conversion, $d(\alpha)/dt$, for TG experiments at constant rate of temperature change, $\beta=dT/dt$ may be expressed by:

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

where $f(\alpha)$ and $k(T)$ are functions of conversion and temperature respectively.

$k(T)$ is expressed by Arrhenius equation:

$$k(T) = A\,e^{-E/RT} \qquad (3)$$

where, Ea is the activation energy, and A is the Arrhenius factor.

The function of conversion $f(\alpha)$ is given by:

$$f(\alpha) = (1-\alpha)^n \qquad (4)$$

where n is the order of the reaction. Insertion of Eqs. (3) and (4) into Eq. (2) gives:

$$\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dt} = (1-\alpha)^n\,A\,e^{-E/RT} \qquad (5)$$

In this work, two methods have been used to analyse the non-isothermal kinetics of PS/DMT blends at different heating rates.

Kissinger method[18]

This technique involves obtaining the temperature values (T_{max}) that occurs at the maximum rate, while $d(d\alpha/dt)/dt$ is zero, differentiation of Eq. (5) with respect to time (t) and setting the resulting expression to zero gives:

$$E\beta/RT^2_{max} = An\,(1-\alpha_{max})^{n-1}\,e^{-E/RT_{max}} \qquad (6)$$

In equation (6), Kissinger assumes that the product $n(1-\alpha_{max})^{n-1}=1$, and is independent of the value of β and the following equation was obtained:

$$\ln(\beta/T^2_{max}) = \ln(AR/E) + \ln[n\,(1-\alpha_{max})^{n-1}] - E/RT_{max} \quad (7)$$

Kissinger method has been employed to analysis of TG data of PS/DMT blends, because it is independent of any thermodegradation mechanism. This allows the activation energy to be determined from a plot of $\ln(\beta/T^2_{max})$ against $(1000/T_{max})$. The activation energy (E) is calculated from the slope, and the pre-exponential factor (A) from the intercept of the obtained straight line. A typical plot obtained by Kissinger method is shown in figure 7.

The kinetic parameters calculated from this method

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TABLE 1: Average values of kinetic parameters of non-isothermal degradation of PS/DMT blends determined by Kissinger's method

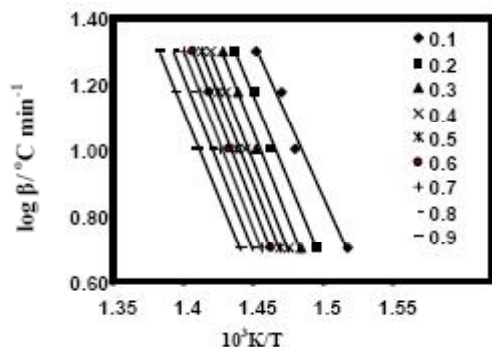| PS/DMT	100/0	95/5	90/10	85/15	80/20	70/30	0/100
r^2		0.9995	0.9982	0.9979	0.9995	0.9989	0.9944	0.9818
(E) KJmol^{-1}	190	207	232	222	203	181	195
Log A	9.6	10.8	12.7	12.0	10.5	8.9	13.9

Figure 8: Application of Flynn-Wall-Ozawa method for 95/5 PS/DMT blend.

are shown in TABLE 1.

It has been reported that the calculated activation energy for PS, (Mw = 24500) was found to be 205 kJ/mole, and to decrease with the increase in Mw values[15]. Our data using Kissinger method gave 190kJ/mole for pure PS, and very close to the above reported value.

Flynn-wall-ozawa method[19-21]

This method is derived from the integral method, also being independent of degradation mechanism. It is directly based on equation (5) that can be arranged as shown below:

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta}(e^{-E/RT})\,dT \qquad (8)$$

Which is integrated with the initial condition of ($\alpha = 0$) at $T = T_o$, to obtain the equation below:

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta}\int_{T_o}^T (e^{-E/RT})\,dT \qquad (9)$$

On assuming that A, $(1-\alpha)^n$ and E are independent of T, while A, and E are independent of α, then by using Doyle's approximation of E/RT >20, for the integrated equation[22], can be simplified as in the following logarithmic equation below:

$$\log F(\alpha) = \log(AE/R) - \log\beta - 2.315 - 0.4567(E/RT) \qquad (10)$$

Where $F(\alpha)$ is the conversion functional relationship, β is the

heating rate in (°C/min).

For different heating rates at constant degree of conversion (α), Eq. (10) can be formulated and called Flynn-Wall-Ozawa equation, as shown below:

$$\log\beta = -0.4567(E/RT) - 2.315 + \log(AE/R) - \log F(\alpha) \qquad (11)$$

Where (α) is the degree of conversion = (0.0- 0.9).

From Eq. (11), values of log β were plotted against 1000/T, and E- values at different degree of conversion for 95/5 PF/ DMT blend were calculated. As Doyle's approximation has been applied for the integral in this method, (α) =0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9 have been used. A typical plot obtained plot by the Flynn-Wall-Ozawa isoconversional kinetic method for 95/5 PS/DMT blend is shown in figure 8 above

In this work, the calculated activation energy (E) is called apparent activation energy because it is the sum value of activation energies of chemical reactions and physical processes in thermal degradation, and is calculated from of the slope of these lines. The values of pre-exponential factor are calculated from the intercept of the straight line with y-axis, for each conversion using the first reaction order kinetic mode. For pure PS, values of (E) are almost constant in the conversion range $\alpha = 0.1$- 0.9. According to this fact, one can conclude that in this conversion range, the mechanism of thermal degradation almost remains constant[23]. For Pure DMT in conversion range $\alpha = 0.1$- 0.9, values of (E) increases with the increase in degree of conversion. Pure PS has higher (E) than for pure DMT. (E) Values of PS/DMT blend decreases with the increase in blending ratio and they do change linearly with the ratio of PS in the blend. Calculated values of kinetic parameters (E and log A) of non-isothermal degradation for each PS/DMT blend in the conversion range (0.1- 0.9) are shown in TABLE 2.

The average values for kinetic parameters (E and logA) of non-isothermal degradation of PS/DMT blend are calculated in the range of applicability of Flynn-Wall-Ozawa method and are listed in TABLE 3.

From the data in TABLES 1 and 3, it can be seen that by using Kissinger and Flynn-Wall-Ozawa methods, almost equal values of activation energies and pre-exponential factor are obtained for the whole conversion range. It is a fact that activation energy, pre-exponential factor and conversion function values should be

TABLE 2: Kinetic parameters of non-isothermal degradation of PS/DMT blends determined by Flynn-Wall-Ozawa method

PS/DMT blend		Conversion, α								
		0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
100/0	r^2	0.9907	0.9938	0.9987	0.9982	0.9984	0.9979	0.9980	0.9959	0.9922
	E KJ mol^{-1}	157	171	177	178	176	177	177	172	161
	log A	10.9	12.1	12.7	12.8	12.8	12.9	12.9	12.7	11.9
95/5	r^2	0.9795	0.9930	0.9941	0.9961	0.9972	0.9977	0.9977	0.9981	0.9983
	E KJ mol^{-1}	170	187	195	196	196	196	196	194	188
	log A	11.9	13.4	14.1	14.2	14.3	14.4	14.4	14.3	13.9
90/10	r^2	0.9877	0.9884	0.9918	0.9943	0.9963	0.9976	0.9975	0.9977	0.9767
	E KJ mol^{-1}	167	167	185	193	195	197	197	190	152
	log A	4.0	11.8	13.3	14.0	14.2	14.4	14.5	14.0	11.2
85/15	r^2	0.9062	0.9201	0.9682	0.9808	0.9895	0.9906	0.9919	0.9920	0.9742
	E KJ mol^{-1}	165	159	180	184	191	188	186	181	160
	log A	0.2	11.3	12.9	13.3	14.0	13.8	13.7	13.4	11.8
80/20	r^2	0.9107	0.9056	0.9753	0.9900	0.9929	0.9947	0.9945	0.9941	0.9912
	E KJ mol^{-1}	182	173	184	193	192	193	193	192	192
	log A	1.0	12.4	13.3	14.1	14.0	14.2	14.2	14.1	14.2
70/30	r^2	0.9967	0.9675	0.9804	0.9973	0.9985	0.9983	0.9965	0.9955	0.9926
	E KJ mol^{-1}	145	160	146	165	171	173	171	170	162
	log A	1.1	1.5	10.4	12.0	12.4	12.7	12.5	12.6	12.0
0/100	r^2	0.9676	0.9961	0.9961	0.9942	0.9875	0.9812	0.9822	0.9785	0.9746
	E KJ mol^{-1}	87	91	94	103	112	125	141	160	180
	log A	7.8	8.2	8.5	9.4	10.3	11.6	13.2	15.1	17.2

TABLE 3: Average values of kinetic parameters of non-iso-thermal degradation of PS/DMT blends determined by Flynn-Wall-Ozawa method

PS/DMT	100/0	95/5	90/10	85/15	80/20	70/30
Conversion, α	0.2-0.8	0.3-0.8	0.3-0.8	0.3-0.8	0.4-0.9	0.5-0.8
r^2	0.9973	0.9968	0.9958	0.9855	0.9929	0.9972
(E) KJ mol^{-1}	175	196	193	185	193	171
Log A	12.7	14.3	14.0	13.5	14.1	12.6

used simultaneously to describe the thermal stability of plasticized polystyrene. When log A and E values exhibit a linear relationship for the same reaction carried out in a series of different conditions, it is known as a kinetic compensation effect[24,25]. The linear relationship was observed on the plot between log A and E for PS/DMT blends and is shown in figure 9.

As can be seen in figure 9, there is a linear relationship between log A and E for PS/DMT blends. According to Agrawal[26], a true compensation effect exists when the Arrhenius plots of (ln k) vs. 1/T display a single point of concurrence (T_{iso}) at which all rates are equal (k_{iso}). A plot of (ln k) vs. 1/T is shown in figure 10, below:

As seen in figure 10, A point of concurrence was observed for PS/DMT blends at blend ratio of 100/0, 85/15, 80/20, and 70/30, but not at higher blending ratio of 95/5 and 90/10. The concurrence point was
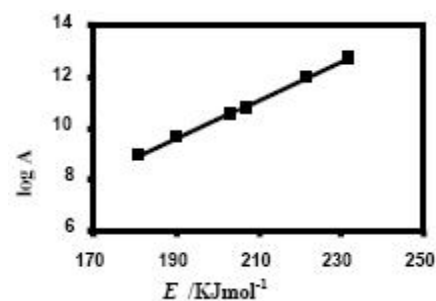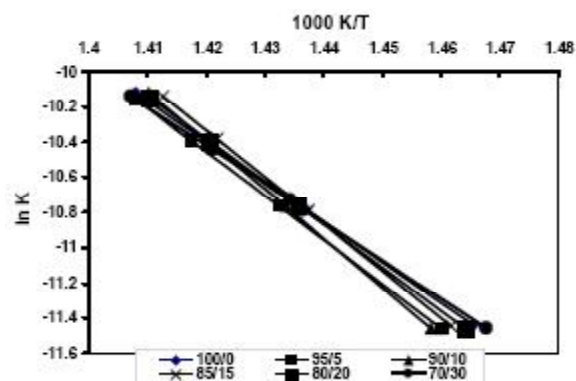

Figure 9: Compensation relationship in non-isothermal degradation of PS/DMT blends

Figure 10: Arrhenius plots *ln k* vs *1/T* for the non-isother-mal degradation of PS/DMT blends

found at Ln k= -10.7 for 100/0, 85/15, 80/20 and 70/30 PS/DMT. This may indicate that a true compensa-

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tion effect exists at these lower ratios. On the other hand, at higher ratios of PS/DMT blends, this point of concurrence does not exist and therefore, a condition for existence of the true compensation effect is not fulfilled.

CONCLUSIONS

1. From the investigations of the thermal degradation of PS/DMT blends with non-isothermal thermogra vimetry in an inert nitrogen atmosphere, it was concluded that:

2. The dynamic thermal degradation of pure PS occurs through one degradation step at the heating rates, of 5, 10, 15, 20°C min^{-1}, where thermal degradation of PS/DMT blends occur through two degradation steps at the used heating rates.

3. Blending of PS with DMT plasticizer, shifts the onset temperature and the temperature at the maximum rates of degradation to lower values. Also, the mass lose for pure PS starts between (400-460°C), while the mass lose of PS/DMT blend starts below 400°C. In the later case, thermal degradation of plasticized PS films is higher than for pure PS films.

4. Kissinger and Flynn-Wall-Ozawa methods were used to determine some kinetic parameters such as (log A and E) of thermal degradation of PS/DMT blends at different heating rates and blending ratios. Almost the same results were obtained by the two methods.

5. The apparent activation energy (E) of pure PS has lower value than blended PS and found to increase at low blending ratio.

6. An isokinetic point has been obtained at lower blending ratios, but not at higher blending ratios. Therefore, it can be concluded that there is a true compensation effect in the case of non-isothermal degradation of PS/DMT at low blending ratio.

ACKNOWLEDGMENT

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