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.

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[22]. 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-
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 somehow 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 gravimetric analysis (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 plasticizer 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 range 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-
mal degradation of PS and DMT plasticizer obtained in the temperature range of 30-550°C at the heating rates 5, 10, 15, 20°C min⁻¹ are shown in figure 1 (a and b) above.

As seen in figure 1(a), it is evident that the thermal degradation of pure PS proceeds by one-step process between 300 and 450°C, 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 500°C, depending on the heating rate, which characterized by a single peak 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 15°C min⁻¹ and it appears below 200°C. 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-
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 (T01) (the intersections of the extrapolated baseline with the tangents drawn in the inflection points of the TG curve), the temperature at the maximum rate of degradation step (T1m), the degree of conversion α is defined as:

\[ \alpha = \frac{(m_0 - m)}{(m - m_f)} \]  

Where m₀, m and mᵢ 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 (T₀₁) and the temperatures at the maximum rate of degradation in the first degradation step (T₁m) 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 T₀₁ and T₁m 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 (α₁m) and the mass percent lose (Δmᵢ), 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, (α₁m) 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
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, \( \frac{d(\alpha)}{dt} \), for TG experiments at constant rate of temperature change, \( \beta = \frac{dT}{dt} \) may be expressed by:

\[
\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dt} = k(T)f(\alpha)
\]

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

\[
k(T) = A e^{\frac{-E}{RT}}
\]

where, \( E_a \) is the activation energy, and \( A \) is the Arrhenius factor.

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

\[
f(\alpha) = (1 - \alpha)^n
\]

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

\[
\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dt} = (1 - \alpha)^n A e^{-E/RT}
\]

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

\[
\frac{E\beta}{RT_{\text{max}}^2} = n(1 - \alpha_{\text{max}})^{n-1} e^{-E/RT_{\text{max}}}
\]

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

\[
\ln(\beta/T_{\text{max}}^2) = \ln(A) + \ln[n(1 - \alpha_{\text{max}})^{n-1}] - E/RT_{\text{max}}
\]

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 \( \ln(\beta/T_{\text{max}}^2) \) against \( 1000/T_{\text{max}} \). 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

<table>
<thead>
<tr>
<th>Blend</th>
<th>( r^2 )</th>
<th>( E ) (kJ mol(^{-1}))</th>
<th>( \log A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS/DMT 100/0</td>
<td>0.9995</td>
<td>190</td>
<td>9.6</td>
</tr>
<tr>
<td>95/5</td>
<td>0.9982</td>
<td>207</td>
<td>10.8</td>
</tr>
<tr>
<td>90/10</td>
<td>0.9979</td>
<td>232</td>
<td>12.7</td>
</tr>
<tr>
<td>85/15</td>
<td>0.9995</td>
<td>222</td>
<td>12.0</td>
</tr>
<tr>
<td>80/20</td>
<td>0.9989</td>
<td>203</td>
<td>10.5</td>
</tr>
<tr>
<td>70/30</td>
<td>0.9944</td>
<td>181</td>
<td>8.9</td>
</tr>
<tr>
<td>0/100</td>
<td>0.9818</td>
<td>195</td>
<td>13.9</td>
</tr>
</tbody>
</table>

Flynn-Wall-Ozawa method

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:

\[
\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} (e^{-E/RT}) dT
\]

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

\[
\int_{0}^{\alpha} \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \int_{T_o}^{T} (e^{-E/RT}) dT
\]

On assuming that \( A, (1-\alpha)^n \) and \( E \) are independent of \( T \), while \( A \) and \( E \) are independent of \( \alpha \), 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:

\[
\log F(\alpha) = \log(\frac{AE}{R}) - \log\beta - 2.315 - 0.4567(E/RT)
\]

Where \( F(\alpha) \) is the conversion functional relationship, \( \beta \) is the heating rate in (°C/min).

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

\[
\log\beta = -0.4567(E/RT) - 2.315 + \log(\frac{AE}{R}) - \log F(\alpha)
\]

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

From Eq. (11), values of \( \log \beta \) 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, \( (\alpha) = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, \) 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 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 3.

The average values for kinetic parameters \( (E) \) and \( \log A \) 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

<table>
<thead>
<tr>
<th>PS/DMT blend</th>
<th>Conversion, α</th>
<th>E KJ mol⁻¹</th>
<th>log A</th>
<th>r²</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>100/0</td>
<td>157</td>
<td>171</td>
<td>177</td>
<td>178</td>
</tr>
<tr>
<td></td>
<td>10.9</td>
<td>12.1</td>
<td>12.7</td>
<td>12.8</td>
</tr>
<tr>
<td></td>
<td>0.9975</td>
<td>0.9930</td>
<td>0.9941</td>
<td>0.9961</td>
</tr>
<tr>
<td>95/5</td>
<td>170</td>
<td>187</td>
<td>195</td>
<td>196</td>
</tr>
<tr>
<td></td>
<td>11.9</td>
<td>13.4</td>
<td>14.1</td>
<td>14.2</td>
</tr>
<tr>
<td></td>
<td>0.9877</td>
<td>0.9884</td>
<td>0.9918</td>
<td>0.9943</td>
</tr>
<tr>
<td>90/10</td>
<td>167</td>
<td>167</td>
<td>185</td>
<td>193</td>
</tr>
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<td></td>
<td>4.0</td>
<td>11.8</td>
<td>13.3</td>
<td>14.0</td>
</tr>
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<td></td>
<td>0.9062</td>
<td>0.9201</td>
<td>0.9682</td>
<td>0.9808</td>
</tr>
<tr>
<td>85/15</td>
<td>165</td>
<td>159</td>
<td>180</td>
<td>184</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>11.3</td>
<td>12.9</td>
<td>13.3</td>
</tr>
<tr>
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<td>0.9107</td>
<td>0.9036</td>
<td>0.9753</td>
<td>0.9900</td>
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<tr>
<td>80/20</td>
<td>182</td>
<td>173</td>
<td>184</td>
<td>193</td>
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<td>1.0</td>
<td>12.4</td>
<td>13.3</td>
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<td>0.9967</td>
<td>0.9675</td>
<td>0.9804</td>
<td>0.9973</td>
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<td>70/30</td>
<td>145</td>
<td>160</td>
<td>146</td>
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</tr>
<tr>
<td></td>
<td>1.1</td>
<td>1.5</td>
<td>10.4</td>
<td>12.0</td>
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<tr>
<td></td>
<td>0.9676</td>
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<td>0.9961</td>
<td>0.9942</td>
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<tr>
<td>0/100</td>
<td>87</td>
<td>91</td>
<td>94</td>
<td>103</td>
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<td></td>
<td>7.8</td>
<td>8.2</td>
<td>8.5</td>
<td>9.4</td>
</tr>
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</table>

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

<table>
<thead>
<tr>
<th>PS/DMT</th>
<th>Conversion, α</th>
<th>E KJ mol⁻¹</th>
<th>Log A</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>0.2-0.8</td>
<td>175</td>
<td>12.7</td>
</tr>
<tr>
<td>95/5</td>
<td>0.3-0.8</td>
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<td>14.3</td>
</tr>
<tr>
<td>90/10</td>
<td>0.3-0.8</td>
<td>193</td>
<td>14.0</td>
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<td>85/15</td>
<td>0.3-0.8</td>
<td>185</td>
<td>13.5</td>
</tr>
<tr>
<td>80/20</td>
<td>0.4-0.9</td>
<td>193</td>
<td>14.1</td>
</tr>
<tr>
<td>70/30</td>
<td>0.5-0.8</td>
<td>171</td>
<td>12.6</td>
</tr>
<tr>
<td>0/100</td>
<td>0.5-0.8</td>
<td>171</td>
<td>12.6</td>
</tr>
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</table>

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 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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CONCLUSIONS

1. From the investigations of the thermal degradation of PS/DMT blends with non-isothermal thermogravimetry 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.

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REFERENCES