Some Aspects of the Thermo-kinetic Non-isothermal Study on the Thermooxidative Degradation of Polytetrafluoroethylene Containing Additives

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Abstract

The thermooxidative degradation of polytetrafluoroethylene (PTFE), both pure and containing additives such as: carbon (graphite) (C), bronze (BZ) and glass fibre (GF), has been studied by non-isothermal thermo-differential analysis (DTA). The values of kinetic parameters obtained from the DTA data, on the basis of thermo-kinetic equations, were compared with the values obtained from the non-isothermal thermo-gravimetric analysis (TG-DTG) and a good agreement was achieved. The analysis of the characteristic temperatures and of the kinetic parameters from DTA-DTG data revealed that the thermal stability and mechanism of thermooxidative degradation depend on the nature and concentration of additives. The results were confirmed by the existence of a real compensation effect. The following equation was derived for the compensation effect: \( \ln A = 0.1410 E - 0.15 \).

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Key Words:
thermal-kinetics; non-isothermal; thermooxidative degradation; PTFE; additives.

Introduction

Since the products obtained from PTFE are not suitable in certain practical applications, various additives have been used to improve some properties of the resulting composites [1,2]. The practical applications of these materials in various fields [1] require studies on their thermal stability and degradation mechanism.

In the present paper such studies are reported by applying the thermo-differential analysis, DTA, under non-isothermal conditions, which afford a thermo-kinetic study on the thermooxidative degradation of
additives containing PTFE, not to be found in literature. The thermo-kinetic study on the additive influence on the thermal stability and mechanism of thermo-oxidative degradation of the PTFE consisted of the analysis of both the characteristic temperatures and the kinetic parameters from the DTA [3,4] and TG-DTG data for PTFE in both pure state as well as PTFE containing some additives such as: carbon (graphite), glass fibres (GF) and bronze (BZ).

The following methods under non-isothermal conditions were applied for estimating the kinetic parameters: the Freeman-Carroll differential [5a] and Coats-Redfern [5b] integral methods adapted for DTA [6,7], the FÆ tu [8] integral method and the method for estimation of the initial reaction rate [6] based on the following thermo-kinetic equations:

\[ \frac{\Delta \ln \left( \frac{A}{a_r} \right)}{\Delta \ln \frac{A}{a_r}} = n - \frac{E_a}{R} \left( \frac{1}{T} \right) \]  

Freeman - Carroll (1)

\[ \ln \left[ \frac{\ln(1 - \alpha)}{T^2} \right] = C - \frac{E_a}{R} \frac{1}{T} \]  

Coats - Redfern (n = 1) (2)

\[ \ln \left( \frac{\Delta T}{1 - \frac{a}{A}} \right) = C \left( \frac{E_a}{R} \frac{1}{T} \right) \]  

\( \text{FÆ tu} \) (3)

where, \( T \)-temperature of the sample; \( \Delta T \)-ordinate of the DTA curve, \( \Delta T = T - T_0 \); \( T_0 \)-temperature of the reference material; \( A \)-total area of the DTA peak; \( a \)-current DTA area at temperature \( T \); \( a_i = A - a \); \( \alpha = a/A \) (conversion degree); \( b \)-abscissa of the DTA curve (min); \( C, C \)-constants independent on \( T \); \( \Delta T_{\text{max}} = T_{\text{max}} - T_0 \); \( T_{\text{max}} \)-temperature at the maximum of the DTA curve (Figure 1); \( E_a \)-activation energy; and \( n \)-reaction order.

The results obtained by the thermo-kinetic studies are in agreement with those obtained from TG-DTG data and were also confirmed by the study by compensation effect.

**EXPERIMENTAL**

PTFE Samples provided by Hoechst - Germany have been used in the experiments, namely: Hostaflon TF (sample 1); Hostaflon TF with 25% C (sample 2); Hostaflon TF with 25% GF (sample 3); Hostaflon TF with 20% BZ (sample 4).

The following non-isothermal techniques have been applied: differential thermal analysis (DTA), thermogravimetry (TG) and derived thermogravimetry (DTG), on a MOM-Budapest derivatograph which records the T, TG, DTG curves simultaneously.

The experimental conditions have been the same: sample weight of 18 mg, heating rate 10 C/min, ambient atmosphere, reference material \( \text{Al}_2\text{O}_3 \) freshly calcined at 1000 C, DTA and DTG sensitivity 1/10, maximum temperature attained 1000 C.
RESULTS AND DISCUSSION

The DTA curves in Figure 2 were drawn for pure (1) and additive containing PTFE with carbon (2), glass fibres (3) and bronze (4). The pure (1) additives containing PTFE such as, GF (3) and BZ (4) can be seen to show a single exothermal peak within the same temperature range. The sample containing carbon shows two distinct exothermal peaks. The first is attributable to the PTFE degradation, being situated within the same temperature range as for the pure PTFE, and the last is attributed to the carbon in the sample, thermally degraded in air within the same temperature range, as mentioned in literature.

In Table 1 the characteristic temperatures in DTA curves are given.

The DTG curves of the samples under study are depicted in Figure 3. It can be seen that the pure PTFE as well as that containing GF (3) and BZ (4) are degraded in one stage while that with carbon (2) in two distinct stages, in agreement with the observations resulting from the DTA curves.

The thermogravimetric variables characteristic of the analyzed samples were obtained from the TG-DTG curves and listed in Table 2.

The composition of the samples was confirmed by the agreement between the theoretical (W∞% theoretic) and experimental (W∞% exp) mass losses for the stage corresponding to the PTFE degradation in the TG curve. In case of the sample II, which is degraded in two stages, the included carbon is degraded during the 2nd stage as proved also by the agreement between the theoretical

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### Table 1. Characteristic temperatures for DTA.

<table>
<thead>
<tr>
<th>No</th>
<th>Sample</th>
<th>Stage I</th>
<th>Stage II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>T_i(°C)</td>
<td>T_m(°C)</td>
</tr>
<tr>
<td>1</td>
<td>Pure PTFE</td>
<td>510</td>
<td>590</td>
</tr>
<tr>
<td>2</td>
<td>PTFE with 25% C additive</td>
<td>500</td>
<td>580</td>
</tr>
<tr>
<td>3</td>
<td>PTFE with 25% FS additive</td>
<td>510</td>
<td>580</td>
</tr>
<tr>
<td>4</td>
<td>PTFE with 20% BZ additive</td>
<td>480</td>
<td>560</td>
</tr>
</tbody>
</table>

T_i - initial temperature of the DTA peak (°C); T_m - temperature at the maximum DTA peak (°C); T_f - final temperature of the DTA peak (°C).

### Table 2. Characteristic temperatures for DTG.

<table>
<thead>
<tr>
<th>No</th>
<th>Sample</th>
<th>Weighed amount (mg)</th>
<th>Stage I</th>
<th>Stage II</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>T_i(°C)</td>
<td>T_m(°C)</td>
</tr>
<tr>
<td>1</td>
<td>Pure PTFE</td>
<td>18</td>
<td>510</td>
<td>585</td>
</tr>
<tr>
<td>2</td>
<td>PTFE with 25% C additive</td>
<td>18</td>
<td>480</td>
<td>580</td>
</tr>
<tr>
<td>3</td>
<td>PTFE with 25% FS additive</td>
<td>18</td>
<td>490</td>
<td>585</td>
</tr>
<tr>
<td>4</td>
<td>PTFE with 20% BZ additive</td>
<td>18</td>
<td>500</td>
<td>570</td>
</tr>
</tbody>
</table>

T_i - initial temperature of the DTA peak (°C); T_m - temperature at the maximum DTA peak (°C); T_f - final temperature of the DTA peak (°C); W∞% exp. - experimental weight loss; W∞% theoretic-theoretical weight loss.
These results indicate the samples under study are physical mixtures.

The kinetic parameters \((n, E_a)\) resulting from DTA data as estimated on the basis of the thermo-kinetic equations (1)-(4) are given in Table 3 in comparison with those obtained from DTG data by means of the Freeman-Carroll differential and Coats-Redfern integral methods.

Tables 1-3 show a good agreement between the characteristic temperatures and activation energies obtained from DTA and DTG data.

The analysis of the initial degradation temperatures resulted from DTA and DTG curves shows the thermal stability of the samples containing additives to decrease in comparison with the pure PTFE. This conclusion

**Table 3.** Kinetic parameters \(\left(\frac{dT}{dt} = 10^0 C / min\right)\).

<table>
<thead>
<tr>
<th>No</th>
<th>Sample</th>
<th>TG-DTG</th>
<th>DTA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(E_a) (kJ/mol)</td>
<td>(E_a) (kJ/mol)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Freeman-Carroll method</td>
</tr>
<tr>
<td>1</td>
<td>Pure PTFE</td>
<td>1</td>
<td>344.05</td>
</tr>
<tr>
<td>2</td>
<td>PTFE with 25% C additive</td>
<td>1</td>
<td>296.20</td>
</tr>
<tr>
<td>3</td>
<td>PTFE with 25% FS additive</td>
<td>1</td>
<td>298.78</td>
</tr>
<tr>
<td>4</td>
<td>PTFE with 20% BZ additive</td>
<td>1</td>
<td>332.48</td>
</tr>
</tbody>
</table>
Some Aspects of the Thermo-kinetic Non-isothermal Degradation of PTFE

The value of the activation energy of the thermooxidative degradation of pure PTFE (346.33 kJ/mol) lies within the range of $E_a$ values of PTFE depolymerization (309-355 kJ/mol) [9]. It follows that the pure PTFE is predominantly degraded by depolymerization, hence by a simple chain mechanism.

With the samples containing additives the degradation by depolymerization decreases from the sample 4, containing less additive (20% BZ) and showing an activation energy (330 kJ/mol) closed to that of the sample 1.

With the samples 2 and 3 the additive concentration is equally higher (25 %) and the activation energies do not decrease significantly. The modification in the degradation mechanism as suggested by the modification of the average activation energies of the samples containing additives in comparison with the pure PTFE might be caused by the additive addition process [1,10]. This process implies various mechanical operations causing the polymer breaking and, hence, the decrease in the average molecular weight. Thus, the physical interactions with the additive, which depend on its nature and amount become weaker and the degradation mechanism is modified as expressed by the decrease in the average activation energy.

With the sample 2, containing 25% carbon, the average activation energies for the 2nd stage were found to be of equal values from DTA (133.50 kJ/mol) and TG - DTG data (130.30 kJ/mol), corresponding to the thermooxidation of carbon in the sample.

The thermooxidative degradation stage of PTFE in the samples proceeds within the same temperature range (480-620°C) and the reaction orders are of the same value. Hence, the reactions are related to one another. By applying two different thermal methods (DTA and TG-DTG) the results were in good agreement, affording the study by compensation effect as well.

In Table 4 the compensation parameters introduced by Nicolaev [5] and Gorbachev [5d] are listed.

The data in Table 4 indicate the same compensation parameters $a$ and $S_p$, meaning, according to Zsako

| No | Sample                  | $T_{interval}$ (°C) | $T_{max}$ (°C) | $E_a$ (kJ/mol) | Compensating parameters
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Nikolaev</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$T_{iz0}$, k</td>
</tr>
<tr>
<td>1</td>
<td>Pure PTFE</td>
<td>510-620</td>
<td>858</td>
<td>348.34</td>
<td>0.1400</td>
</tr>
<tr>
<td>2</td>
<td>PTFE with 25% C Additive</td>
<td>480-610</td>
<td>853</td>
<td>300.53</td>
<td>0.1410</td>
</tr>
<tr>
<td>3</td>
<td>PTFE with 25% FS additive</td>
<td>490-600</td>
<td>858</td>
<td>298.73</td>
<td>0.1400</td>
</tr>
<tr>
<td>4</td>
<td>PTFE with 25% BZ additive</td>
<td>500-610</td>
<td>843</td>
<td>330.56</td>
<td>0.1426</td>
</tr>
</tbody>
</table>

Table 4. Compensating parameters.
[5e], that the same bond type is splitted by degradation, namely the covalent bonds present.

On the other hand, ln A decreases in the same direction with the activation energy suggesting weaker and weaker covalent bonds in the 1 > 4 > 2 > 3 order, generating a real compensation effect. The graph illustrating the real compensation effect is depicted in Figure 4, and the obtained equation is of the following form:

\[ \ln A = 0.1410 \cdot E^{-0.15} \]

The validity of the compensation effect is confirmed by the Arrhenius plotting, \( \ln k_i = f(1/T) \), (Figure 5), where an intersection domain of the straight lines with the correlation coefficient between 0.9959-0.9990 is made evident. The center of the intersection area represents the isokinetic temperature, which constitutes a criterion of existence of the kinetic compensation, in accordance with the literature data [11,12].

**CONCLUSION**

The non-isothermal thermo-kinetic study made on the pure PTFE as well as on the PTFE containing carbon, glass fibres and bronze led to the following conclusions:

- The kinetic parameters calculated from DTA data on the basis of thermo-kinetic equations were in good agreement with those calculated from TG-DTG data.
- The thermal stability of the samples containing additives is lower than that of pure PTFE and the following order was found: 1 > 4 > 2 ≥ 3.
- The degradation mechanism is influenced by the additive’s nature and concentration as confirmed by the existence of a compensation effect.

**REFERENCES**


5. Segal E. and Fătu D., *Introduction to Non-isothermal Kinetics*; Academic Ed. Bucharest, 102 (5a); 113 (5b); 202 (5c); 205 (5d); 204 (5e) (1983).