Effect of graphene content on thermal degradation of PTFE

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ABSTRACT
In this work we report on the effect of graphene nanoplatelet inclusion on the thermal degradation of polytetrafluoroethylene (PTFE) in nitrogen. PTFE/graphene nanocomposites, containing up to 4 vol% graphene were produced by solution-assisted blending followed by sintering. Decomposition parameters were determined by direct fitting of the Sestak-Berggren equation to the experimental data. It was found that the activation energy of thermal decomposition increased up to as much as 20% and was practically independent of the graphene content in the studied PTFE/graphene nanocomposites. This was attributed to the tortuosity of the graphene layers hampering the diffusion of the gaseous decomposition products.

Keywords: PTFE; thermal degradation; Sestak-Berggren equation; graphene nanocomposites

Introduction
Polytetrafluoroethylene (PTFE) is a fluoropolymer which exhibits high crystallinity and molecular weight which gives it excellent thermal stability and chemical inertness. Therefore, PTFE is used in various industries where specialised applications are required over a wide range of temperatures. However, PTFE exhibits poor thermal conductivity, deforms under load (creep), and experiences high wear rates. To overcome these limitations, fillers may be incorporated into the polymer matrix to prepare composites with enhanced properties [1].

In the past few years, the incorporation of carbon based nano-sized fillers into PTFE has received significant interest from the research community due to the enhancement of specific properties when compared to micro-scale fillers [2–4]. Another advantage of nano-sized fillers is that they have shown to be effective at relatively low loadings. Nano-sized carbon fillers, like graphene nanoplatelets, have shown to be very effective to improve the wear resistance of PTFE when compared to graphite [3]. The homogeneous dispersion of the graphene nanoplatelets in the PTFE matrix is critical to acquire the optimum property enhancement. Researchers developed recently methods to improve the dispersion of graphene in PTFE by using electrostatic self-assembly [5] and using perfluorinated solvents as dispersing aids [6]. Smith and Pantoya [7]
found that graphene improved the thermal conductivity of PTFE three times more than when using carbon nanotubes due to its platelet shape. Furthermore, the aspect ratio and platelet shape of nano-fillers play an integral role in delaying thermal degradation of a polymer matrix [8].

Additives are not generally incorporated into PTFE to improve its thermal stability, but mainly to improve the thermal conductivity. However, the incorporation of carbon nanotubes into PTFE is known to improve the thermal stability of fine particle PTFE dispersions [9]. Also, the use of platelet shaped nano-sized fillers are known to improve the thermal stability of polymers [10, 11]. Therefore, graphene may also improve the thermal stability of PTFE by forming an interconnected network in the composite matrix [7] According to our knowledge, the effect of graphene on the thermal stability of PTFE has not been addressed in literature. On the other hand, few studies already focused on the thermal stability of polyvinylidene fluoride (PVDF)/graphene composites [12, 13]. Most studies on the thermal degradation of PTFE and filled PTFE were, however, dealing with the thermal kinetics and the recovery of the monomer (C₂F₄) from PTFE waste [14–16].

In this study, the thermal degradation stability of graphene filled PTFE composites was measured using thermogravimetry (TG) in nitrogen. The Sestak-Berggren [17, 18] equation was directly fitted to the experimental data to resolve corresponding thermo-kinetic decomposition parameters at different graphene loadings. This method was chosen for its general applicability to thermal decomposition studies, and precluded the need for a possibly biased choice of reaction model.

Materials and methods

The PTFE moulding powders (Grade TFM 1700) were obtained from 3M Dyneon (Germany). TFM 1700 is a non-free flowing modified PTFE which exhibits a mean particle size of about 25 µm and a density of 2.16 g cm⁻³. The graphene nanoplatelets (GNPs) were obtained from XGsciences (USA) (Grade M-25) and incorporated into the PTFE through solution blending with perfluorohexane (PFH) (Pelchem, South Africa). The GNPs were used as received with no chemical modification.

The guidelines specified by Van Rooyen et al. [6] were followed to prepare the composite discs for thermal gravimetric analysis. The GNPs were incorporated according to volume fraction (vol%) of the total GNP/PTFE powder system. The GNP content varied between 0.25 and 4 vol%. The GNPs were firstly dispersed in perfluorohexane for 1 h at 30 °C in an ultrasonic bath (Scientech, 100W, South Africa). Afterwards the GNP/solvent mixture was blended with 5 g of a selected PTFE powder and stirred for 1 h. The GNP/PTFE powder was filtered and dried in a vacuum oven (Instruvac, OV-11) at 70 °C for 24 h to remove any residual solvent. Approximately 30 mg of the PTFE/GNP powder was weighed and pressed into composite discs (Ø5 mm) using 12.7 MPa as preform pressure. The preform discs were sintered at 380 °C using a programmable cycle in a sintering oven (Carbolite HT, United Kingdom). For both polymers, three sets of samples were prepared at different graphene loadings, and the TG analysis was performed at three heating rates. Details of specific samples are given in Table 1.

Thermogravimetry

Thermogravimetry (TG) on the GNP/PTFE composite and PTFE reference discs were performed on a SDT Q600 (TA Instruments, USA) simultaneous TG/DSC analyser. The disc samples were heated from ambient temperature up to 800 °C in a nitrogen atmosphere using heating rates of 10, 15 and 20 °C.min⁻¹ and N₂ purge rate of 100 ml.min⁻¹.

Microscopy

A SUPRATM 40VP (Carl Zeiss SMT AG, Jena, Germany) ultra-high resolution Field Emission Scanning Electron Microscope (FESEM) operating at a 5 kV acceleration voltage was used to investigate cryo-fractured
cross sectional regions of the 1 and 4 vol% graphene filled PTFE composites.

Table 1 Sample size in mg.

<table>
<thead>
<tr>
<th>Graphene /%</th>
<th>Heating rate /°C.min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
</tr>
<tr>
<td>0</td>
<td>32.2</td>
</tr>
<tr>
<td>0.75</td>
<td>31.1</td>
</tr>
<tr>
<td>2</td>
<td>28.1</td>
</tr>
<tr>
<td>4</td>
<td>27.4</td>
</tr>
</tbody>
</table>

Theory

Using the activation energy of decomposition or thermal degradation to evaluate polymer thermal stability is not a new idea [19, 20], and can readily be deduced from the kinetic methodology.

According to solid state kinetic theory, a substance decomposes according to the kinetic equation [21]:

\[
\frac{d\alpha}{dt} = kf(\alpha) \tag{1}
\]

with \( f(\alpha) \) a function describing the kinetic model, \( \alpha \) the fractional extent (conversion) of the reaction, \( t \) the time, and the kinetic (Arrhenius) constant \( k \):

\[
k = Ae^{-E_a/RT} \tag{2}
\]

where \( A \) is the pre-exponential factor, \( R \) is the universal gas constant. In our work we substitute \( f(\alpha) \) the Sestak-Berggren equation:

\[
f(\alpha) = \alpha^m (1 - \alpha)^n (- \ln(1\alpha))^p \tag{3}
\]

And compare the resulting integral using Euler’s method:

\[
\alpha_{n+1} = \alpha_n + kf(\alpha_n)\delta t \tag{5}
\]

To construct the integral an initial value \( \alpha_0 = 0.000001 \) is assigned. The activation energy, \( E_a \), was varied between 0 and 500 kJ.mol⁻¹, and to conform with the well established kinetic models the values \( m \) and \( p \) can were restricted to 0, \( \frac{1}{2}, \frac{2}{3}, \) and \( \frac{3}{4} \), while \( n \) was allowed 0, \( \frac{1}{2} \) and \( \frac{2}{3} \).

Integration and rearrangement of Equation 1, yields equation 5:

\[
t_\alpha = \frac{g(\alpha)e^{E_a/RT}}{A} \tag{3}
\]

This equation describes that the time it takes for a polymer to degrade to any given value of \( \alpha \) is directly proportional to the activation energy \( (E_a) \) of the degradation reaction.

Results and discussion

The TG curves for graphene dispersed in TFM1700 are shown in Figure 1. Very little difference is visible between the curves for samples with differing graphene content, except for the final residue value. Final residues (Table 2) correlate reasonably well to the initial graphene content.

Table 2 Residue after each run

<table>
<thead>
<tr>
<th>Graphene /%</th>
<th>Heating rate /°C.min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
</tr>
<tr>
<td>0</td>
<td>0.02</td>
</tr>
<tr>
<td>0.75</td>
<td>0.3</td>
</tr>
<tr>
<td>2</td>
<td>0.45</td>
</tr>
<tr>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

To evaluate the decomposition kinetics, the procedure described in section 4 was followed. The best fit was obtained when \( n=2/3 \) and other exponents equal to zero (Equation 3). Table 3 lists the \( E_a \) for each run, with the correlation between theoretical and experimental data in Table 4.

Figure 2 shows the theoretical fit of the Euler integral (Equation 4) showed in dashed lines, with experimental data for each experimental run. The corresponding activation energy is shown on Figure 3.

The value of \( E_a \) increases substantially with GNP loading for the TFM1700 polymer, but no significant changes between 0.75 and 4 vol%
GNP loading is apparent. This increase indicates improved resistance to thermal degradation of the polymer sample.

Figure 1 TG curves for PTFE (TFM1700) with different graphene loadings.

Table 3 Activation energies that resulted in best correlation between experimental and theoretical data.

<table>
<thead>
<tr>
<th>Graphene (vol%)</th>
<th>Heating rate /°C.min⁻¹</th>
<th>Activation Energy (E_a)/kJ.mol⁻¹</th>
<th>Average</th>
<th>Stdev</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10</td>
<td>252</td>
<td>259</td>
<td>288</td>
</tr>
<tr>
<td>0.75</td>
<td>15</td>
<td>320</td>
<td>314</td>
<td>308</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>328</td>
<td>317</td>
<td>309</td>
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<tr>
<td>2</td>
<td>10</td>
<td>303</td>
<td>317</td>
<td>309</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>317</td>
<td>322</td>
<td>314</td>
</tr>
<tr>
<td></td>
<td>10°C.min⁻¹</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4 Correlation between experimental and theoretical data.

<table>
<thead>
<tr>
<th>Graphene (vol%)</th>
<th>Heating rate /°C.min⁻¹</th>
<th>Correlation Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10</td>
<td>0.9992</td>
</tr>
<tr>
<td>0.75</td>
<td>10</td>
<td>0.9999</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.9998</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.9999</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.9999</td>
</tr>
<tr>
<td>0.75</td>
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<td></td>
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<td>0.9999</td>
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<tr>
<td>4</td>
<td>10</td>
<td>0.9999</td>
</tr>
<tr>
<td>0.75</td>
<td>15</td>
<td>0.9998</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.9999</td>
</tr>
</tbody>
</table>

It can be argued as graphene is introduced into the polymer matrix the graphene layers restrict the diffusion of the gases by generating a tortuous pathway. This effect was recently confirmed in a study dealing with the helium permeability of PTFE/GNP [22].

Figure 2 Theoretical fit of SB equation to experimental data.
Figure 2 Activation energy for the decomposition reaction.

Figure 4 shows SEM images of PTFE composites at 1 and 4 vol% graphene loadings which clearly indicated the formation of a tortuous matrix at higher loadings.

Figure 3 SEM images of PTFE composites at 1 and 4% loadings of graphene

Conclusions

In this work graphene filled PTFE nanocomposites were prepared by solution-assisted blending followed by sintering, and the influence of graphene concentration on the thermal degradation properties were evaluated. For determination of the activation energy theoretical curves were directly fitted to experimental data, using the Sestak-Berggren equation. From our results it is clear that graphene may be used to improve the thermal degradation of the polymer samples. The effect observed might be due to some channeling of the volatile degradation products. With increasing graphene content, however, the thermal stability is systematically increased up to a nominal value which may be well beyond that of the unfilled PTFE. This improvement can be assigned to the formation of a tortuous path along with a shielding layer, generated by the graphene platelets, which impede both the evolution and exhaust of the gases.

Acknowledgements

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References


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