Supporting information

Green reduction of graphene oxide by polydopamine to construct flexible film: superior flame retardancy and high thermal conductivity

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1. Preparation of the films

Table 1 the composition of the prepared film

<table>
<thead>
<tr>
<th>Sample</th>
<th>GO</th>
<th>GPI</th>
<th>GPH</th>
<th>GPF</th>
<th>GPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene oxide</td>
<td>1.0</td>
<td>9.6</td>
<td>4.8</td>
<td>2.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Dopamine</td>
<td>0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The film is prepared according to the stoichiometric ratio described in Tab. 1. The

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reduction of the graphene oxide by dopamine is recorded by XRD, the corresponding patterns are shown in Fig. 1. A sharp peak located at 9.70° of GO can be observed from Fig. 2, which is the typical diffraction peak of GO. According to Bragg’s equation, the \( d \) spacing is 0.91 nm. As the content of the dopamine increases, new diffraction peaks are arouse, and when the stoichiometric ratio of (graphene oxide to dopamine) is decreased to 2.4:1, the typical diffraction peak of GO is completely disappeared, which indicated that the graphene oxide sheets are almost totally transfer to reduced graphene oxide (rGO).

![Fig. 1 XRD patterns of series film](image)

2. Effective medium theory

To account for the association between thermal conductive phenomenon and the
laminated structure of the film, the effective medium theory is adopted for interpreting the thermal resistance. 

\[
K_{11} = K_{22} = K_m \frac{2 + f \left[ \hat{A}_1 (1 - L_{11}) (1 + \cos^2 \theta) + \hat{A}_3 (1 - L_{33}) (1 - \cos^2 \theta) \right]}{2 - f \left[ \hat{A}_1 L_{11} (1 + \cos^2 \theta) + \hat{A}_3 L_{33} (1 - \cos^2 \theta) \right]} \\
K_{33} = K_m \frac{1 + f \left[ \hat{A}_1 (1 - L_{11}) (1 - \cos^2 \theta) + \hat{A}_3 (1 - L_{33}) \cos^2 \theta \right]}{1 - f \left[ \hat{A}_1 L_{11} (1 - \cos^2 \theta) + \hat{A}_3 L_{33} \cos^2 \theta \right]}
\]

\[
\hat{A}_i = \frac{K_{ii}^C - K_m}{K_m + L_{ii} \left( K_{ii}^C - K_m \right)}
\]

\[
<\cos^2 \theta> = \frac{i^\hat{N}(\hat{\psi} \cos^2 \theta \sin \theta \, \hat{d} \hat{d})}{i^\hat{N}(\hat{\psi} \sin \theta \, \hat{d} \hat{d})}
\]

Where \(K_{11}\) and \(K_{22}\) represent the in-plane thermal conductivities and \(K_{33}\) is the across-plane thermal conductivity. \(\theta\) is the angle between the materials plane and the local particles symmetric axis. \(\rho(\theta)\) is a distribution function describing the ellipsoidal particle orientation, \(f\) is the volume fraction of the filler, \(K_{ii}^C\) \((i=1, 2, 3)\) are the equivalent thermal conductivities conductivities along the symmetric axis of this aligned composites unit cell. \(K_m\) is the thermal conductivity of the matrix phase, \(L_{ii}\) are the geometrical factors dependent on the particle shape and are given by the following.
equation:

\[
L_{11} = L_{22} = \frac{p^2}{2(p^2 - 1)} + \frac{p}{2(1 - p^2)^{3/2}} \cos^{-1} p \quad \text{for } p \leq 1 \quad E_4
\]

\[
L_{33} = 1 - 2L_{11} \quad E_5
\]

\[
K_{ii}^c = \frac{K_m K_p}{K_m + (2p + 1) \dot{\Lambda}_{ii} K_p} \quad E_6
\]

Here a dimensionless parameter, \( \dot{\alpha} \), is defined by

\[
\dot{\alpha} = \frac{R_{bd} K_m}{h} \quad E_7
\]

Where \( R_{bd} \) is thermal boundary resistance and \( h \) is the thickness of the nanosheets.

For the laminate composites, considering the aligned graphene, assuming ideal case, \( p \rightarrow 0 \), \( L_{11} = 0 \) and \( L_{33} = 1 \). Thus, \( E_2 \) and \( E_6 \) can be expressed as following:

\[
K_{11}^c = K_{22}^c = K_p \quad E_8
\]

\[
K_{33}^c = \frac{K_m K_p}{K_m + \dot{\alpha} K_p} \quad E_9
\]

\[
\dot{\alpha}_1 = \frac{K_p - K_m}{K_m} \quad E_{10}
\]

\[
\dot{\alpha}_3 = (1 - \dot{\alpha}) - \frac{K_m}{K_p} \quad E_{11}
\]
Thus equations of effective medium theory reduce to:

\[
K_{11} = K_{22} = K_m \quad \frac{2 + f \left[ K_p - K_m \left( 1 + \langle \cos^2 \theta \rangle \right) \right]}{2 - f \left[ \frac{K_p - K_m}{K_p h} \left( 1 - \langle \cos^2 \theta \rangle \right) \right]}
\]

\[
K_{33} = K_m \quad \frac{1 + f \left[ K_p - K_m \left( 1 - \langle \cos^2 \theta \rangle \right) \right]}{1 - f \left[ \frac{K_p h}{h + R_{bd} K_p} \left( \cos^2 \theta \right) \right]}
\]

Where \( K_m \) is the thermal conductivity of the matrix phase, \( K_p \) is the thermal conductivity of the laminated nanosheets, \( f \) is the volume fraction of the particles, \( \theta \) is the angle between the materials axis, \( X_3 \), and the local particles symmetric axis, \( R_{bd} \) is thermal boundary resistance, and \( h \) is the thickness of the reduced graphene.

In the case of GPF, from the sectional SEM image, Materials axis \( X_3 \) is perpendicular to the graphene sheets symmetric axis (\( X_1 \) and \( X_2 \) direction), which means that \( \theta \) is tend to be zero. Thus, \( R_{bd} \) can be expressed as:

\[
R_{bd} = \left( \frac{f K_{33}}{K_{33} - K_m} - \frac{1}{K_p} \right) h
\]

In this case, \( h \) is approximately 0.5 nm, \( K_{33} \) is 0.69 W m\(^{-1}\) k\(^{-1}\), and it can be approximatively calculated that \( R_{bd} \) is less than \( 0.5 \times 10^{-9} \) K m\(^{2}\) W\(^{-1}\), of charred layer of GPF(d)(e)
3. $\pi-\pi$ stacking

The XRD pattern of GPF shown in Fig. 2 in the papers demonstrate the reduction of the GO. In detail, the peaks in the curve can be collected ($2\Theta=17.76, 20.40, 21.88, 22.24, 25.64$ and $28.50$), respectively, the corresponding $d$ spacing are $0.500, 0.435, 0.406, 0.399, 0.347, 0.312$nm. The narrow spacing might be aroused by the $\pi-\pi$ stacking between the reduced GO and polydopamine$^{6,7}$.

4. Tensile strength of the prepared films

![Graph](image)

**Fig. 2** Strain-stress curves of the prepared films

The strain stress curves of the prepared films are presented in Fig. 2. It can be
observed that the tensile strength of the films shows little difference. The tensile strength of GPE, GPF, GPH, GPI is 24.5, 25.0, 24.4 and 21.6 respectively. Among these films, GPE get a relative low tensile strength, which may be aroused by the totally reduction of the GO, which impairs the hydrogen bond between the rGO sheets and polydopamine.

5. Fire performance of the prepared films

The fire performances of the prepared films are depicted in Fig. 4. It can be found that all the films have excellent flame retardancy. However, based on the digital images of the samples after fire tests shown in Fig. 5, the flame stability of the film varies as the compositions of the film. Due to the less content of polydopamine, GPH and GPI can be burnt out, by leaving the large holes. This phenomenon demonstrates that polydopamine play a significant role in the flame retardant of the film.
**Fig. 3** Fire performance of the prepared films

**Fig. 3** Digital images of The samples after fire tests
References


