A critical review on in situ reduction of graphene oxide during preparation of conducting polymeric nanocomposites

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Graphene oxide (GO), prepared by chemical oxidation of graphite, serves as a building block for developing polymeric nanocomposites. However, their application in electrical conductivity is limited by the fact that the oxygen sites on GO trap electrons and impede charge transport. Conducting nanocomposites can be developed by reducing GO. Various strategies have been adopted to either reduce GO ex situ, before the composite preparation, or in situ during the development of the nanocomposites. The current state of research on in situ reduction of GO during the preparation of conducting polymeric nanocomposites is discussed in this review. The mechanism and the efficiency of reduction is discussed with respect to various strategies employed during the preparation of the nanocomposite, the type of polymer used, and the processing conditions employed, etc. Its overall effect on the electrical conductivity of the nanocomposites is also discussed and the future outlook in this area is presented.

1. Introduction

Graphite’s lamellar structure is made up of individual layers that are held together by van der Waals forces and are considered to be independent entities (graphene). These independent entities are known to possess unique electronic and mechanical properties. Some of the remarkable electronic and mechanical properties of graphene reported are ~200 000 cm² V⁻¹ s⁻¹ of charge carrier mobility, high Young’s modulus of ~1100 GPa and extraordinary fracture strength of 125 GPa. Apart from high electrical conductivity, they possess very high specific surface area of 2630 m² g⁻¹ and interesting transport phenomena such as the quantum Hall effect. Besides flexibility in properties, mono layer graphene sheets offers myriad possibilities of chemical modification and functionalization. Thus, graphene can be potentially used as energy-storage materials, polymer composites and sensors etc. Yan et al. reported that graphene and few-layer graphene can be utilized for thermal management of advanced electronics wherein graphene acts as heat spreaders in transistors. Luo et al., summarized various graphene based applications in energy storage such as solar cells, lithium ion secondary batteries and supercapacitors. In a recent article, Mittal et al.† reported that graphene exhibits restacking of sheets due van der Waals forces and strong π–π stacking effects. The interaction between graphene sheets and polymer matrix plays a vital role in achieving high electrical percolation. Graphene sheets can also act as a cationic initiator for polymerization of polystyrene (PS) and poly(styrene-isoprene). Graphene polymer composites can be used for tissue engineering applications such as osteogenesis in 3D scaffolds, selective gas/vapor sensors and in removal of heavy metal/pathogenic bacteria from aqueous media. GO based composites showed a significant surface enhanced Raman scattering (SERS), which can be useful in developing ultrasensitive SERS-based immunosensing platforms. Graphite to individual 2D graphene conversion is widely carried out by chemical oxidation of graphite layer. The formed oxides serve as a precursor for cost-effective and mass production of graphene-based materials. These exfoliated layers of graphene sheets with oxygen moieties are referred to as graphene oxide (GO). GO offers flexibility in the large scale production of graphene based nanocomposite. GO is widely synthesized via Brodie, Staudenmaier and Hummers methods. All these methods focus on the oxidation of individual layers using strong acids and oxidants for the introduction of oxide groups such as epoxy, hydroxyl or carboxyl. This oxidation results in the disruption of sp² bonding. In addition, these oxygen sites trap electrons that results in electrically insulating materials. High electrical conductivity can be achieved by effective removal of oxygen species. Various strategies that are reported in the literature for restoring electrical conductivity are chemical reduction, thermally reduction, microwave assisted reduction, photocatalysis and in situ reduction of GO during processing. Apart from these techniques, some literature exist that
utilized UV treatment for further reduction of GO. There are plenty of reviews available on the techniques mentioned above. However, the state of research on in situ reduction of GO, during the preparation of the nanocomposite, has not received much attention although the field is gaining significant interest among the scientific community.

Given the brevity of this review, we focus here mainly on the in situ reduction of GO during the preparation of conducting nanocomposites. The in situ reduction of GO is carried out mainly during in situ polymerization or during melt processing. The following section will highlight the current state of research on in situ reduction of GO to design and develop conducting polymeric nanocomposites from GO as the starting material.

2. In situ polymerization and simultaneous reduction of GO

The in situ polymerization involves polymerization of polar or hydrophilic monomers that can interact and intercalate into the stack of GO sheets. This results in exfoliation and isolation of GO sheets. To accomplish this, GO is initially dispersed in a polar solvent by ultrasonication. The dispersed GO sheets are then mixed with monomers and subsequently in situ polymerized at high temperature and under inert atmosphere. The in situ polymerization at high temperature ensures proper dispersion and reduction of GO. Hence, the obtained reduced GO composite shows 3–4 orders of higher conductivity compared to GO based composites. This strategy was adopted by Liu et al. in which simultaneous dispersion and thermo-reduction of GO occurs during in situ melt polycondensation reaction. GO was initially dispersed in ethylene glycol and then the composites were prepared via in situ polymerization of terephthalic acid (PTA) (Fig. 1). Further, it was demonstrated that polyester chains were successfully grafted onto GO sheets during polymerization, accompanied by the thermo-reduction from GO to reduced graphene oxide. The reported increase in conductivity of the composite is ca. 0.56 S m⁻¹ in striking contrast to GO based composites (7 × 10⁻⁴ S m⁻¹). They concluded that the chemical bonding between the polymer chain and GO is favorable for the improvement of interfacial interactions in the composites. In a recent study, Jin et al. adopted similar strategy to graft PBS (poly(butylene succinate)) chains onto graphene oxide during in situ polymerization, which is accompanied by the thermo-reduction from GO to graphene. In another recent work, an one-step approach was utilized to reduce and functionalize graphene oxide (GO) during the in situ polymerization of phenol and formaldehyde. The in situ reduction of graphene oxide provides homogenous dispersion of graphene into polymer matrix and additionally improves the electrical and thermal conductivity in the composite.

3. In situ reduction of GO during compositing process

The in situ reduction of GO during compositing process involves dispersion of GO followed by thermal reduction resulting in a composite with monolayer reduced GO. This strategy offers a simple fabrication procedure that prevents restacking and aggregation of reduced GO sheets in a given polymer matrix. Fig. 2 illustrates the method of in situ reduction during compositing process.

Recently, Tang et al. explored this strategy for poly(vinylidene fluoride) PVDF based GO composites, wherein they showed well-isolated reduced GO sheets in PVDF. Initially, they dispersed GO in DMF to yield highly exfoliated GO followed by mixing with PVDF. Thus, obtained PVDF/GO composites were then hot pressed at 200 °C for 2 h. Hot pressing leads to in situ reduction of GO that is evident from the change in color from brown to black.

Fig. 1 The synthesis of reduced polymer composite via in situ melt polycondensation (Liu et al. reproduced by the permission of The Royal Society of Chemistry).
This color change is attributed to the efficient removal of oxygen functional groups and partially restoring the graphitic structure. From Fig. 2, it is evident that PVDF/GO composite was initially brown suggesting uniform dispersion of GO in PVDF. However, after reduction, the films turned black. Restoring graphitic structure can lead to $\pi$-conjugation, which renders electrical conductivity in the composites. Further, they demonstrated a three-order increase in conductivity with respect to GO composites at a relatively low fraction of 0.16 vol% of reduced GO. Due to immobilization of GO, thin layer of sheets percolate into composites and lead to low percolation threshold. The single layer of reduced GO was further confirmed by TEM (as shown in Fig. 2) and suggested that polymer with higher thermal stability could even enhance the conductivity by complete reduction of GO to graphene.

In another study,\textsuperscript{37} PVDF/GO composites were prepared by solution mixing in DMF. The resultant composite was coagulated with water. The obtained PVDF/GO mixture was then hot pressed at $200\,^\circ\text{C}$ at 50 MPa into sheets of about 0.4 mm thickness. After hot pressing, the color of the composite changed from grey to black suggesting thermal reduction of GO into reduced GO. These sheets were used as masterbatch for the preparation of PVDF/GO composites using a melt compounding. They demonstrated a significant improvement in conductivity of the composite i.e. $3 \times 10^{-7}$ S cm$^{-1}$ at a loading of 0.17 vol% of reduced GO. Further, at 1 vol% of reduced GO, a conductivity of $2 \times 10^{-3}$ S cm$^{-1}$ was obtained and the change in conductivity with processing temperature was studied. The processing temperature affects the percolation threshold of TRG. For instance, PVDF–TRG composite processed (hot pressed) at $200\,^\circ\text{C}$ exhibited a percolation threshold of 0.12 ± 0.02 vol% (as shown in Fig. 3) in contrast to the composite processed at 190 and 210 $\,^\circ\text{C}$ which showed similar percolation thresholds of 0.17 ± 0.02 vol% and 0.17 ± 0.01 vol%, respectively (Table 1).

The reduction of GO in situ during compression molding was also studied by Ding-Xiang et al.\textsuperscript{38} wherein they distributed GO on the surface of ultra-high molecular weight poly(ethylene) (UHMWPE) particles followed by compression molding. It is evident that GO sheets are distributed at the interface of UHMWPE particles and further reduction of GO was assisted by hot pressing at $280\,^\circ\text{C}$ and 10 MPa pressure for 30 min. Hot pressing ensured reduction of GO to reduced GO in situ. The distribution of reduced GO sheets at the interface yielded a low percolation threshold of 0.66 vol% in UHMWPE and an electrical conductivity of ca. 3.4 S m$^{-1}$.

Yan et al.\textsuperscript{39} utilized segregated architectures to distribute reduced GO at the interface of polymer granules rather than distributing in volume in the matrix. These segregated architectures lead to reduction of percolation threshold hence resulting in an increase in electrical conductivity. They utilized polystyrene (PS) of different particle size and observed PS with higher particle size to yield lower percolation threshold. They

### Table 1: Critical percolation threshold and electrical conductivity of reduced GO–PVDF composites hot-pressed at different temperature\textsuperscript{38} (reproduced by permission of The Royal Society of Chemistry)

<table>
<thead>
<tr>
<th>Temperature ($^\circ\text{C}$)</th>
<th>Critical percolation ($P_c$) (vol%)</th>
<th>Conductivity ($\sigma_\infty$) (S cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>0.17 ± 0.02</td>
<td>75.29 ± 16.23</td>
</tr>
<tr>
<td>200</td>
<td>0.12 ± 0.02</td>
<td>1496 ± 136.38</td>
</tr>
<tr>
<td>210</td>
<td>0.17 ± 0.02</td>
<td>573.74 ± 63.54</td>
</tr>
</tbody>
</table>

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reported percolation threshold of 0.09 vol% in PS and conductivity of order of ca. $10^{-2}$ S m$^{-1}$ at ~1 vol% of reduced GO (Fig. 4).

In another study by Shen et al., GO was mixed with poly(vinyl pyrrolidone) (PVP) and glucose (which acts as a reducing agent). GO–PVP and GO–glucose was then mixed with poly(lactic acid) (PLA) in DMF. The resultant solution containing GO–PVP and GO–glucose was then coagulated using methanol. The formed precipitate was dried, transferred to a mold and hot pressed at 210°C. This process results in the reduction of GO facilitated by both thermal and chemical processes. The resultant composite with 1.25 vol% of GO–glucose showed a significant high conductivity of 2.2 S m$^{-1}$ in striking contrast to neat PLA ($10^{-15}$ S m$^{-1}$). The high electrical conductivity was attributed to the improved exfoliation and dispersion of reduced GO glucose further facilitating in the formation of interconnected conducting network within the PLA matrix. Fig. 5 shows the electrical conductivity as a function of particle concentration for different PLA composites.

Zhu et al. reported reduction of GO by dispersing in propylene carbonate (PC) at pH 3 by bath sonication. The obtained PC solution was heat treated at 150 °C for 12 h resulting in reduced GO. Composite samples were dried in vacuum at 80 °C, and resulted in a conductivity of 2100 and 1800 S m$^{-1}$ for the samples, which were heat treated at 150 and 200 °C, respectively. Further, vacuum annealing at 250 °C for 12 h resulted in a conductivity of 5230 S m$^{-1}$ and 2640 S m$^{-1}$ for the samples which were subjected to heat treatment at 150 and 200 °C, respectively. In this work, they also discussed the dispersion of GO in the PC matrix, and observed that the dispersion of GO in PC may not be due to electrostatic repulsion.
but can be due to the high dipole moment of PC. Fig. 6 shows the state of dispersion of GO in PC as well as in the solvent. In a recent study, in situ reduction of GO was reported during the compositing process in the presence of surface functionalized octadecylamine (ODA). The presence of long octadecyl chain resulted in the hydrophobicity in GO and also facilitated in its efficient reduction. Further, by hot pressing at 210 °C in the presence of PS matrix, electrically conducting samples were obtained. Thermal reduction in presence of PS resulted in a sharp transition from insulator to conductor. The GO-ODA showed 2 orders of higher electrical conductivity when subjected to thermal treatment as displayed in Fig. 7. Hence, it can be concluded that surface modification of GO along with thermal reduction may assist in both improved dispersion and simultaneous increase in electrical conductivity.

Another strategy commonly used to reduce GO is by changing polymer chemistry. The latter can play an important role in assisting thermal reduction of GO during hot pressing. Glover et al. studied the in situ reduction of GO in poly(vinyl pyrrolidone), poly(vinyl acetate), and poly(vinyl pyrrolidone/vinyl acetate) and they demonstrated that the chemical architecture exhibited by these polymer had strong influence on the extent of thermal reduction. They compared time/temperature relationship for GO reduction in air and in dimethylformamide under the same temperature conditions. The efficiency of reduction was reported based on the change in the C/O (carbon/oxygen) ratio (see Table 2). They showed that reduction of GO depends on time/temperature history and also on the polymer chemistry. They reported an increase in electrical conductivity by 2 orders in all the composites.

### 4. Mechanism of in situ reduction: synergistic effects from functionalization and heat

The thermal gravimetric analysis (TGA) of GO is characterized by three transitions which can be attributed to vaporization of hydroxyl group (<100 °C) and loss of carbonyl group as CO or CO₂ at 120–150 °C and 200–260 °C. From TGA of GO, it is clear that temperature above 200 °C is critical for reduction of oxygen moieties on the GO surface and hence a processing temperature above 200 °C will result in efficient reduction of GO. It is equally important to select a polymer that degrades well above 200 °C. Henceforth, optimum processing time, the thermal stability of

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Exposure time</th>
<th>Medium</th>
<th>C content (%)</th>
<th>O content (%)</th>
<th>Atomic C/O ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>—</td>
<td>—</td>
<td>56</td>
<td>39</td>
<td>1.9</td>
</tr>
<tr>
<td>55</td>
<td>4 months</td>
<td>Water</td>
<td>63</td>
<td>27</td>
<td>3.2</td>
</tr>
<tr>
<td>150</td>
<td>10 min</td>
<td>Air</td>
<td>56</td>
<td>39</td>
<td>1.9</td>
</tr>
<tr>
<td>150</td>
<td>240 min</td>
<td>Air</td>
<td>60</td>
<td>36</td>
<td>2.2</td>
</tr>
<tr>
<td>175</td>
<td>10 min</td>
<td>Air</td>
<td>59</td>
<td>37</td>
<td>2.1</td>
</tr>
<tr>
<td>175</td>
<td>240 min</td>
<td>Air</td>
<td>73</td>
<td>23</td>
<td>4.2</td>
</tr>
<tr>
<td>200</td>
<td>10 min</td>
<td>Air</td>
<td>69</td>
<td>26</td>
<td>3.5</td>
</tr>
<tr>
<td>200</td>
<td>240 min</td>
<td>Air</td>
<td>81</td>
<td>16</td>
<td>6.8</td>
</tr>
<tr>
<td>200</td>
<td>240 min</td>
<td>DMF</td>
<td>72</td>
<td>12</td>
<td>8.0</td>
</tr>
<tr>
<td>250</td>
<td>10 min</td>
<td>Air</td>
<td>80</td>
<td>20</td>
<td>5.3</td>
</tr>
<tr>
<td>250</td>
<td>240 min</td>
<td>DMF</td>
<td>73</td>
<td>12</td>
<td>8.2</td>
</tr>
</tbody>
</table>
polymer and the resistivity of the nanocomposites as a function of annealing time is necessary to understand the mechanism of thermal reduction of GO. Glover et al. studied the effect of various polymers with respect to the temperatures. The C/O ratio in GO was monitored, as described in Table 2.

In addition, the polymer chemistry i.e. polarity and aromaticity dictates efficient reduction and the overall state of dispersion. The exact mechanism of reduction of GO is not yet known, which is due to lack of direct measurement of the reduction process and the chemical reactions that take place during processing in the melt. However, with the limited results, Ye et al. arrived at some understanding. The decrease in the reducing temperatures in the presence of polymer is related to the interactions between GO sheets and the polymer matrix. Further, Rourke et al. proposed that GO are large sheets of graphene with oxidative debris adhered to sheets by π–π stacking or van der Waals interactions.

Fig. 8 illustrates schematically the GO sheets and its interaction with the polymer. From Fig. 8, it is clear that aromatic polymer such as polystyrene (PS) initially adsorb on the graphene sheets by π–π stacking between the continuous phenyl rings and the conjugated basal planes of graphene. This adsorption facilitates intercalation of GO sheets. Further, the π–π stacking counter balances the interactions between graphene sheets and oxidative debris, thus facilitating strong adhesion of polymer chains on the sheets. This adhesion will eliminate the oxidative debris from the surface of the sheet. Both the attachment of polymer chain and the elimination of oxidative debris leads to the reduction of GO thermally, and requires low energy and low reducing temperatures. It is envisaged that polar polymers, such as PMMA, forms hydrogen bonding with the oxidative debris. This further assists in peeling off the oxidative debris from the sheet. As a result, the reduction of GO in polar polymers require relatively less energy and reducing temperatures.

Apart from enhanced electrical conductivity during in situ reduction of GO, observed to compatibilize immiscible poly-(methyl methacrylate)/polystyrene (PMMA/PS, 80/20) blends.
The droplet diameter of the dispersed phase (PS) phase significantly reduced in the presence of GO. During processing, at higher temperatures, the in situ thermal reduction of GO renders more hydrophobicity in GO and further suppresses the coalescence of PS droplets. However, the electrical conductivity of the samples were not reported in this study.

Recently, Tan et al., covalently functionalized GO with a copolymer and converted GO to reduced GO in situ during molding of PMMA/PS blends. This facile method resulted in localization of GO at the interface of PMMA/PS blends and further resulted in low percolation threshold of 0.02 vol%. This is the lowest reported value in context to graphene as a nanofillers. Further, from Fig. 9, it is evident that the conductivity increased by 2 orders of magnitude for the composite containing P(St-co-MMA) grafted GO. The TEM image indicated localization of GO sheets at the interface.

5. Shear induced in situ reduction of GO

From the above discussion, it is clear that temperature and external forces like compression strain can assist in the in situ reduction of GO. However, in practice, heat can be accompanied by shear forces for further reduction of GO. In this context, Ye et al. studied the in situ reduction of GO in quiescent melt and under shear. They demonstrated that the composites which were sheared in the melt had a higher degree of reduction as compared to quiescent condition. They observed that the reduction was quite high under low shear, which further confirms the effect of shear on reduction of GO. This efficient reduction is associated with enhanced π–π stacking and the interaction between graphene sheets and the matrix. Further, they showed that an increase in conductivity of ca. 4 orders after shear. This was ascribed to significant reduction of GO during melt blending under high shear forces. Moreover, they observed that the central part of the composite sample (as shown in Fig. 10) exhibited higher reduction than the outer part by monitoring the enthalpy. This change in enthalpy was attributed to energy consumption required for the reduction of GO. As the outer part of the sample experiences higher shear force than the central part, the degree of reduction is higher at the center.

Another less explored strategy for in situ reduction of GO is the use of masterbatch. You et al. prepared a master batch of graphene oxide with styrene-ethylene/butylene-styrene (SEBS) triblock copolymer by melt mixing at 225 °C and they obtained a high degree of reduction. The resultant master batch was further diluted with polystyrene in the subsequent melt mixing process for improving mechanical properties. They reported three orders of magnitude increase in conductivity in reduced GO that was extracted from SEBS as shown schematically in Fig. 11.

6. Conclusions and outlook

Recent advances in in situ reduction of GO during the preparation of conducting polymeric nanocomposites has been reviewed here. The effect of presence of oxygen species on the
in situ GO shows promising reduction of GO and this method needs to the electrical percolation threshold. Shear induced reduction of reduction of GO provide a homogeneous dispersion and reduce conducting polymer composites is a better way as compared to interesting to note that of various strategies adopted for scarce and need to be explored more. Fig. 13 shows a pie chart e electrical conductivities achieved by in situ involving ducting nanocomposites. Fig. 12 outlines various strategies strategy. This opens new avenues in designing GO based con-duction polymerization, hot press, and shear are critically assessed eective for complete reduction of GO but the different strategies, shear in combination with heat was observed to be the most effective strategy. This opens new avenues in designing GO based con-ducting nanocomposites. Fig. 12 outlines various strategies involving in situ reduction of GO and Table 3 highlights the electrical conductivities achieved by in situ reduction of GO. The effect of polymer chemistry on the in situ reduction of GO is scarce and need to be explored more. Fig. 13 shows a pie chart of various strategies adopted for in situ reduction of GO. It is interesting to note that in situ polymerization and simultaneous reduction of GO provide a homogeneous dispersion and reduce the electrical percolation threshold. Shear induced reduction of GO shows promising reduction of GO and this method needs to explored in detail in future.

From the existing literature concerning the reduction of GO it is apparent that in situ reduction of GO to design highly conducting polymer composites is a better way as compared to ex situ reduction processes which often involves harsh treatments. More emphasis should be given in this direction and more research should be pursued towards in situ reduction of GO during the composite preparation.

**References**


