Effect of reduced graphene oxide–carbon nanotubes hybrid nanofillers in mechanical properties of polymer nanocomposites

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Abstract: Graphene and carbon nanotubes (CNTs) have tremendous interest as reinforcing fillers due to their excellent physical properties. However, their reinforcing effect in polymer matrix is limited due to agglomeration of graphene and CNTs within the polymer matrix. Mechanical properties by the admixture of reduced graphene oxide (rGO) and CNTs in Poly (methyl methacrylate) (PMMA) prepared by solution mixing method has been investigated. The prepared samples are characterized using X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM) and Raman spectroscopy. The hybrid composite shows improvement in the mechanical properties compared to rGO/PMMA and MWCNTs/PMMA composites due to better interaction between rGO-MWCNTs and polymer matrix.

1. Introduction

Two dimensional (2D) graphene and one dimensional (1D) carbon nanotubes (CNTs) exhibit exceptional physical properties and are being used for different applications [1,2]. Such properties make them ideal nanofillers for polymer composites with enhanced electrical, mechanical and thermal properties for various potential applications [3,4]. However, poor dispersion of graphene and CNTs in polymer matrices hinders the potential applications of graphene and CNTs polymer composites. In order to fully realize the reinforcing effect of graphene and CNTs in polymer matrix, two critical issues have to be resolved (i) dispersion of graphene and CNTs, (ii) interfacial adhesion between fillers (graphene or CNTs) and polymer matrix [5]. Due to large surface area of graphene and CNTs, they possess large van der Waals forces which makes very difficult to be effectively dispersed in polymer matrix. Several efforts have been taken in order to obtain homogeneous dispersion of CNTs/graphene in the polymer matrix and better interfacial interaction between nanofillers and matrix [6-8]. Graphene-CNTs hybrid filler polymer composites are now developing as a new hybrid nanofiller material with better properties.

Polymer composites containing hybrid carbon nanofillers with enhanced electrical, mechanical and thermal properties have been reported by different groups. Chatterjee et al. [9] demonstrated that graphene nanoplatelets/CNTs epoxy composites shows better mechanical properties than single filler systems. Graphene oxide (GO)–CNT/ Polyvinyl alcohol (PVA) composites show superior mechanical properties compared to GO/PVA and CNTs/PVA composite due to the complete exfoliation of GO and CNT via good dispersion [10]. Enhancement in the electrical, flexural and fracture properties are observed by Kim et al. [11] in the multiwalled carbon nanotubes (MWCNTs)-graphene nanoplatelets/epoxy composite. Kumar et al. [12] reported that polyetherimide (PEI)/(graphitic...
nanoplatelets (GNP)/functionalized MWCNTs) composite shows enhancement in electrical conductivity, thermal conductivity and dynamic mechanical properties than PEI/GNP and PEI/MWCNTs composites at same filler loadings. Yang et al. [5] demonstrated improvement of thermal conductivity and tensile strength of MWCNTs/multi-graphene platelets/epoxy composite. Zhang et al. [13] reported that increase in mechanical and thermal properties is observed in PVA/reduced graphene oxide (rGO)-treated CNT (t-CNT) composite as compared to PVA/CNT and PVA/rGO composites. Patole et al. [14] reported that admixture of two types of carbon fillers provide better improvement in thermal and mechanical properties compared to the neat polymer.

In this study effect of rGO-MWCNTs hybrid nanofiller on the mechanical properties of polymer composites have been investigated. The mechanical properties of rGO-MWCNTs/polymer hybrid composite has been compared with MWCNTs/polymer and rGO/polymer composite.

2. Materials and methods

Commercially procured MWCNTs and graphite powder (GFG 50), sodium nitrate (NaNO₃), sulphuric acid (H₂SO₄), potassium permanganate (KMnO₄), hydrogen peroxide (H₂O₂), hydrazine hydrate, N-N Dimethyl formamide (DMF), Poly(methyl methacrylate) (PMMA) have been used in this work. Graphite oxide (GO) has been prepared by Modified Hummers method [15]. In order to prepare GO, 1.0 g of graphite powder and 0.5 g of NaNO₃ have been mixed together and then 25 mL of concentrated H₂SO₄ has been added to that mixture. The mixture has been placed in an ice bath in order to decrease its temperature. After stirring for 2 hr, 3 g of KMnO₄ has been added slowly and again stirred for another 1 hour continuously. After that the ice bath is removed and the mixture is cooled down to room temperature. The temperature of the mixture is increased after addition of 100 mL of distilled water. Again 300 mL of distilled water is added and again continuously stirred for another one and half hour. At this stage the colour of the mixture changes to mud brown. For the termination of the reaction 10 mL of H₂O₂ has been added to the mixture. For the removal of unwanted ions and acid the prepared GO has been washed using distilled water until it becomes neutral. The material has been recovered by filtering and the obtained material is dried in vacuum at 100 °C for 3 hours. For the reduction of GO hydrazine hydrate is used [16].

The mostly used methods for the preparation polymer composites are melt mixing [17,18], in-situ polymerization [19] and solution casting [20]. Each and every method has their own advantages and disadvantages. In the present case, we have adopted solution mixing method to prepare the desired rGO-MWCNTs/PMMA hybrid nanocomposite (HC). In this method for the preparation of HC, MWCNTs, rGO and PMMA have been separately dissolved in DMF. The resulting solutions are sonicated and stirring in order to get homogeneous dispersion. After that the three solutions are mixed together and again sonicated followed by stirring. In order to get the hybrid nanocomposites films, the solutions are put in a glass petri dish and dried in an oven. Several batches of HC are prepared by varying rGO wt% (0.05, 0.1, 0.3, 0.5, 1, 3 wt%) keeping MWCNTs wt% constant (0.3 wt%). The as-prepared samples are characterized using Scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), Raman spectroscopy and tensile test using ASTM D 3039.

3. Result and Discussion

The morphology of rGO and CNTs are investigated through SEM. Randomly oriented crumpled sheets of rGO are shown in Figure 1(a) which is due to good exfoliation of rGO sheets. Entangled CNTs are observed from SEM image of CNTs (Figure 1(b)). The HRTEM images of rGO and CNT are shown in Figure 1(c) and (d). From the HRTEM image of rGO, it is observed that the prepared rGO are mostly multilayer in nature. Multilayer nature of CNTs is observed from HRTEM image of CNT.
Figure 1 (a), (b) SEM images and (c), (d) HRTEM images of rGO and MWCNTs respectively.

XRD pattern of graphite powder, GO, rGO and MWCNTs are shown in Figure 2 (a). A characteristics peak of graphite is obtained at 26.4° with interlayer spacing of 3.34 Å. In the XRD pattern of GO due to incorporation of oxygen functional groups in graphite the interlayer spacing increases and the peak is shifted to 11.5°, but after reduction due to removal of oxygen functional groups the interlayer spacing again decreases and peak shifted to 24.7°. The diffraction peak of MWCNTs is obtained at 26.1° which arises from graphitic carbon of MWCNT.

Figure 2 (a) XRD pattern of graphite, GO, rGO and MWCNTs, (b) Raman spectra of GO, rGO and MWCNTs.
Raman spectroscopy is generally used to characterize crystal structure, disorder and defects in graphene-based materials. The Raman spectra of GO, rGO and MWCNTs are shown in Figure 2(b). For GO and rGO the D peak which is due to the defect is at 1347 and 1339 cm$^{-1}$ respectively. Since there are no content of amorphous carbon in the GO and rGO, the D peaks are attributed to the defects. The G peaks of GO and rGO are present at 1572 and 1576 cm$^{-1}$ respectively which arises due to crystalline nature of graphitic structure\cite{16}. From the Raman spectrum of MWCNTs is seen that the D and G peaks are at 1339 and 1584 cm$^{-1}$.

From the SEM images of HC (Figure 3), it is observed that most of the 2D rGO and 1D MWCNTs are buried and exfoliated in the PMMA matrix. From the SEM images it is seen that most of the MWCNTs and rGO are covered by PMMA and some folded rGO sheets are visible. With increasing rGO wt% more folded rGO sheets are visible. Also from SEM and TEM images it is seen that MWCNTs and rGO form a network structure in the polymer matrix which may help for improving the mechanical properties of the resulting HC as compared to MWCNTs/PMMA composite and rGO/PMMA composite. Presence of 1D MWCNTs on the surface of rGO sheets in the polymer matrix are also seen that may reduce the restacking of rGO sheets.

The XRD pattern of PMMA, HC with 0.05, 0.1, 0.3, 0.5, 1 and 3 wt% of rGO are shown in Figure 4(a). It is seen that for PMMA the two broad reflection peaks are obtained at 13$^\circ$ and 30$^\circ$ which show amorphous character of PMMA. But in case of HC the reflection peaks are only due to PMMA, here XRD peaks due to MWCNT and rGO are not observed probably due to higher PMMA concentration and better exfoliation of MWCNTs and rGO in polymer matrix\cite{21}.

![Figure 3 SEM images of as prepared HC with (a) 0.05, (b) 0.3, (c) 3 wt% rGO, (d) TEM image of HC with 0.3 wt% rGO](image-url)
Figure 4 (a) XRD pattern of PMMA and HC with various wt% of rGO, (b) Raman spectra of PMMA, MWCNTs/PMMA composite (0.3 wt%), HC at different wt% rGO.

Raman spectroscopy is also used to study the interaction between polymer matrix and nanofiller. Raman spectra of PMMA, MWCNTs/PMMA composite with 0.3 wt% and HC at 0.05, 0.3, 1 and 3 wt% of rGO is shown in Figure 4(b). Decrease in the Raman peak intensity of PMMA is observed with addition of MWCNTs in PMMA. Again with the addition of rGO in MWCNTs/PMMA shifting in the D and G peaks occurs. Also in the HC, the intensity of the D and G peaks are less than that of rGO and MWCNT which is attributed may be due to the network structure of rGO-MWCNTs within the polymer matrix, grafting of the polymer on the surface of rGO sheets and MWCNTs provide higher defect level. Also with increase in rGO concentration the D and G peaks are shifted indicating increase in interfacial interaction between filler and matrix. Tensile measurements of the composites are done in order to study the mechanical properties. Figure 5(a) shows the tensile stress–strain graphs of the composites. The tensile strength and Young’s modulus of PMMA are 21.19 MPa and 1.42 GPa respectively.

Figure 5 (a) Stress-Strain curves of HC at different wt% of rGO, rGO/PMMA composite with 0.6 wt% (R (0.6)) and MWCNTs/PMMA composite with 0.6 wt% (C (0.6)) (b) Tensile strength and Young’s modulus of HC at different rGO wt%.
The tensile strength and Young’s modulus of PMMA is increased to 23 MPa and 1.48 GPa with the addition of 0.1 wt% rGO into MWCNTs/PMMA composite with 0.3 wt%. More tensile strength and Young’s modulus is observed in HC than MWCNTs/PMMA composite and rGO/PMMA composite at the same total filler wt%. Similarly Young’s modulus of HC more compared to MWCNTs/PMMA composite but lower than that of rGO/PMMA composite. These increase in mechanical properties of HC is may be due to the formation of the network structure by rGO and MWCNTs which provide larger contact area for stress transfer at the polymer matrix and the nanofiller interface and better contact between polymer and rGO-MWCNTs hybrid nanofillers [22]. Further increase in rGO wt% in HC the tensile strength and Young’s modulus increases and maximum strength and modulus are obtained at 0.5 wt% rGO. With further increase in rGO wt% the tensile strength and Young’s modulus of HC decreases which may be due to aggregations of rGO sheets [22]. At higher wt% of rGO, agglomerations of rGO may be may be take place which results in improper dispersion of rGO sheets within the polymer matrix which results in decreasing mechanical properties of HC.

4. Conclusion
In this study solution mixing method is adopted to prepare 2D rGO-1D MWCNTs/PMMA hybrid polymer composites. Due to formation of network structure of MWCNTs and rGO in PMMA, it gives more contact area for stress transfer from polymer matrix to the hybrid nanofiller. As a result of which enhancement in the tensile strength and Young’s modulus as compared to MWCNTs/PMMA and rGO/PMMA composites have been observed.

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