Synthesis and Characterization of Reduced Graphene Oxide Reinforced Polymer Matrix Composite

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Abstract: Graphene and its derivatives, owing to their superior properties have been being used as reinforcement to improve the properties of polymer matrix. In this work, the influence of Reduced Graphene Oxide (RGO) on the properties of Poly Vinyl Alcohol (PVA) has been studied. RGO was synthesized from graphite powder starting with synthesis of Graphene Oxide (GO) by Modified Hummer’s Method followed by the reduction of GO with Hydrazine Hydrate. Synthesized RGO was characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS). PVA composites with different RGO loading were fabricated by simple solution mixing method. The fabricated composites were characterized by Optical Microscopy, XRD, UV-Visible Spectroscopy, Thermo Gravimetric Analysis (TGA), Differential Thermal Analysis (DTA) and Shore hardness test. The reports from those tests have ensured that after incorporating RGO in PVA matrix, band gap energy was decreased, crystallinity and shore hardness were increased and thermal stability was improved up to a certain level of RGO loading.

1. Introduction
Graphene has become a topic of both intensive and extensive research owing to its extraordinary mechanical, electrical, optical and thermal properties. Much credit goes to its unique molecular structure. It is a 2-D sheet of hexagonally arranged C atoms where each atom is sp² hybridized [1]. Due to sp² hybridization of C atoms, graphene molecule has free pi electrons located above and below the 2D sheet [1]. These electrons act like massless particle and are responsible for high electronic mobility and conductivity [2]. Besides, these pi electrons overlap and help to enhance the strength of C-C valence bond [1] which is responsible for high mechanical strength. Other important factors that make graphene so special are small C-C bond length [1], zero band gap, ballistic conductivity [2], thermal conductivity, impermeability and so on. All these factors working together make graphene a special material and create its demand in various fields like composite materials, bioengineering, nanotechnology, energy technology and so on [3]. Among its versatile applications, one of the alluring applications is to use it to improve the properties of current materials and substances [3]. Graphene has been using as reinforcement to improve various properties of many polymer. Well dispersed graphene in polymer matrix forms very interactive network structure which enhances different properties of polymer [4].

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Polyvinyl alcohol (PVA) is a polymer which offers many properties to be improved. The only challenging aspect is well dispersion of graphene in PVA matrix on which efficiency of reinforcement depends [4]. One judicious solution is to introduce oxygenated functional groups to the surface of graphene which enhance dispersion of graphene in polymer matrix [4]. This special molecular structure of graphene having oxygenated functional on its surface is called Reduced Graphene Oxide (RGO) [5]. The properties of this graphene derivative is very similar to that of graphene except the dispersion behavior. This study is aimed at fabrication of RGO/PVA composites and observing the influence of RGO on various properties of PVA.

2. Experimental

2.1 Synthesis of Graphene oxide (GO)
Modified Hummer’s Method [6] was conducted for the synthesis of GO from graphite powder. 5g Graphite powder was mixed with 2.5gm NaNO₃ and the mixture was taken in a volumetric flask containing 115 ml 98% H₂SO₄. After that the flask was kept under magnetic stirring for around 30 minutes. Then it was taken to the ice bath to maintain the temperature <20⁰C, where 15 g KMnO₄ was added to the solution very slowly. The solution was then stirred at 35⁰ for 1 hour. Then the solution was taken to oil bath where 250 ml de-ionized H₂O was slowly added to the solution for 15 minutes at 95⁰C. Then H₂O & H₂O₂(30%) were added to this solution and stirred at 65⁰C for 2 hrs. The solution was changed to olive green color. The solution was then washed and filtrated and centrifuged at 8000 rpm for 15 minutes. The obtained gel was dried and again mixed with DI water to ultra-sonicate for 1 hour. The obtained product was dried at 70⁰C for 24 hours to get the GO powder.

2.2 Synthesis of Reduced Graphene oxide (RGO)
At first, GO solution was prepared with 260 mg of obtained GO and 260 ml de-ionized water by ultra-sonication for 1 hour. Subsequently, 5 ml of 99% Hydrazine Hydrate was added to solution and heated for 8 hours at 70⁰C. Finally the product was dried at 60⁰C for 24 hours and RGO was obtained shown in ‘figure 1(a)’.

2.3 Synthesis of RGO reinforced PVA
1 gm PVA for each sample was dissolved in 100 mL DI water and heated at 90⁰C for 30 minutes to prepare PVA solution. For the preparation of RGO solution, calculated amount of RGO was dissolved in 100 mL DI water and heated at 70⁰C. Then the solution was ultra-sonicated for 1 hour. At last the PVA solution and the RGO solution were mixed and heated at 60⁰C followed by ultra-sonication for 1 hour. The obtained solution was poured into cultured dish and dried at 70⁰C for around 24 hours. Obtained product was RGO/PVA composites shown in ‘figure 1(b)’.

![Figure 1](image.png)

**Figure 1.** (a) RGO powder (b) RGO/PVA composites in cultured dish
3. Results and Discussion

3.1 SEM with EDS

Scanning Electron Microscopy (SEM) was conducted to observe the surface morphology of RGO. SEM topography shows presence of wrinkles and crumplles on RGO surface. Wrinkle [7] shown in ‘figure 2(a)’ is a common phenomenon of a 2D material [7] and forms mainly due to negative thermal expansion of RGO [7]. Crumplles [7] are ‘paper-ball like’ shape shown in ‘figure 2(b)’ which occur due to an isotropic compression and thermal reduction [7].

![Figure 2. SEM topography images of RGO (a) wrinkles (b) crumplles](image)

Energy-dispersive X-ray spectroscopy (EDS) was performed to find out the composition of RGO. ‘Figure 3’ indicates the presence of considerable amount of C, S, O and Na. From the EDS report, the amount (mass %) of C, S, O and Na is 89.08, 5.09, 2.64 and 1.94 respectively. The amount of other elements is negligible. Molecular structure of RGO confirms that presence of C and O is very expected. The intruder elements S and Na were incorporated into RGO molecule from H2SO4 and NaNO3 respectively during the synthesis. This indicates that washing during the synthesis of RGO was not conducted properly.

![Figure 3. EDS report of RGO](image)
3.2. Optical microscopy
Optical Microscopy was conducted to reveal the dispersion behaviour of RGO in PVA matrix. The dark spot appeared in pure PVA matrix is inclusion ‘figure 4(a)’, though it is very negligible. In case of 3% RGO loading, dispersion seems to be homogeneous, although a very negligible amount of agglomerated RGO is observed. In case of 5% RGO loading, considerable amount of agglomeration is observed ‘figure 4(c)’. In case of 10% RGO loading, highest agglomeration is observed ‘figure 4(d)’. ‘Figure 4(e)’ shows agglomerated RGO in 10% RGO/PVA composite.

Figure 4. Optical microstructure of (a) Pure PVA (b) 3% RGO/PVA (c) 5% RGO/PVA (d) 10% RGO/PVA (e) Agglomeration in 10% RGO/PVA

3.3. XRD
Cu Kα having wavelength of 1.5406 Å was used at 40 kV in this test. For graphite, GO and RGO XRD was conducted to get a good idea about d-spacing of those substances. From ‘figure 5’ it is evident that graphite shows its characteristic peak at around 26.5° whose corresponding d-spacing is 0.33 nm. GO shows a broad peak at around 11° and its corresponding d-spacing is 0.8 nm. The reason behind this increase in d-spacing is intercalation of oxygen containing functional groups in the interlayer of graphite during oxidation of graphite to get GO. GO also shows a weak peak at around 26.5° which is nothing but an indication of incomplete oxidation. RGO shows a very strong broad peak at around 25.8° and corresponding d-spacing is 0.35 nm. The value is smaller than that of GO but larger than that of graphite. The reason behind this is during reduction of GO, some oxygenated functional groups were removed from the interlayer of GO but still contains some of that which is totally absent in case of graphite. RGO also shows a weak peak at around 43° which is an indication of incomplete reduction of GO.

Intensity peak of pure PVA is almost flat having a very weak peak at around 20° which is shown in ‘figure 6’. This peak is an indication of non-crystalline nature of pure PVA. As the RGO loading increases, the peak height also increases and the peak width becomes narrower which indicates that crystallinity of PVA increases. However, all RGO/PVA composites show peak at around 20°.
Figure 5. XRD report of Graphite, GO and RGO

Figure 6. XRD report of pure PVA and RGO/PVA composites

3.4. UV-Visible Spectroscopy
This test was conducted to observe the absorbance of pure PVA and RGO/PVA composites. Absorbance values have been presented graphically in ‘figure 7(a)’. From the graph it is cleared that with increasing RGO loading absorbance of PVA increased. ‘Figure 7(b)’ shows Tauc’s plot method [8] which was accomplished with the help of obtained absorbance value and the thickness of the materials [8]. This method was used to determine the band gap of the samples. Obtained band gaps of different samples by Tauc’s plot have been presented in ‘figure 8’. It is very clear that pure PVA had the highest band gap of 3.57 eV and with RGO loading band gap of PVA composites decreased. Therefore, electric conductivity of PVA composites increased with increasing RGO loading as it is inversely proportional to band gap energy [9].
Figure 7. (a) Absorbance of PVA with different RGO loading (b) Tauc’s Plot to determine band gap

Figure 8. Band gap comparison among PVA samples with different RGO loading

3.5. TGA and DTA
TGA and DTA were carried out to observe the effect of RGO on the thermal property of PVA. From ‘figure 9’ it is clear that decomposition of pure PVA and PVA composites took place through several stages. The maximum decomposition rate of pure PVA, 3%RGO/PVA, 5% RGO/PVA and 10% RGO/PVA is 0.74% /°C, 0.66% /°C, 0.71% /°C and 0.78% /°C respectively and corresponding temperature is 491.71°C, 526.14°C, 417.54°C and 230.36°C. From the results it is clear that up to 3% RGO loading, maximum decomposition rate decreased and corresponding decomposition temperature increased which is a good indication of improved thermal stability. But beyond 3% RGO loading, maximum decomposition rate started to increase and corresponding decomposition temperature decreased. The reason behind this behaviour is that beyond 3% RGO loading, interfacial bonding between RGO and PVA matrix was poor [4] due to considerable amount of RGO agglomeration which has been cleared from Optical Microscopy.
3.6. Shore hardness test

Hardness values of pure PVA, 3% RGO/PVA, 5% RGO/PVA and 10% RGO/PVA obtained from this test are 35.6, 44.8, 50.2 and 60.4 (in D scale) respectively shown in ‘figure 10’. The reason behind this increase in hardness value with increasing RGO loading is, when RGO was incorporated to PVA matrix, it increased the crystallinity of PVA [10] which has been evident from XRD report.

Figure 9. TGA and DTA report of (a) Pure PVA (b) 3% RGO/PVA (c) 5% RGO/PVA (d) 10% RGO/PVA
Figure 10. Hardness of PVA with different RGO loading

4. Conclusion
RGO synthesis from graphite powder was successfully carried out. Fabrication of RGO/PVA composites by solution casting was possible but good dispersion of RGO was achieved up to 3% RGO loading and beyond that agglomeration of RGO occurred which has been evident from optical microscopy. This agglomeration affected the interfacial bonding between RGO and PVA matrix which in turn affected the thermal property of PVA confirmed by TGA and DTA. However, with increasing RGO loading, crystallinity of PVA increased which has been cleared from XRD report and due to this, shore hardness of PVA increased with RGO loading. In addition, UV-Vis spectroscopy has confirmed that absorbance of PVA increased and band gap decreased with RGO loading.

5. References
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