Graphene Decorated Quantum-Dots Filled Multiscale Nanocomposites

Sanchit Katyal[1], Rathinjai Chauhan[2] and Prof. Pankaj Balkrishna Tambe[3]

SMEC, VIT University, Vellore-632014, Tamil Nadu, India

[1]sanchitkatyal.99@gmail.com

[2]rathinjai@gmail.com

[3]pankajtambe@vit.ac.in

ABSTRACT - The field of materials has been the hot topic amongst the research community and graphene is among them which is a wonder material with many special properties, isolated for the first time only in 2004. Since the discovery of graphene, advancements within different scientific disciplines have exploded, with huge gains being made particularly in electronics and biotechnology already. The problem lies in its manufacturing as it is an expensive and tedious process. It is the thinnest compound known to man at one atom thick, the lightest material known, the strongest compound discovered (between 100-300 times stronger than steel), best conductor of heat at room temperature (at $(4.84 \pm 0.44 \times 103)$ to $(5.30 \pm 0.48 \times 103)$ W•m-1•K-1) and also the best conductor of electricity known (studies have shown electron mobility at values of more than 15,000 cm2•V-1•s-1). The project involves isolating graphene from graphite oxide using (modified) Hummers' method and then using it as a reinforcement material in epoxy resin which will be further used to produce high strength composite material. The primary objective of the research is to find a point of optimality where the ratio of epoxy to graphene gives the perfect combination of strength and durability.

Keywords: Graphene, Modified Hummers' method, Characterization.

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I. INTRODUCTION

Graphene is a wonder material with many unique properties. It was known to scientists for several years but was isolated for the first time only in 2004, a feat that fetched its discoverer the Nobel Prize six years later. In simple terms, it is a single, thin layer of pure carbon wherecarbon atoms are bonded together in a hexagonal honeycomb lattice [8]. In more complex terms, it is an allotrope of carbon in the structure of a plane of sp2 bonded atoms. The uniqueness of graphene comes from its structure because chemically, it is only carbon; similar to graphite which is nothing but layers of graphene stacked one atop the other. Graphene-based polymer Nanocomposites were extensively studied in last one decade for various applications. The incorporation of asmall concentration of graphene in thepolymer matrix can result in a remarkable enhancement in mechanical properties of polymer nanocomposites.

II. MOTIVATION

The presence of graphene can enhance the conductivity and strength of bulk materials and help create composites with superior qualities. Graphene can also be added to metals, polymers, and ceramics to create composites that are conductive and resistant to heat and pressure. The problem that prevented graphene from initially being available for developmental research in commercial uses was that the creation of high-quality graphene was a very expensive and complex process (of chemical vapors disposition) that involved the use of toxic chemicals to grow graphene as a monolayer by exposing Platinum, Nickel or Titanium Carbide to ethylene or benzene at high temperatures. The challenge faced during the course of study was isolating asignificant amount of graphene from raw materials while at the same time maintaining the purity of the end product (Graphene). While this research is very highly regarded, the quality of the graphene produced will still be the limiting factor in technological applications. Once graphene can be produced on very thin pieces of metal or other arbitrary surfaces (of tens of nanometres thick) using chemical

vapourdisposition at low temperatures and then separated in a way that can control such impurities as ripples, doping levels and domain size whilst also controlling the number and relative crystallographic orientation of the graphene layers, then we will start to see graphene become more widely utilized as production techniques become more simplified and cost-effective.

III. LITERATURE SURVEY

The incorporation of G-D-GQDs and G-D-GQDsAg in PVDF matrix increases the thermal stability and crystalline of PVDF. New methods for thermally deoxygenating GO to create reduced graphene oxide without the use of hydrazine as a reducing agent. Graphene-based Nanocomposites represent the most technologically promising developments to emerge from the interface of polymer material. Graphene photodetectors and imaging systems, light modulators and switches, screening systems, and 2D graphene plasmonics applications can be quite competitive. The improved Hummers method described can be used to prepare GO in large scale and it is one-step towards the synthesis of graphene and its derivatives through environmentally friendly approaches. The results indicated that the distance spacing of graphite oxide was longer than that of graphite and the crystal structure of graphite was changed. This modification does not decrease the yield of product, eliminating the evolution of NO2/N2O4 toxic gasses and simplifying the disposal of waste water because of the inexistence of Na+ and NO3− ions. It is shown that at low nanofiller content, graphene platelets perform significantly better than carbon nanotubes in terms of enhancing the Young modulus of the nanocomposite.

IV. EXECUTION STAGES OF RESEARCH WORK

Following is the step by step procedure followed for the making and purification of Graphene:

1) Taking 360ml of AR grade Sulphuric Acid along 3 grams of graphite powder in a conical flask.
2) Adding 40ml of Orthophosphoric Acid into the flask.
3) The entire solution is kept in an ice bath which is then stirred using a magnetic stirrer.
4) Carefully addition AR grade Potassium permanganate in small quantities to avoid excessive heat generation.
5) Waiting for some time for the entire solution to reach a temperature of 60 degree Celsius and then maintaining this constant temperature for theduration of 7 hours.
6) In order to prevent coagulation, it is necessary to keep the entire solution over the magnetic stirrer.
7) Now that the solution has changed its color to dark grayish, 400ml of distilled water is added which is followed by a rise in temperature followed by effervescence (As a safety measure, the entire solution is kept in an ice bath).
8) 3ml of Sulphuric acid is added to the solution which results in a change of color from gray to muddy brown.
9) In a separate beaker, a solution of 35% HCl (25ml) and 250ml of distilled water are made.
10) The solution prepared in step 8 is mixed with the solution prepared in step 9 in eight centrifuge tubes in avolumetric ratio of 3:1.
11) The tubes are loaded in the centrifuge machine for theduration of 15 minutes at 3000 rpm at room temperature.
12) As a result of the centrifuge process, we are left with a brown precipitate in the tubes which is removed using a spatula. Centrifuge process is done to remove acid which cannot be directly achieved by heating the solution.
13) This graphite oxide is converted to graphene oxide using Sonication process.
14) 50 ml of DMF is added to graphite oxide in a beaker before sonication.
15) This beaker is kept in an ice bath as thetemperature was increasing due to the addition of DMF and kept inside the apparatus for half an hour. Hence, graphene oxide is produced.
16) Graphene oxide (GO) is converted to reduced graphene oxide (rGO) by directly heating it to very high levels in a furnace.
17) For this purpose, Box furnace is used in the MET laboratory of VIT university. It is kept at 160 degree Celsius for eight hours.

18) This rGO obtained has some acid in it which cannot be removed by direct heating. Hence, Centrifuge process is again used.

19) In the sample, 80 ml of THF is poured. Then, this solution is put in two vials and kept in the centrifuge apparatus at 3000 rpm.

20) After centrifuging, theprecipitate is obtained at the bottom. The above clear liquid contains some acid which is poured in the sink.

21) This precipitate has some residual moisture and hence, kept in an oven at 40 degree Celsius for three hours approximately and hence, nano-sized Graphite flakes are obtained.

After graphene production, thefollowing are the steps done to make its composite:

1) The very first sample was a composite that contained pure epoxy without any type of reinforcement; the consecutive samples had graphene concentration as 0.05%, 0.1%,and 0.2% respectively. The liquid epoxy resin used is LapoxL-12 (4,4'-Isopropylidenediphenol, oligomeric reaction products with 1-chloro-2,3-epoxypropane) and hardener used is.

2) 120 grams of epoxy resin is added in each of these samples.

3) According to calculations, thehardener is added to theepoxy resin in the ratio of 10:1 and composite are made in layers of 16 each for the three samples.

V. CALCULATIONS

For producing the composite, it is required that 120 g of epoxy is mixed with G-D-GQDs.

SAMPLE 1

For S1, 0.05 weight percentage concentration of graphene is selected.

S1 = ((0.05)/100)*120 g

S1 = 0.05*1.2 g

S1 = 0.06 g of graphene

SAMPLE 2

For S2, 0.1 weight percentage concentration is selected.

S2 = ((0.1)/100)*120 g

S2 = (0.1*1.2) g

S2 = 0.12 g of graphene

SAMPLE 3

For S3, 0.2 weight percentage concentration is selected.

S3 = ((0.2)/100)*120 g

S3 = (0.2*1.2) g

S3 = 0.24 g of graphene

VI. COST ANALYSIS

Table 1: Cost Analysis

CONTENT	QUANTITY	INR
AR grade Sulphuric Acid	500 ml	500
AR grade Potassium permanganate	500 ml	270
AR grade Di-methyl Formamide	500 ml	300
Orthophosphoric Acid	500 ml	580
Epoxy Resin	500 ml	8106
Acetone Dry	500 ml	454
Ethanol AR grade	500 ml	600
TOTAL		10,810 INR

Hence, total cost incurred in manufacturing of graphene is very less compared to other methods and is not dangerous also.

VII. CHARACTERIZATION OF G-D-GDQs

GO samples were synthesized by using hummers' method without using $NaNO_3$ and purified by centrifugation. The graphene produced was measured to be 92% ± 3%. This result indicates that the solution of concentrated

H_2SO_4 containing $KMnO_4$ is capable of oxidizing graphite to GO in a yield close to that of Hummer method even without the assistance of $NaNO_3$.
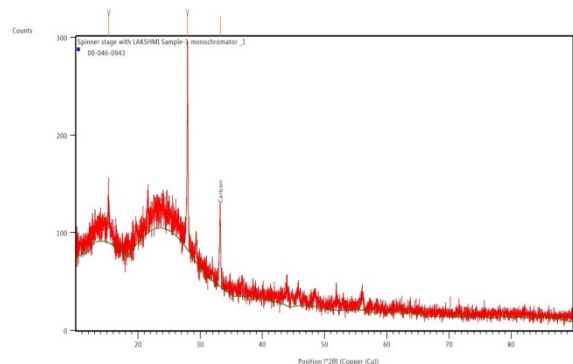

Figure 1XRD Spectrum

Table 2 XRD Results

Pos. [°2θ]	Height [cts]	FWHM Left [°2θ]	d-spacing [Å]	Rel. Int. [%]
15.2794	41.44	0.3070	5.79900	20.97
27.9631	197.57	0.1535	3.19084	100.00
33.2323	78.09	0.1791	2.69598	39.53

Figure 1 shows the XRD spectra of graphite powder, graphene oxide and solvothermally reduced graphene oxide. From the analysis, it was observed that a sharp peak centered at 26° is a characteristic peak of graphite. When graphite is oxidized the d-spacing of oxidized graphite increases and the peak is shifted towards lower diffraction angle. This is verified with the peak centered on 10° confirming oxidation of graphite takes place. The solvothermal reduction shows a diffraction peak at 24.6^o having d-spacing of 3.6 A. In general, reduced graphene oxide show a peak centered on 23°, but in this case the diffraction peak is achieved at 24.6^o.
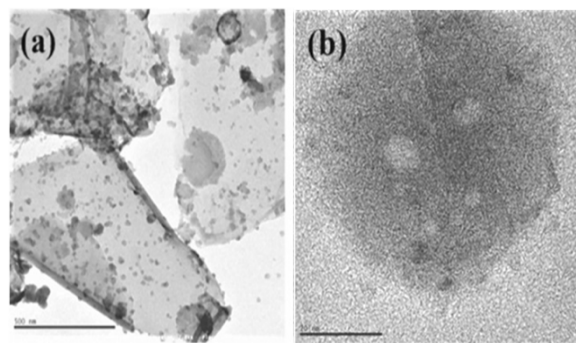

Figure 2 TEM Analysis

Figure 2 shows a layer of reduced graphene oxide over which small dots are distributed. The magnified image of those dots shows their dimensions are less than 30nm, confirming the presence of graphene quantum dots (GQDs). Thus, the product obtained after solvothermal reduction of graphene oxide is referred as graphene decorated graphene quantum dots (G-D-GQDs).

The reason for the formation of these quantum dots is because when DMF is heated above its boiling point it decomposes and yields carbon monoxide and dimethylamine. Carbon monoxide is a strong reducing agent, which can easily reduce hydroxyl, epoxy and carboxyl functional groups. The Epoxy functional group can readily react with dimethylamine. The graphene oxide was dispersed in DMF and heated in an autoclave at 160^oC for the duration of 8 hours. At this temperature, DMF is decomposed into dimethylamine and carbon monoxide. Carbon Monoxide shall reduce the functional group of graphene oxide, while dimethylamine reacts with epoxy functional groups.

VIII TENSILE TESTING

For validating the mechanical properties of G-D-GQD composite, tensile testing using Universal Testing Machine was carried out. The test was done as a comparison between four types of samples. The very first sample was a composite that contained pure epoxy without any type of reinforcement; the consecutive samples had 0.05, 0.1 and 0.2 weight percentage of the graphene nanoparticles. The load was applied in gradual increments. For the sake of keeping the results accurate, two test samples of same concentrations were tested.

The result of tensile testing clearly shows that the mechanical property of the composite is enhanced when graphene particles are added as reinforcements. The sample having 0.05 weight percentage of graphene reinforcement beaks at a peak load of 12.86 kN whereas the sample containing 0.2 weight percentage of the same reinforcement breaks at a peak load of 14.88 kN. This shows an improvement in load bearing capacity by 13%, while at the same time the change in amount of reinforcement material is marginal.

Table 3 Tensile Test Result 1

S N o.	Tensile strain at Maximum Load (%)	Load at Break (Standard) (kN)	Tensile stress at Break (Standard) (MPa)	Concent ration of graphen e (%)
1	2.58523	12.86	265.52	0.05
2	2.57187	12.81	253.51	0.05
3	2.76219	13.05	273.63	0.1
4	2.86302	12.48	259.74	0.1
5	2.90324	14.88	303.83	0.2
6	2.68765	14.84	289.90	0.2
7	1.23224	8.19	108.68	Pure Epoxy

As the maximum load bearing capacity of samples are increased at the time there is a significant improvement in the Young's Modulus as well as the Ultimate Tensile Strength.

Table 4 Tensile Test Result 2

Maximum Load (kN)	UTS (GPa)	Young's Modulus (GPa)	Maximu m Extensio n (mm)
12.86	0.266	14.962	2.06818
12.81	0.254	14.225	2.0575
13.05	0.274	15.179	2.20975
12.48	0.270	15.153	2.9041
14.88	0.304	15.535	2.32259
14.84	0.290	15.318	2.15012
8.189	0.109	10.403	0.99339

The following graphs describes the maximum extension of the sample at peak load. It is clearly observed that as the amount of reinforcement is increased, the maximum extension also increases and reaches a maximum value of 2.9041mm after which it decreases indicating that there is a decline in the elastic properties after a certain percentage of reinforcement is inceased.

Another thing to be observed from here is that however the elastic properties decrease, the tensile properties does not follow the same trend which means an optimum point has to be found while using this type of composite for practical applications.
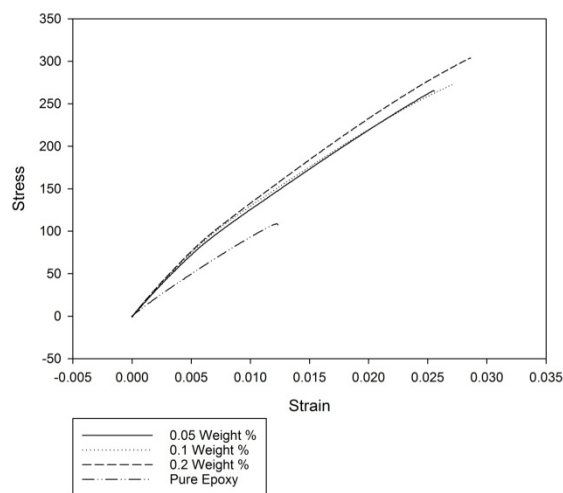
Figure 3 Stress vs Strain Curve

IX. FLEXURAL TESTING

Table 5 Flexural Test Results

S No.	Maximum Load (N)	Maximum Flexure Stress (MPa)	Concentration of graphene (%)
1	500.30	246.43744	0.05
2	569.05	281.91306	0.05
3	810.31	400.20306	0.1
4	685.76	316.68350	0.1
5	772.42	364.33542	0.2
6	803.57	382.00616	0.2
7	634.32	214.1723	Pure Epoxy

X. CONCLUSION

It is concluded that graphene powder made by modified Hummers' method is successfully completed in a systematic and correct manner which is ensured by characterizing the material at every stage of the process and comparing its respective results. The process cost is also less expensive in comparison with other methods for graphene preparation. Characterization of graphite, graphite oxide, and reduced graphite flakes is done using XRD analysis and Transmission electron microscopy. The project also involves incorporating graphene in the epoxy resin to produce composite material and then mechanical testing of the composite is done using tensile and flexural tests. Observing these tests, it can be seen how graphene can take considerable amounts of theload as its concentration is increased in the composite material.

X. SCOPE FOR FUTURE WORK

Graphene is strong, stiff and very light. Currently, aerospace engineers are incorporating carbon fiber into the production of aircraft as it is also very strong and light. However, graphene is much stronger whilst being also much lighter. Therefore, it is expected for it to be usedin creating a material that can replace steel in the structure of aircraft, improving fuel efficiency, range and reducing weight. Due to its electrical conductivity, it could even be used to coat aircraft surface material to prevent electrical damage resulting from lightning strikes. In this example, the same graphene coating could also be used to measure strain rate, notifying the pilot of any changes in the stress levels that the aircraft wings are under. These characteristics can also help in the development of high strength requirement applications such as body armor for military personnel and vehicles.

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