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Preparation and Characterization of Graphene / PMMA Composite

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ABSTRACT: Normal graphite powder was used to synthesis the graphene flakes via graphene oxide by Hummer's method . Graphene/PMMA composites of different wt.% concentration (0 , 0.1 , 0.3 ,0.5 , 1 and 2) % were prepared by Hand lay-up method . Graphene , graphen oxide and graphene/PMMA composites were characterized by XRD , FT-IR ,UV-VIS , SEM and DLS. Graphene exhibit a broad peak at (002) plane with d-spacing d_{002}=3.4Å . SEM image showed graphene as flakes with highly agglomerated state and many wrinkles . The absorption of G/PMMA composites films increased with the increase of the concentration of graphene flakes while energy gap decreased from (4- 2.8) eV with the increase of the graphene flakes concentration. The mechanical properties include hardness , which is done at room temperature, results of the work shows the values of hardness which increased with the increase of the graphene flakes concentration .

KEYWORDS: Graphene , PMMA , Optical Properties, Hardness , XRD, SEM ,UV-VIS.

I. INTRODUCTION

Two dimensional (2D) graphene has a unique properties and wide range of applications , since the awarded of Nobel prize in physics for the discovering of graphene, it has a large effect in the natural science communities [1-5]. Graphene is an ideal nano filler for function composite due to exceptional properties likes , high surface area , along with its electrical , thermal and mechanical [7,8].

Nanocomposites of graphene on a base of its have a considerable attention due to the improvement in physical properties like electrical , thermal and mechanical as it compared with other nanocomposites and pure polymer [9-11]. So graphene reinforced polymer composites is a challenge and in this work the preparation of graphene and study its optical and mechanical properties of the composites samples are performed .

II. EXPERIMENTAL WORK

A. Materials

Natural graphite rod (99.995%) ,($KMnO_2$,99%) , ($NaNO_3$,99.5%) , (H_2O_2,32%) and (Hcl,37.5%) from (Sigma-Aldrich) and (H_2SO_4,98%) from (LOBA Chemie) and ($N_2H_4.H_2O$,99%) from (Merck) and (CH_3OH,99.8%) from (Fluka) and Chloroform ($CHCl_3$,99%) from Scharlab S. L. and Poly methyl methacrylate PMMA, methyl methacrylate from Duracryl plus.

B. Preparation of Graphene and Nanocomposites

Graphene (G) was prepared by reducing graphene oxide (GO) that was synthesized by Hummer's method [12].

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1. Preparation of Graphene Oxide

The essential material used for synthesis the graphene by Hummer's method is the powder produce from milling of graphite rod . In that method 1g graphite powder and 0.5g of sodium nitrate were added to the concentrated sulfuric acid (in an ice bath) followed by the addition of 3g from $KMnO_2$ gradually and with temperature below 35°C . Afterwards magnetic stirrer is used for mixture at room temperature for 24 h , then a thick paste is formed . the reduction of $KMnO_2$ is performed by adding 5ml of H_2O_2 32% . This addition turns the color of the paste to the light brown , then the paste washed by deionized water and 5% HCl (HCl(11.52) + H_2O (88.75)) ml. Finally the resultant product was dried at 80°C for 4h in order to get grphene oxide solid .

2. Reduce of Graphene Oxide

Reduced graphene oxide is obtaining by using hydrazine hydrate as a reducing agent at 100° C for 24h . In this chemical reduction 0.9 g of GO was dispersed into 450 ml deionized water , then using ultrasonic for 1h in order to exfoliated it .Then 9ml of $N_2H_4.H_2O$ was added and the solution was heated for 24h at 100°C . At the end the solution color was changed from brown to the black . The product was kept to cool and afterwards , filtered and washed by methanol and dionized water the dried at 70°C for 4h.

3. Preparation of Nanocomposite Films

The nanocomposites films was prepared by dissolving PMMA in 20ml Chloroform ($CHCl_3$,99%) . In a typical procedure ,wt.% Graphene/PMMA (0 , 0.1 , 0.3 ,0.5 , 1 and 2) % of graphene was dispersed in this blend and the temperature was kept at 80°C for 30 min and the mixture turned to the mold by casting it by hand lay-up method .

4.Preparation of Nanocomposite Bulk (Hardness Samples)

The nanocomposite bulk was prepared by dissolving PMMA in 10 ml methyl methacrylate solvent volumetric ratio 3:1 (three part of powder, 1 part of liquid) . In a typical procedure , (0 , 0.1 , 0.3 ,0.5 , 1 and 2) % of graphene flakes were dispersed in this blend . The mixing process passed by several steps (i): sandy step (powder and solvent) (ii) : viscous step (Sticky filaments) (iii): pasty step (the mixture like pasty) and it is the step that the mixture turns to the mold and casting by Hand lay- up method (iv): hardening step, the sample takes the final form . The blend poured in cylindrical mold with 20.5mm diameter and 0.6mm high. The sample polished by polishing papers with degree of fine-tuning 1000 and 1200.

C. Characterization

The study of crystalline structure is performed by using X-ray diffraction system (XRD- Shimadzu 6000) employing Cu $K\alpha_1$ radiation (X-ray wavelength λ=1.5406 Å) at (R.T.) . The morphologies of G and GO were examined using scanning electronic microscopy (SEM) (VEGA\\Easy Probe) . The chemical groups of the samples were studied by Fourier transformation infrared spectroscopy analysis (FT-IR – Shimadzu Spectrophotometer) using KBr as a background . The optical properties were studied by using Vis-UV (UV-1800- Shimadzu) rays for range (300-900) nm . The hardness is calculated by using shore (B) ,which is a device used for all samples to measure plastics with high hardness ,sample of hardness according to the specifications (ASTM D 2240) . Particles size is measured using particles size analyzer (DLS) (Nano Brook with high speed examination from (1-2) sec.

III. RESULTS AND DISCUSSION

A. XRD Characterization

The XRD pattern (Fig.1) exhibited a strong peak at 2Θ=11.85° with (001) plane , which corresponded to an interlayer spacing of about 7.6 Å for GO, while (Fig.2) exhibited broad peak centered at 2Θ=25.72° for G which is the same peak of graphite correspond with data card (JCPDS Card no.75-1621) at plane (002) with d-spacing d_{002}=3.4Å while constant lattice was a=2.74Å. (Fig.3) showed pure PMMA at 14.79 ° and graphene/PMMA composite with increased and decreased (±1°) of graphene angle and that agree with others [13-14].

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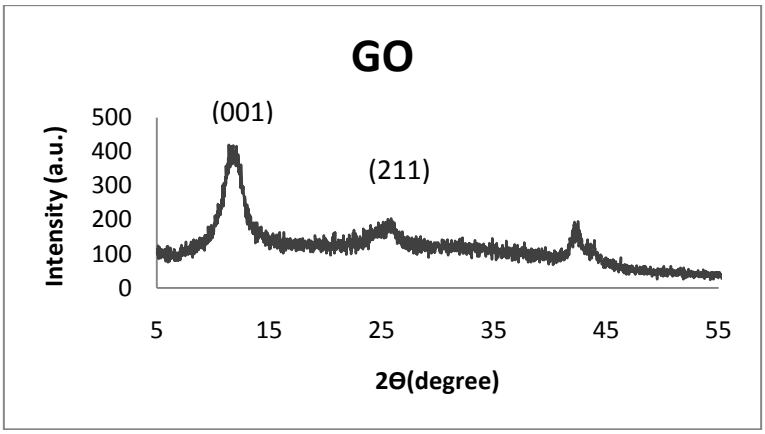

Fig.1-XRD pattern of graphene oxide.

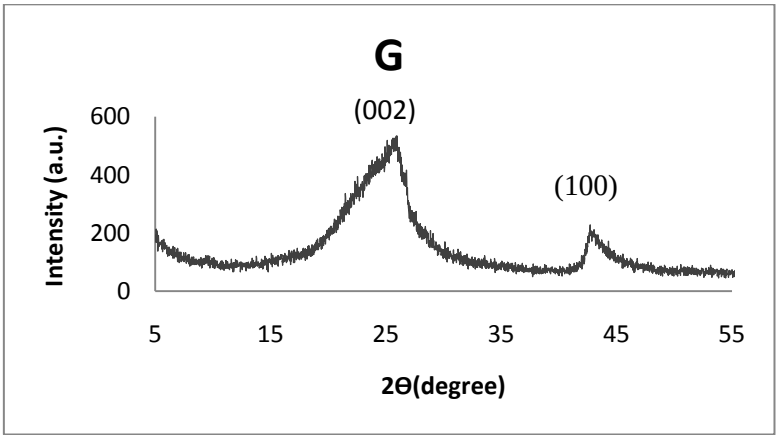

Fig. 2 – XRD patterns of graphene.

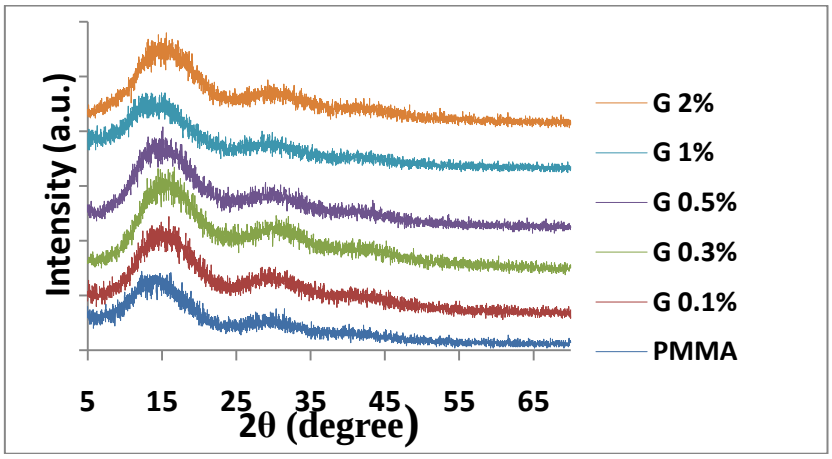

Fig (3) –XRD patterns of Graphene/PMMA .

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B. SEM and DLS Characterization

From SEM images the graphene oxide exhibit like agglomerated Fig.4a with 21nm particles size using DLS Fig.5a while Fig.4b graphene showed flakes with highly agglomerated state and many wrinkles with 200nm particles size Fig.5b [15-16].

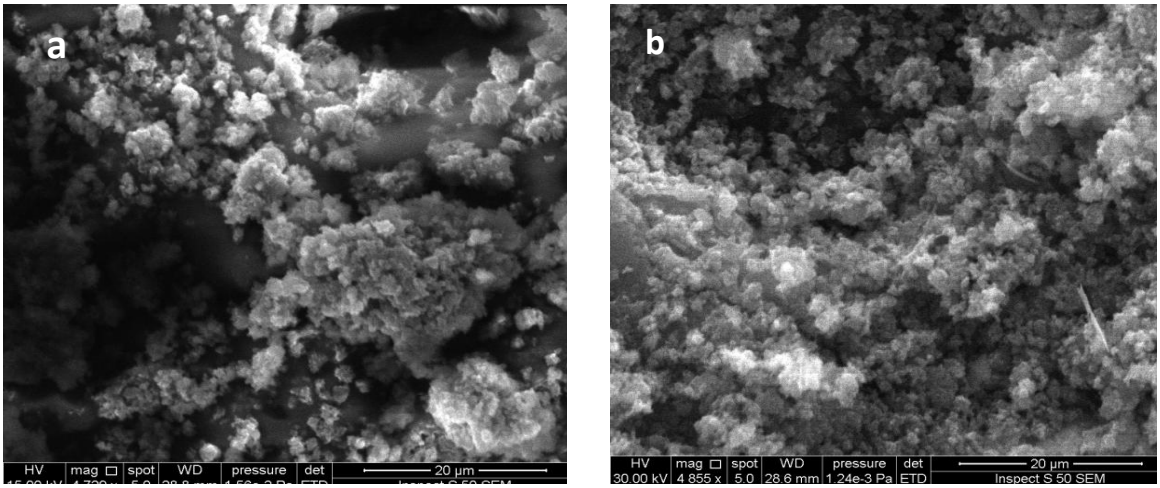

Fig.4 – SEM images : **a**) Graphene Oxide **, b**) Grphene .

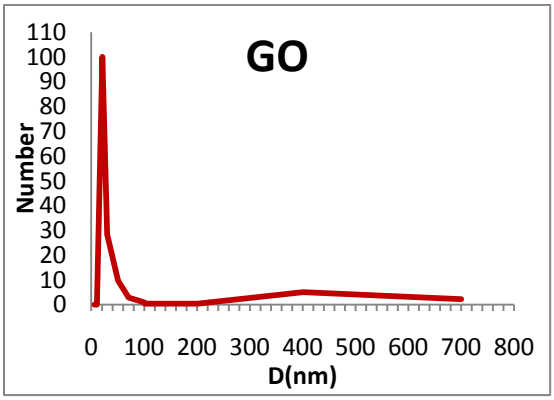

Fig.5a Graphene Oxide

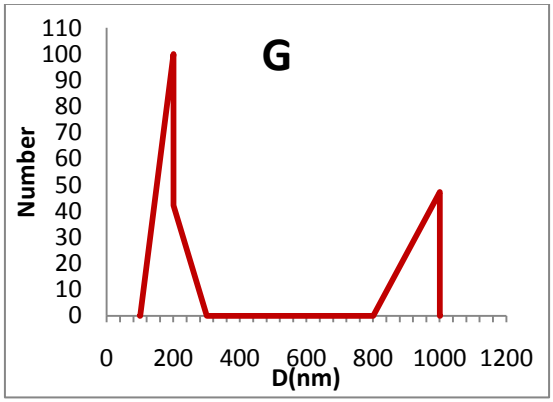

Fig.5b Graphene Flakes

C. FT-IR Analysis

FT-IR peak for graphen oxide Fig.6a between 3000 to 3500 cm^{-1}(O-H) due to absorbed moisture which returns to (C-OH) carboxylic acid , with (C=O) 1712 cm^{-1} (carbonyl/carboxy) , (C=C) 1626cm^{-1} (aromatics) , (C-O) 1358 cm^{-1} (carboxy) , (C-O) 1217 cm^{-1} (epoxy) , (C-O) 1047 cm^{-1} (alkoxy) . Graphene has a few organic number because of reducing graphene oxide Fig.6b[17].

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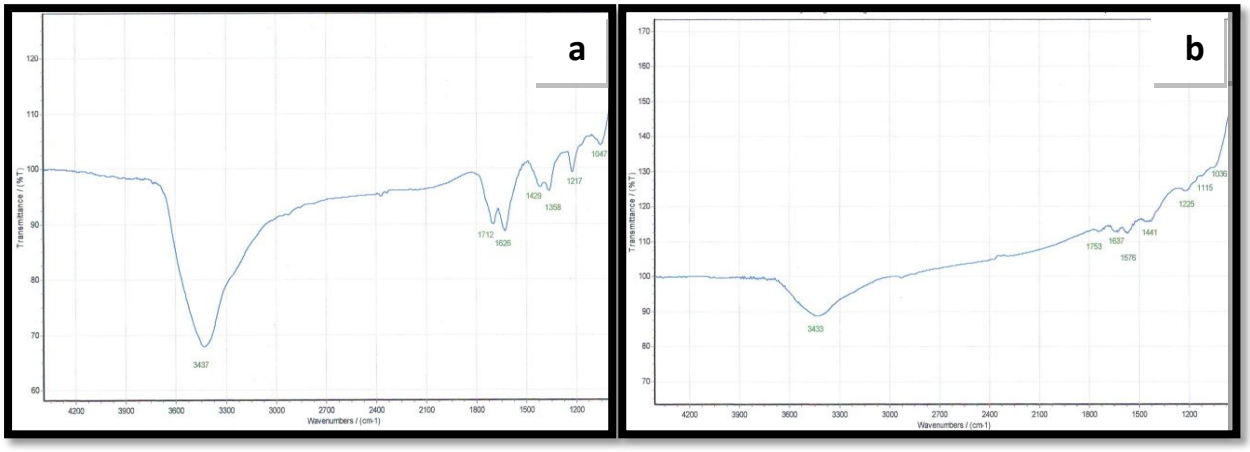

Fig.6. FT-IR spectra :a) Graphene Oxide , b) Graphene .

D. Optical Properties

Synthesized graphene/ PMMA films were characterized by UV-VIS with wavelength range (300-900) nm , from Fig.7 we saw that the increase of absorption as a function of graphene concentration and wavelength . G / PMMA films recorded highest value 92% at 2% concentration of graphene flakes in Infrared region (800-900) nm due to the increase in energy levels formed by the impurity atoms in matrix material between conductive and valance band , these levels work as helping levels for transporting the electrons that absorbed the photon with low energy from energy gap region and that caused the absorbance [18] , while the transmittance decreased as function of wavelength by increasing the composition of graphene flakes (acting in contrasts the absorbance) Except pure PMMA film (0%) the transmittance up to 90% [18], as we saw in Fig.8.

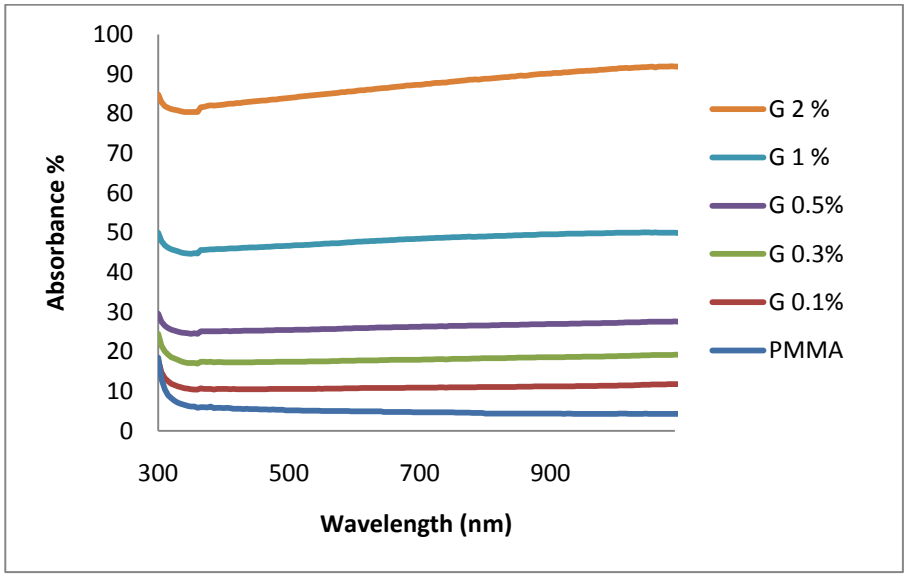

Fig.7. Absorbance as function of wavelength for G/PMMA films .

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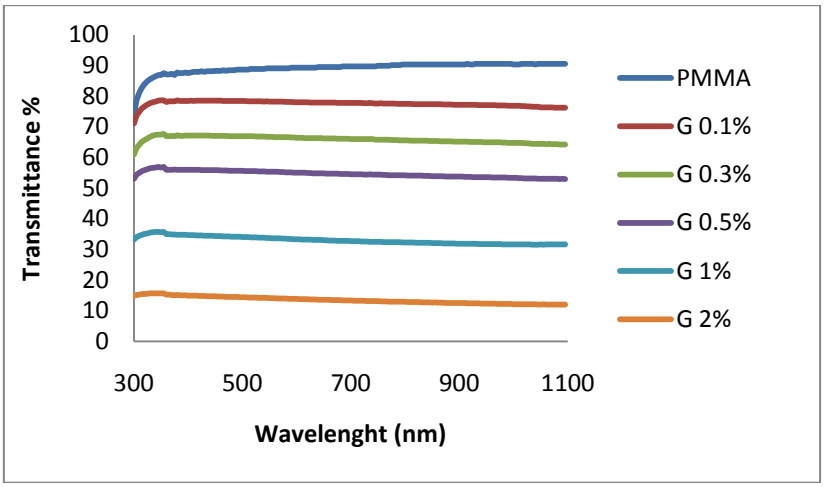
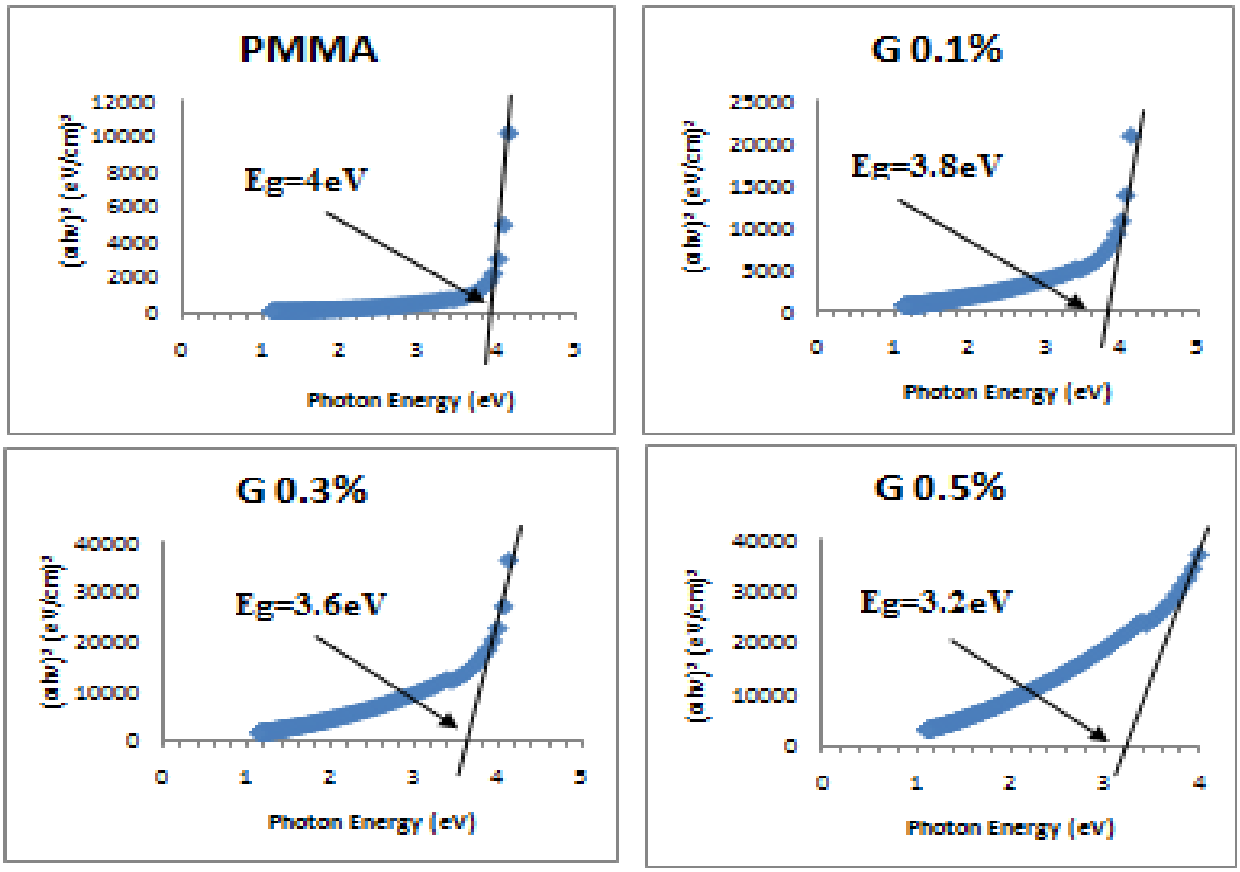


Fig.8. Transmittance as function of wavelength for G/PMMA films .

From UV-VIS energy gap (Fig.9) is calculated which decreased by increasing of the graphene flakes concentration due to the transport of electrons that absorb the photons with low energy from (4 – 2.8) eV and graphene has high conductivity and that caused the decrease [19-20] .



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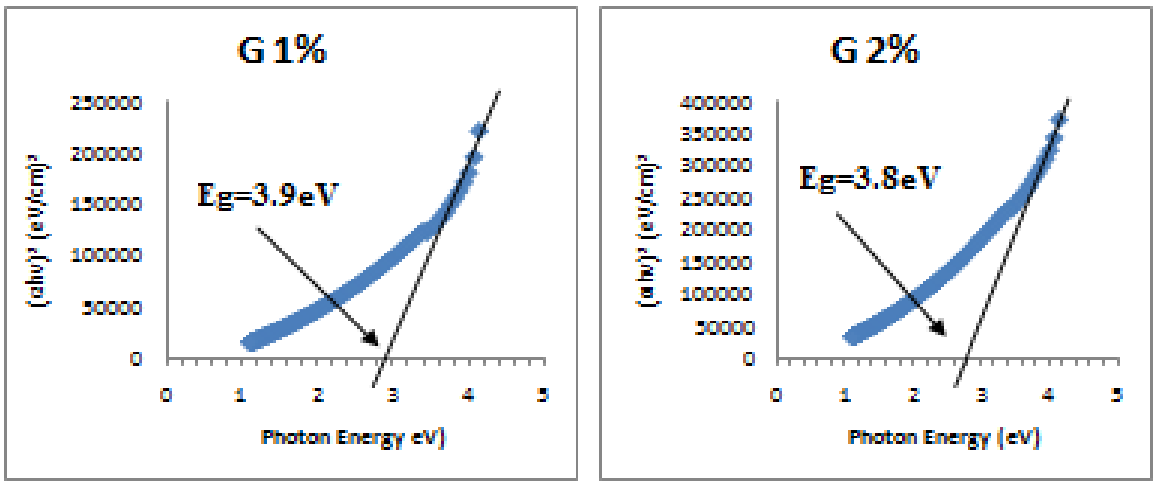

Fig.9 Energy gap of G/PMMA films (0,0.1,0.3,0.5,1and 2)% concentration .

E. The Hardness

Fig. (10) showed the value of hardness of graphene/PMMA bulks increased with the increase of the concentration of graphene flakes (0,0.1, 0.3 , 0.5, 1, 2)% , due to the impurities of graphene flakes permeated the matrix PMMA and reinforced it[14] , the samples were examined by using (shore durometer) type shore B , after 1 or 2 sec. we got the values of hardness.

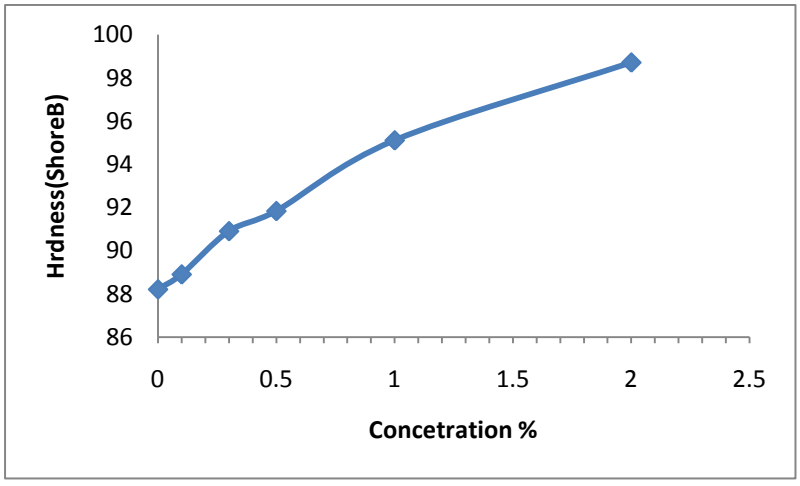

Fig.10 Hardness value of G/PMMA bulks .

IV.CONCLUSIONS

The G/PMMA films and bulks composites were successfully prepared by Hand lay-up method . FT-IR results show that graphene contains very few organic groups . XRD patterns indicate that graphene flakes were fully dispersed in the PMMA matrix , whereas SEM and DLS morphological investigation show that graphene that prepared by Hummer's method have form flakes with highly agglomerated state and many wrinkles .The energy gap was found to be dependent on concentration of graphene flakes and best value record at 2% . The mechanical properties include

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hardness were found to dependent on the concentration of grphene flakes and it is increased by increasing the filler of graphen flakes . the mechanical and optical properties of composites were prepared by Hand–lay up method make this a preferred method for packing application , solar cells , IR- window and microwave absorbing .

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