

Hydrogen Bonds Effects on the Electrical Properties of Pectin/Pva Graphene Nanocomposites

*Issam A. Latif , Sumayah M. Abbas , Muna A. Kadhum

Department of Chemistry, College of Education Ibn Al-Haitham, University of Baghdad, Baghdad, Iraq

* E-mail of the corresponding author: dr_issam2003@yahoo.com

Abstract

Electrical properties were studied for Pectin/PVA graphene composites films and the effect of aqueous interaction on their properties. The conductivity and the dielectric constant of this composite are important because Polysaccharide like pectin is increasingly being used in biomedical applications and as nanoparticles coating materials. The Dielectric and conductivity of composite films were compared in dry and wet condition the differences in the results were attributed to the water molecules and the hydrogen bond which connect the three composite compounds (Pectin, PVA and Graphene) together. These connections were allowed the hydrogen and hydroxyl group's migrations in the composite super molecules. On the other hand, graphene was prepared and with different techniques like Ft-IR, XRD, SEM and AFM characterized.

Keywords: Hydrogen Bonds, nanocomposite , dielectric constant , Pectin/PVA graphene nanocomposite

1. Introduction

Hydrogen bonding is recognized as a useful tool in constructing of a supramolecular motif owing to its directional property. Small molecules with multiple hydrogen bonds are assembled to form a supramolecular polymer which has similar properties to a conventional polymer in terms of theology [1]. The additional interaction to a hydrogen-bond-based supramolecular polymer gives rise to new chemical properties [2]. Polysaccharides hydrogels, like other hydrogels, can have significant water contents, comprising water tightly bound to the polymer chains [3-6]. Water within polysaccharide films plays a pivotal role in establishing their molecular conformations. At low-water concentrations, polysaccharides chains forming extended twofold helices are stabilized by intramolecular hydrogen bonds including the stabilizing water molecules between polysaccharides sheets formed by these chains [7-9]. Importantly the initial molecular interactions between the polysaccharides chains and water molecules at nanoscale dimensions using molecular dynamics, and showed that the extent of hydrogen bond formation and disruption or rearrangement influenced the interchange free volume [10]. Few articles were studied and investigated the electrical properties of polysaccharides with two hydroxyl groups and one carboxylic group in its monomer unit. Pectin is a good candidate for forming a supramolecular polymer composite because a Pectin unit possesses two hydroxyl groups and one carboxylic group which lead to multiple hydrogen bonds that form a flexible and robust film [11]. Pectin is used in advanced biomedical applications, such as drug delivery, tissue engineering and hemodialysis membranes. PVA/pectin is a very good composite the two polymers are hydrophilic and the hydrogen bonds are combining the Pectin and PVA molecules together.

Graphene has been studied in the context of many applications, such as energy-related materials, sensors, paper -like materials, field-effect transistors (FET), and biomedical applications, due to its excellent electrical, mechanical, thermal properties and polymer composites [12,13]. Graphene normally operate in ambient environments, and can bind with water molecules by the weak van der Waals bonds, which corresponds to the hydrophobic properties of non-functionalized carbon Nanosystems [14]. The gas molecules (such as H₂O, O₂) adsorbed on graphene can act as donors or acceptors and induce changes in the electrical conductivity, giving rise to such applications as gas sensors with high sensitivity [15]. The influence of gas adsorption becomes more severe when graphene contains defects due to their enhanced reactivity [16, 17]. Water molecules can dissociate over defective sites in graphene, forming C–H and C–OH bonds, which has been demonstrated by both theoretical calculations [18], and vibrational spectroscopy. Therefore, elucidating the impact of defects toward gas adsorption and reactions is crucial for making reliable graphene-based devices that operate in ambient conditions [19]. In this work, we systematically study the effect of hydrogen bonds on the electrical properties of the films and dielectric relaxation phenomena associated with the onset and progress of PVA/Pectin graphene nanocomposites films by the conventional parallel plate geometry adopted for such measurements. The arrangement adopted allowed measurements under controlled water contain conditions, which identified the spontaneous deswelling arising from expulsion of water during structural rearrangement.

2. EXPERIMENTAL DETAILS:

2.1. Materials

All chemicals, including sulfuric acid (98%), hydrochloric acid (36 weight %), hydrogen peroxide (30 weight %), potassium permanganate, sodium nitrate were purchased from Merck-Germany and pectin, PVA (MW =72000g), and N, N-dimethylformamide Sigma Aldrich Co and used as received. Graphene was prepared from natural flake graphite powder (Sinopharm Chemical Reagent Co., Ltd).

2.2. Instruments

For the characterization of graphene and the polymer composites were used the following instruments IR spectrophotometer (8300 FT-IR Shimadzu Spectrophotometer), XRD (Shimadzu XRD-6000) with copper radiation (Cu K α , 1.5406 Å), Atomic Force Microscopy (AFM, AA 3000 Scanning probe Microscope), Scanning electron microscopy (SEM) (VEGA TE SCAN USA), For the dielectric properties were used Precision LCR meter HP 4274A connected with HP 4275 A and Test Fixture HP 16047 A at frequency range 100 Hz to 100K Hz .

2.3. Synthesis of graphene oxide (GO)

Hummer method was used [20] to oxidize the graphite's for the synthesis of GO. First, 0.2 g graphite, 0.1 g sodium nitrate and 10 ml of sulfuric acid were mixed and strongly stirred at 0° C for 15 min in a 500 ml reaction flask immersed in an ice bath. Then 1 g potassium permanganate was added slowly to the above solution and cooled for 15 min. After this, the suspended solution was stirred continuously for 1 h, and 50 ml of water was added slowly to the suspension for 10 min. Subsequently, the suspension was diluted with 80 ml of warm water and treated with 5 ml of H₂O₂ (30%) to reduce residual permanganate to

soluble manganese ions. Finally, the resulting suspension was filtered, washed with distilled water, and dried in a vacuum oven at 60°C for 24 h to obtain GO.

2.3. Graphene synthesis by Reduction of exfoliated GO with hydrazine hydrate

Graphene was synthesized in a typical procedure, GO (100 mg) was loaded in a 250-mL round bottom flask and water (100 ml) was then added, yielding an inhomogeneous yellow-brown dispersion. This dispersion was sonicated using (Soniprep 150 Plus) until it became clear with no visible particulate matter. Hydrazine hydrate (1.00 ml, 32.1 m. Mol) was then added and the solution heated in an oil bath at 100 °C under a water-cooled condenser for 24 h over which the reduced graphene oxide gradually precipitated out as a black solid. This product was isolated by filtration, washed continuously with water (5x100 ml) and methanol (5x100 ml), and dried in oven (50°C) [21] Figure (1)..

2.4. Film fabrication

Six 50 ml beakers were prepared with (0.432 g 16% Pectin - 2.268g 84% PVA), and was added to each one a 20 ml deionized water and mixed completely under constant stirring for one hour while the mixture was heated up to 50° C then the mixture was left to cool down to room temperature (20°C) with stirring of the mixture was carried out to ensure a homogenous composition. Each composite was mixed ultrasonically for 23-25 minutes with different graphene composites weight (0.0, 0.006, 0.012, 0.024, and 0.048 g). To cast the films were poured the above mixtures in a casting glass plate 5x12 cm and let it dry at 50°C for 120 hours. At the expiry of this time, the films were ready which were peeled off the casting glass plate. The films were heat treated in a vacuum oven at 100° C for 5 h to produce a dry Pectin/PVA graphene composites films. When the first required electrical measurement was finished the same films exposed to moisture in a humidity chamber and the films monitored from weight change to an accuracy of 0.0001 g, the second measurements were with moistures films.

2.5 Dielectric constant measurements

The above-fabricated films were cut into 2x1.5 cm pieces to fit a homemade silver electrode for characterization by measuring the dielectric properties using the Precision LCR meter. The dielectric parameter as a function of frequency is described by the complex permittivity

$$\epsilon^* (\omega) = \epsilon'(\omega) - \epsilon'' (\omega) \quad \dots\dots\dots (1)$$

Where the real part ϵ' and imaginary part ϵ'' are the components for the energy storage and energy loss, respectively, in each cycle of the electric field. The measured capacitance, C was in the range 10 pF to 1 nF for dry composite films and from 1 nF to 1 μ F, was for films with water content 6 wt %. The accuracy of the measured capacitance was 60.01 pF for dry films and 61 pf for water content samples. The capacitance was used to calculate the dielectric constant, ϵ' using the following expression.

$$\epsilon' = \frac{C d}{\epsilon_0 A} \quad \dots\dots\dots (2)$$

Where d is the thickness between the two electrodes (film thickness), A is the area of the electrodes, ϵ_0 is the permittivity of the free space, $\epsilon_0 = 8.85 \times 10^{-12}$ F. m⁻¹ and (ω) is the angular frequency; $\omega = 2 \pi f$, f is applied frequency. Whereas for dielectric loss, $\epsilon''(\omega)$ and $\tan\delta$ is tangent delta [22]:

$$\epsilon''(\omega) = \epsilon'(\omega) \cdot \tan \delta(\omega) \quad \dots\dots\dots (3)$$

3. Results and Discussion:

3.1 Film hydration

Hydration of the films under saturated humidity chamber was monitored as a function of time. Films gained water was reached 7.74 wt % after 300 min and reached a maximum value of 12.11 wt % after a total time of 21 h. After this time, the water content in the Pectin/PVA graphene composites films decreased spontaneously in spite of the film being maintained at 100% relative humidity (RH) due to deswelling processes figure 3. The final water content appeared to stabilize at 8.70 wt % after 83 h as shown in Figure 4.

3.2 FTIR analysis

In Figure 5 (a) shows several characteristic peaks of FT-IR for graphene oxide corresponding to O-H vibration at 3200-3400 cm⁻¹, C=O stretching at 1726 cm⁻¹, C=C skeletal vibration from unoxidized graphitic domains at 1627 cm⁻¹, O-H deformation at 1396 cm⁻¹, epoxy symmetrical ring deformation at 1154 cm⁻¹, C-O is stretching mixed with C-OH bending at 1032 cm⁻¹. After reduction as seen in Figure 5 (b) , the peaks corresponding to C=O stretching at 1726 cm⁻¹, disappeared while the peak at 1557 cm⁻¹ (C=C) was retained , the stretching vibrations at 1060 cm⁻¹ on the graphene oxide and reduced graphene oxide spectra indicate the presence of C–C skeletal vibrations of the graphite ring . This showed that reduction results in the formation of sp² carbon structure. Thus it can be concluded that graphene sheets were produced via reduction of graphene oxide.

3.3. XRD analysis

In the XRD pattern of GO Figure (6), the strong and sharp peak at $2\theta = 11.7^\circ$ corresponds to an interlayer distance of 7.6 Å (002). Reduced graphene oxide Figure (7) shows a broad peak that can be fitted by using a Lorentzian function into three peaks centered at $2\theta = 22.30^\circ$, 25.68° and 26.83° , corresponding to interlayer distances of 4.91, 3.72 and 3.39 Å, respectively. These XRD results are related to the exfoliation and reduction processes of GO and the processes of removing intercalated water molecules and the oxide groups. And all XRD pattern was identical with [23,24]. The morphology of the prepared graphene powder sample was examined by SEM and AFM, representative images are shown in Figs. (8,9) respectively. The SEM reveals an agglomerated powder with a ‘thinning’ appearance. In figure 6 show a high profile AFM image of graphene. The suspensions concentration of graphene was (0.21 mg/ml) and deposited on mica. Many researchers were found that the synthesis of graphene materials from reduction of exfoliated GO yields samples which are not based on single separated graphene sheets, but rather on an over-lapped multiple layers, highly agglomerated wrinkled sheet. Evidence for stacks of graphene sheets comes from the broad XRD out-of-plane graphitic reflections, shown in Fig. (6,7). We label these peaks ‘‘002’’ [25 -29].

3.4. Dielectric spectroscopy

3.4.1. Dry Pectin/PVA graphene composites films

Figure (10) shows a typical frequency dependent dielectric characteristics of the dry Pectin/PVA graphene composite films electrode configurations produce identical dielectric responses. The dielectric permittivity (ϵ') was $(8.5-9.5 \pm 0.1)$ (at 10^5 Hz) for these films, consistent with values reported for a range of similar Biopolymer matrices [31]. The low-frequency dielectric permittivity (ϵ') were about $(17.7 - 37.5) \pm 0.1$ (at 100 Hz) indicative of negligible space charge contributions, whereas the dielectric loss corrected for DC loss (ϵ'') was $\sim 2.9 - 3.8$ at low frequencies increasing to $(6.7 - 8.0) \pm 0.01$ at 10^5 Hz is confirming the minimum effect on the of mobile charge carriers such as OH^- in these well-dried films.

3.4.2. Dielectric permittivity of hydrated films

Dehydration that occurred during deswelling reduced the water content to 8.7 wt %. The bounds water-pectin/PVA graphene composites complexes in the crystalline regions are illustrated diagrammatically in Figure (2). Water molecules form bridges between pectin-PVA-and Graphene chains stabilizing the structure. These constitute the non-freezing bound water within the structure, which characteristic changes the relaxation processes due to increased cooperative motion of local chains as reflected in their measured dielectric properties [23, 30]. Figure (11) shows the frequency dependence (dispersion) of the dielectric permittivity (ϵ') for the hydrated pectin/PVA graphene composite films with water contents above 8.7 wt %. The dielectric permittivity has a major contribution from Maxwell-Wagner-Sillars relaxation processes (e.g., interfacial space charge polarization arising from mobile OH^- ions). Dehydration that occurred during deswelling reduced the water content to 8.7 wt %. Water molecules form bridges between pectin-PVA-and Graphene chains stabilizing the structure. These constitute the non-freezing bound water within the structure, which characteristic changes the relaxation processes due to increased cooperative motion of local chains as reflected in their measured dielectric properties. Figure (10,11) shows the frequency dispersion of the dielectric permittivity (ϵ') and the dielectric loss (ϵ'') for the pectin/PVA- graphene composite films before and after the hydration in the humidity chamber. The ϵ' and ϵ'' at low frequencies were increased steadily more than an order of magnitude with increasing graphene weight. This behavior was similar to that reported in the literature for various systems such as polyethylene oxide containing hydrogen ions [31], and nanoporous silica containing water [32]. Figure (11) show no development of a resonance peak in the dielectric loss (ϵ'') observed in the measured frequency range even after dc conductivity correction, indicative of the measured dielectric loss having high contributions from other dielectric relaxation processes in addition to the orientational dipolar relaxation. This high-dielectric loss $(3.5 - 15 \pm 0.1)$ In the low-frequency range (at 100 Hz) rises from relaxation of the Low - mobility charge carriers, namely, hydroxide ions. Such a high-dielectric loss may mask the relaxation observed by Gonzalez-Campos et al [33] at frequencies below 100 Hz for Chitosan films. At low frequency were shown the dielectric permittivity (ϵ') $(75 - 141 \pm 0.1)$ (which is not affected by the dc conductivity) confirming the increasing formation of charged species with hydration that contribute to the space charge polarization component (Maxwell-Wagner-Sillars) of the dielectric permittivity. The dielectric permittivity (ϵ') of this film at 10^5 Hz increased from $(8.5-9.5 \pm 0.01)$ for the dry film to $(4-12 \pm 0.01)$ for the film containing 8.7 wt % water, whereas the dielectric loss (ϵ'') exhibited only a marginal increase from $(2 - 3.5 \pm 0.01)$ to $(2.5 - 4.5 \pm 0.01)$ at this frequency.

4. CONCLUSIONS

Here, we have prepared the pectin/PVA graphene composites films and studied the hydration processes within a controlled humidity chamber. The electrical studies were performed between two parallel plate electrodes using dielectric spectroscopy (100 to 10^5 Hz). These studies have shown that the hydration process in the pectin/PVA graphene composite films have a high effect on the dielectric permittivity of the hydrated composites films, the dielectric permittivity were increased more than predicted by the Maxwell–Wagner mixing rule, the dielectric permittivity increasing can be attributed to the formation of a chain-bound water complexes between Pectin, PVA and Graphene molecules adding to the contributions from dipole Polarizabilities. The real dielectric permittivities of hydrated films were shown 3-5 times higher value than the dry films but the imaginary dielectric permittivity showed a little difference (about 0.2-0.3 time). The hydrated composite films were shown a high difference between the real and imaginary dielectric permittivity, these are very useful composite films for super capacitor manufacturing.

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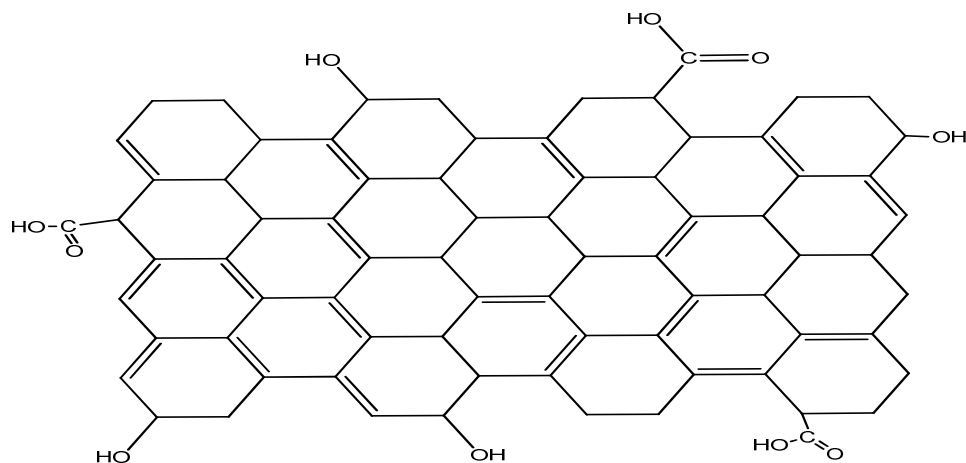


Figure 1: structure proposed for reduced graphene oxide (Graphene)

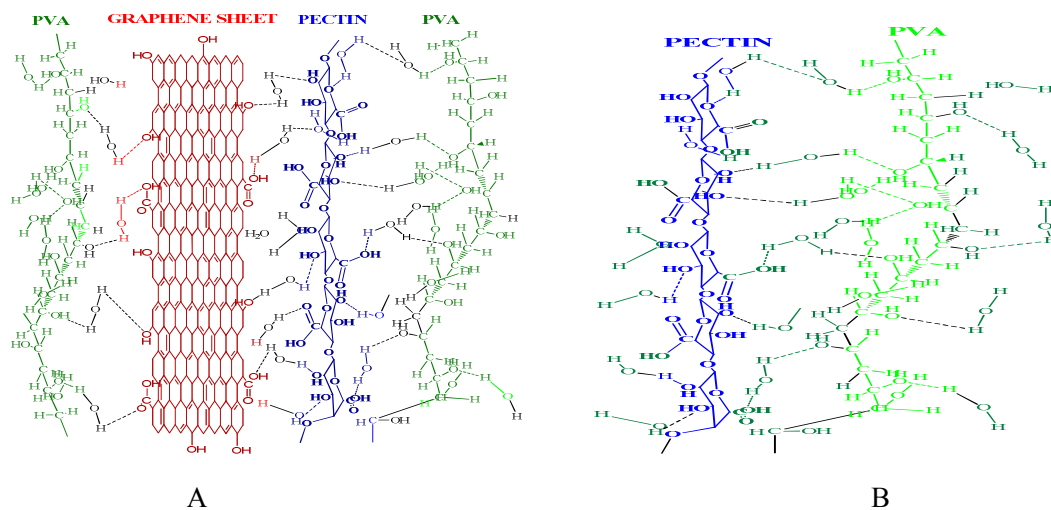


Figure 2: proposed composite structures and hydrogen bonding .A) Represent Pectin/PVA graphene composite. B) Represent Pectin/PVA composite.

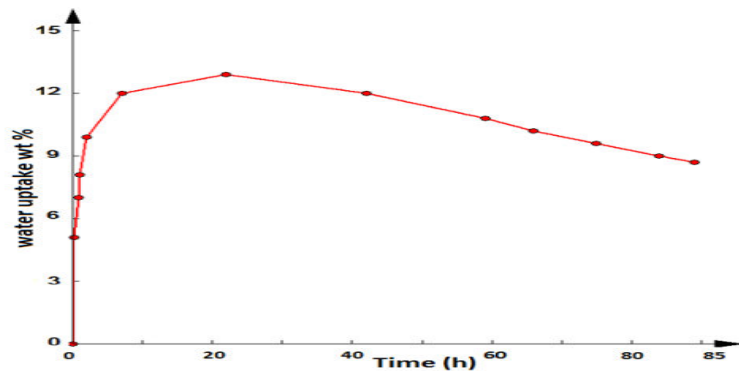


Figure 3 : water uptake by the prepared films

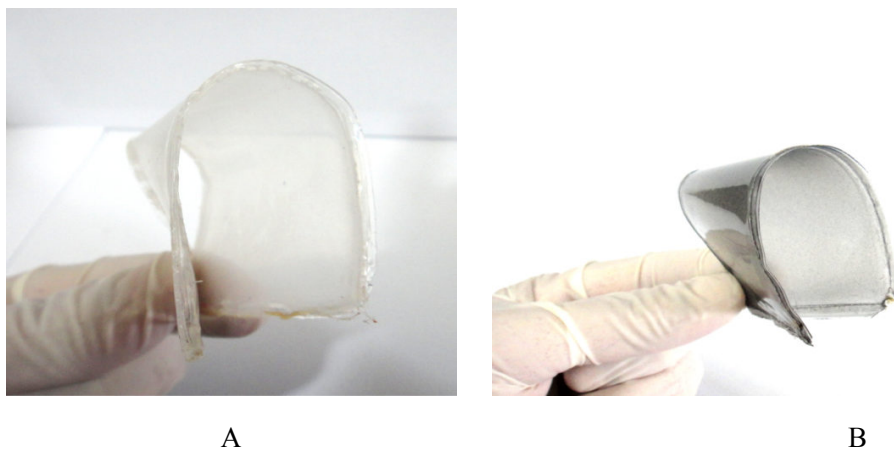


Figure 4: The films no. 3 at 8.7 wt % water content, A) film without graphene. B) Film with graphene

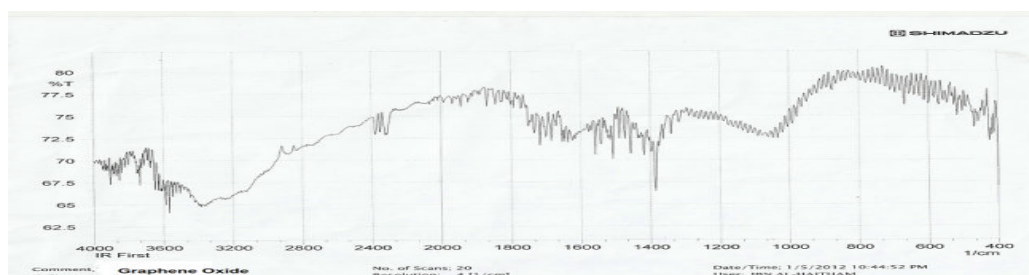


Figure 5 a: FT-IR spectra of graphene oxide

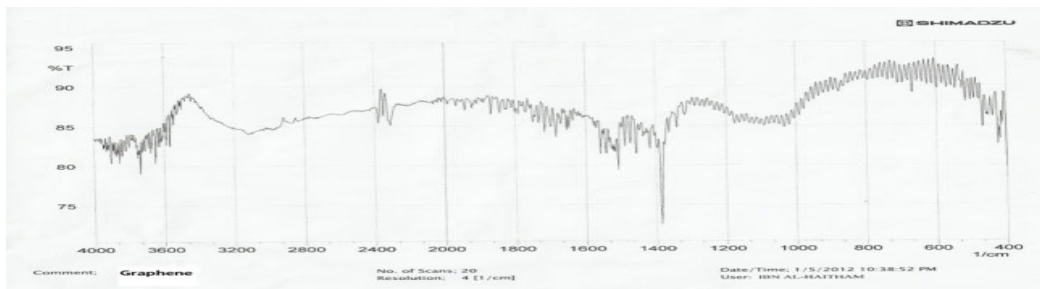


Figure 5b: FT-IR spectra of graphene sheets

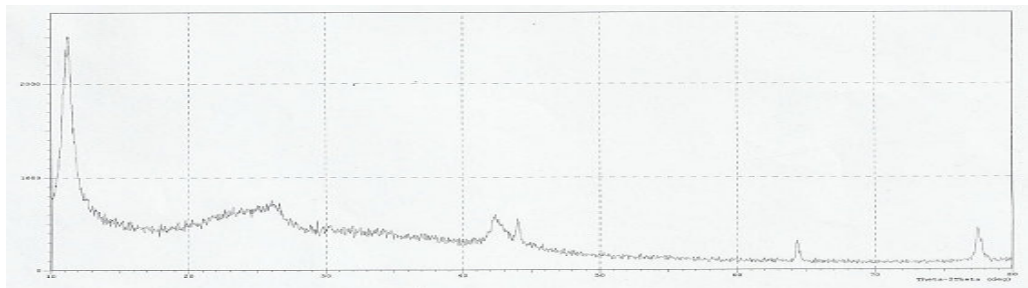


Figure 6 : XRD patterns of graphene oxide

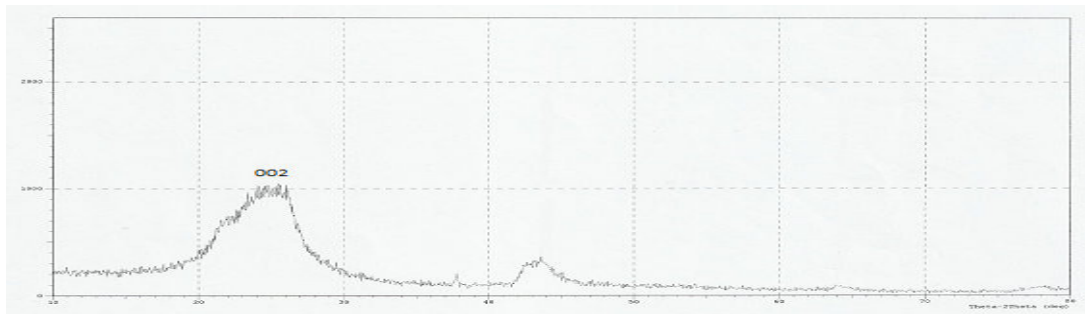


Figure 7: XRD plot of graphene powder sample. Inset shows the multiple Lorentzian peaks fitting of (002) reflection

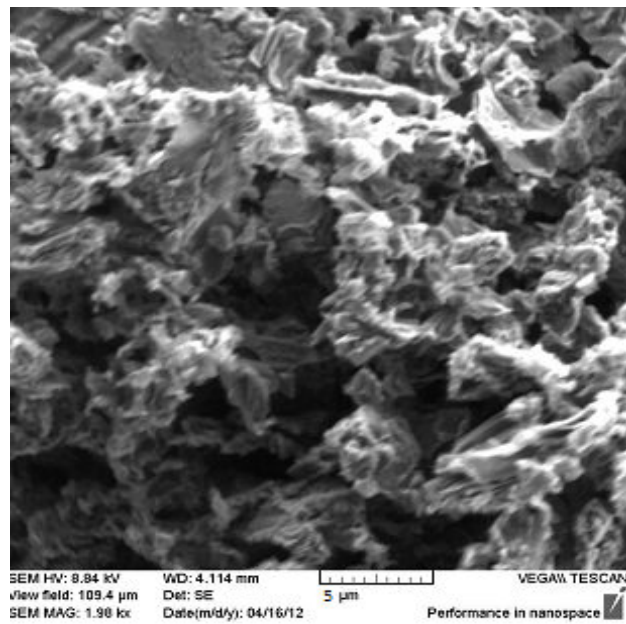


Figure. 8 – SEM image of graphene sample shows that the sheets are highly agglomerated with a fluffy morphology

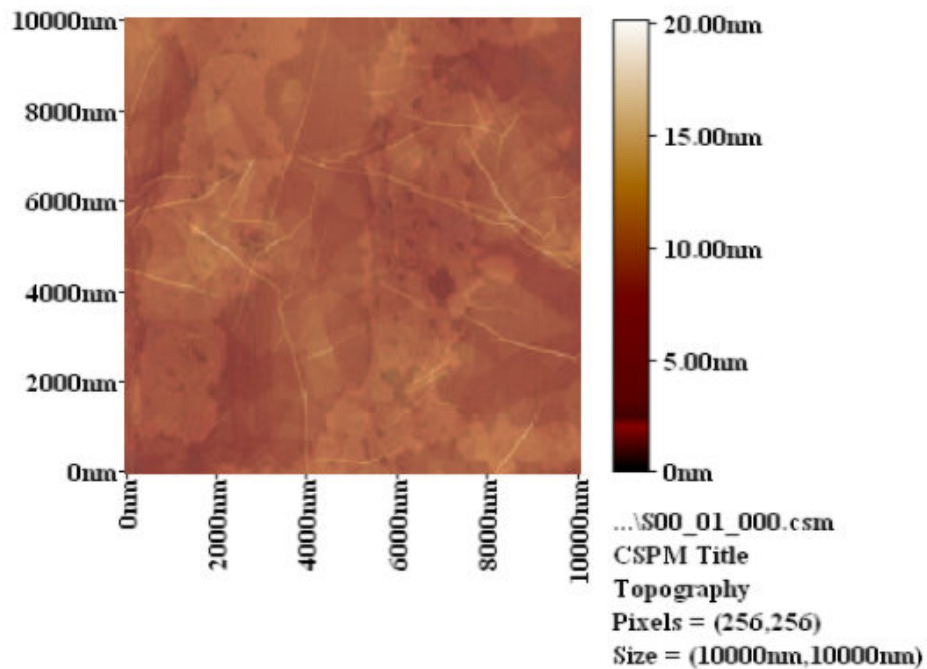


Figure 9- show a high profile AFM image of graphene

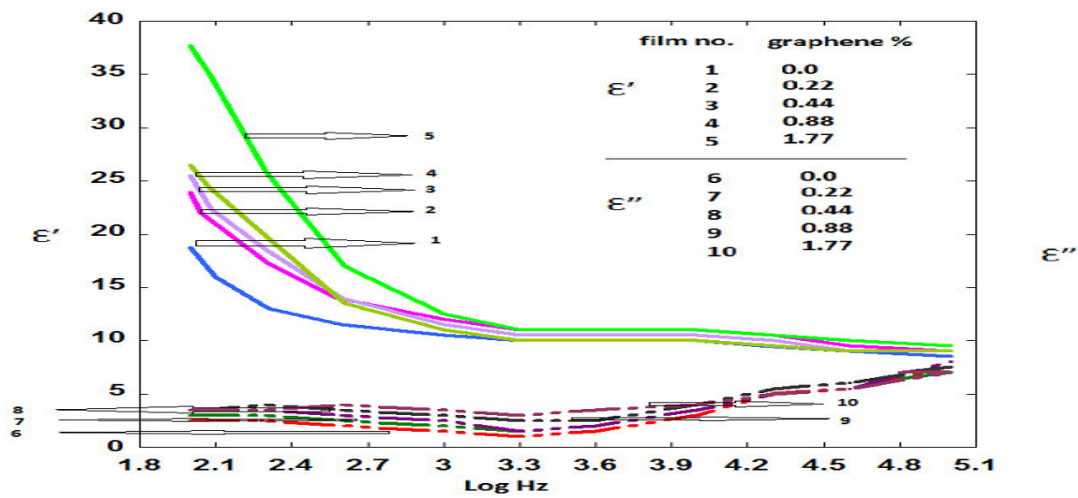


Figure 10: dependent of dielectric characteristics of dry the dry Pectin/PVA graphene composite

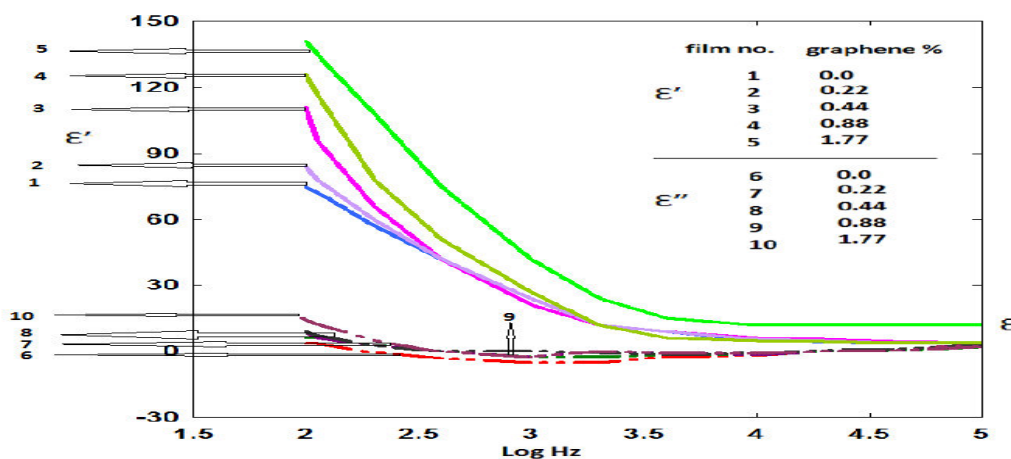


Figure 11: shows frequency dependence of the dielectric permittivity (ϵ') for the hydrated pectin/PVA graphene composite

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