

## Transforming delicate agar to highly stable composite material by incorporating graphite powder for potential multiple applications

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### Abstract

To improve the properties of the biodegradable and biocompatible agar sheets, an attempt is made to fabricate agar based graphite composite (AGC) sheets by simple thermo-physico-mechanical method using hotplate and ultrasonic bath. AGC were prepared by incorporating varying the amounts of graphite as additive in the agar matrix, with ratios ranging from 1:1 to 1:5. The physical characterization of the as prepared AGC and control sheet was done by analyzing the thermal stability, evaporation rate, water holding capacity (WHC) and swelling ratio (SR). SEM, FTIR and XRD analyses were used to investigate the morphology and structural characteristics of AGC. The results showed that AGC with high amount of graphite showed low WHC, SR and high evaporation rate. The AGC were thermally more stable than control and showed stability up to 180°C. SEM, FTIR and XRD data showed the successful and uniform distribution of graphite powder within the agar matrix. From the overall study it was concluded that the delicate nature of agar was transformed into a rigid and thermally stable composite sheets having the potential to be used for several applications.

Key words: Agar; graphite; composite; characterization; thermal stability

## INTRODUCTION

Progress in the field of polymer materials has increased drastically (Tian et al., 2012). Today polymer composites are used everywhere in the world (Murr, 2015). Polymer matrix composites are composed of a polymer resin matrix phase mixed with a variety of short and continuous fibers phase and ground minerals. Reinforcement in polymer matrix composite provides high strength, fracture toughness, light weight, abrasion resistance, puncture and corrosion resistance stiffness and low cost to the composite material (Saunders et al., 1999). The use of (Ihsan Ghani et al., 2023) light weight and strong polymer composites in military aircrafts has greatly enhanced the performance and cost. For (Shahid Zaman et al., 2024) marine industry the big headache and payroll is corrosion. In order to reduce these problems to the minimum level, composites are the best options to do so because of the fact that composites do not corrode like other materials e.g. metals and wood can easily be corroded and rot.

Graphite is a good choice to be used as a reinforcing material because it is cheap, abundant and electrical conductive in nature. Graphite shows intransigence to many of the alkalis, acids and some other corrosive gases, making it one of the best chemically impotent inert materials. The vast applications of graphite in many fields are due to its characteristic chemical and physical properties (Rüdorff, 1959, He et al., 2008). In most of the cases, the incorporation of graphite within the polymer matrix need its activation for easy distribution.

Graphite/polymer composites exhibit high corrosion resistance, low contact resistance and low fabrication cost (Lee et al., 2011). The formulation of graphene nano-platelets reinforced alumina nanocomposites composites were studied by Wu *et al.* It was found that massive increase in hardness is followed by an increase in fracture toughness due to the rise and fall of temperature (Wu et al., 2017). Nanocellulose based agar composite is reported to have improved mechanical, and thermal properties (Shankar and Rhim, 2016). Grapefruit seed extract incorporated agar composite were prepared to achieve material with antimicrobial activity exhibiting improved physical properties (Kanmani and Rhim, 2014). The incorporation of (Kashif et al., 2023) nanoclay in agar to produce a composite material is also reported by intercalation method. The resultant (Muhammad Sheraz et al., 2023) composite had caused evident effect on the thermal, mechanical, swelling and water barrier properties of agar (Rhim, 2011).

Silver/agar nanocomposites with antimicrobial properties are also reported. The resultant composite properties were dependent on the amount of silver used as additive (Rhim et al., 2013). Several studies describing that the incorporation of additives in agar make them a suitable packing material with improved physical, thermal, mechanical and antimicrobial properties (Malagurski et al., 2017, Pinto et al., 2018). Recently, injectable agar based composite for tumour therapy was developed (Wu et al., 2018).

Hence, considering the biodegradable and biocompatible nature of agar and its use as a matrix for developing composite materials having application in several fields, the present attempt is made to fabricate graphite/agar composite with improved thermal and mechanical properties for potential biomedical and industrial application by a simple and economical fabrication method.

## **EXPERIMENTAL**

### **Chemicals and Reagents**

Graphite (powder) obtained from DAEJUNG chemicals and metals Co. Ltd., Korea, Agar was the product of Sigma (Germany).

### **Synthesis of Agar-Graphite Composite Sheets**

Agar-graphite composite (AGC) was prepared by using simple thermo-physico-mechanical method. Different amounts of graphite and agar were mixed in different ratio. Initially, the agar amount was kept fixed as 1g and the graphite was added in increasing order in such a way that the ratio of agar and graphite was maintained as 1:1 (1 g/1 g), 1:2(1 g/2 g), 1:3(1 g/3 g), 1:4(1 g/4 g) and 1:5 (1 g/5 g), respectively. In order to prepare the mentioned AGC, respective amounts (g) of graphite were ultrasonicated in 30 ml distilled water followed by heating on hot plate (Rommelsbacher, type –THS 1590.2, Germany) at 80°C for five minutes. At the same time given amount (g) of agar was added to 70 ml of distilled water and shaken at room temperature for five minutes. 30 ml of hot graphite solution was poured into the already prepared solution of agar making a total of 100 ml. The mixed solution was shaken well for five minutes before heating. It was then heated for about 30 minutes at 90 °C on hot plate with continuous shaking time to time. After complete dissolution of agar the hot suspension was poured directly into the Petri dish and cooled to room temperature where it transformed into the composite hydrogel sheets.

The as-prepared composite hydrogels sheets were then completely dried using mild drying conditions. The same procedure was followed for control (only agar) sheet preparation.

## Physical Characterization

Physical tests were performed in order to investigate the characteristics of AGC sheets. Following physical tests were performed.

### Water Holding Capacity

Strips of equal length and size from dried AGC sheets and control were weighed and dipped in 100 ml of distilled water for 24 h at room temperature. After the defined period sheets were taken out and weighed.

### Swelling Ratio

Composite sheets of similar weight and diameter were cut from the already synthesized agar based graphite composite sheets and were immersed into the distilled water. The wet strips were first dried by soft tissue paper and then weighted. The Swelling ratio of each type of composite and control after 24 hour was calculated by using the following formula:

$$\text{Swelling ratio} = \frac{M_t - M_o}{M_o} \times 100$$

$M_o$  and  $M_t$  are the initial dry weight (g) and final wet weights (g), respectively of the prepared AGC and control.

### Thermal Properties

Thermal analysis of composite was carried at different temperature. Each composite sheets was cut of same diameter from already synthesized AGC and control sheets and were then kept in oven and heated in Oven (Model DW-MD4, Pakistan) at 25°C, 40°C, 60°C, 80°C, 100°C, 120°C, 140°C, 160°C, 180°C, 200°C, 220°C and 240°C for 30 min. Physical change in the form of bending, curving or disintegration was observed.

## **Scanning Electron Microscopy (SEM)**

The surface morphology, cross sectional view and the distribution of graphite particles within the agar matrix of the as prepared composite were studied by using a 30KV Scanning Electron Microscope (JSM5910, JEOL, JAPAN). All the samples were oven dried before the analyses.

## **Fourier Transform Infrared (FTIR) Spectroscopy**

The powder sample was mixed with potassium bromide (KBr) in the ratio of 1:1000. A semitransparent disk of 1 mm of the powdered mixture was obtained by applying the pressure of 20 MPa for 5 minutes. Using the FTIR spectrometer (Thermo Scientific Nicolet6700, VEGA3, USA), the FTIR spectra was obtained at the wavelength range of 4000-400  $\text{cm}^{-1}$ .

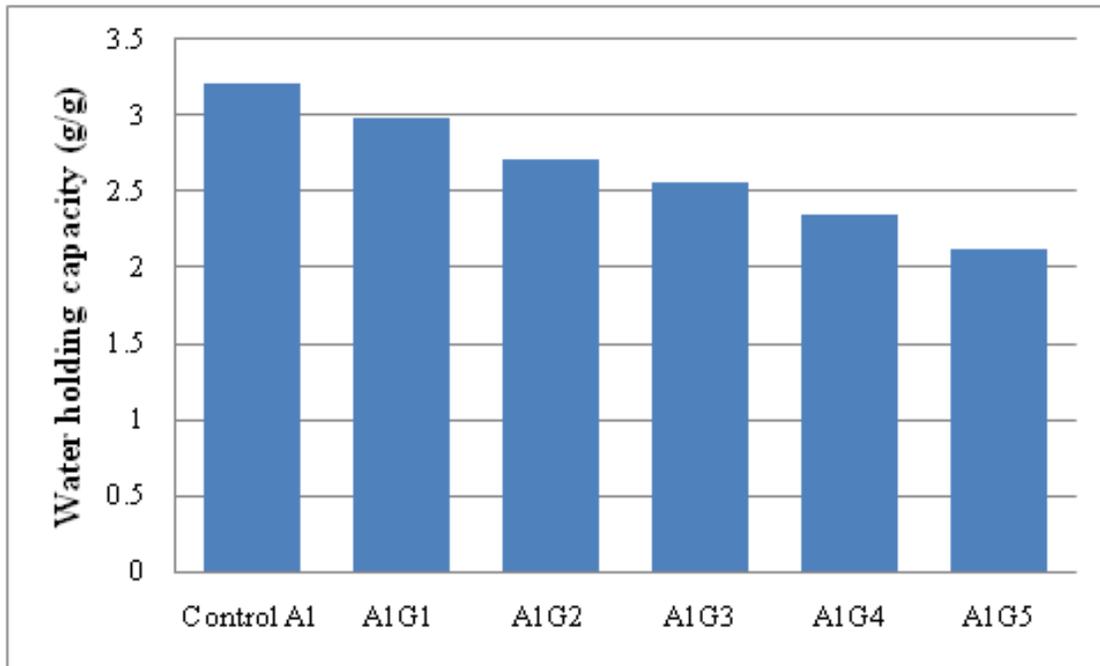
## **X-ray diffraction (XRD) Analysis**

Powder X-ray diffraction (XRD) analysis of the specimens was performed using an X-ray powder diffractometer with Cu anode (PAN alytical Co. X'pert PRO, UK), running at 40 kV and 30 mA, scanning from 3° to 70° at 3°/min.

# **RESULTS AND DISCUSSIONS**

## **Water Holding Capacity (WHC)**

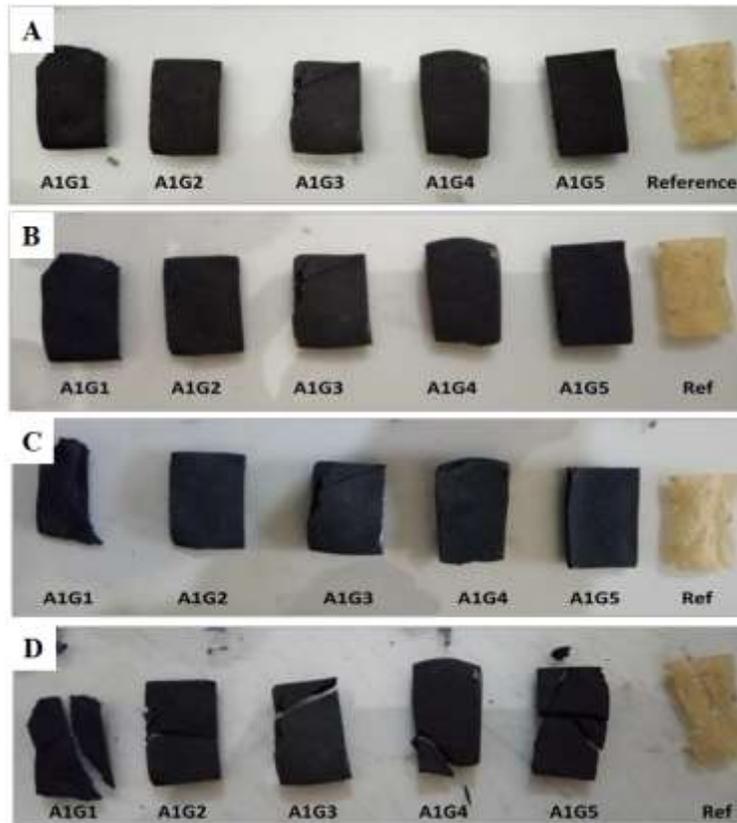
The WHC data of AGC clearly shows that the maximum WHC is attained for A1G1 agar based graphite composite sheet. The WHC of the composite sheets decreased with increase graphite amount in the composite sheets. This is because of the hydrophobic nature of graphite (Raffaini and Ganazzoli, 2009). However if we take a quick look to the Fig 1, it can be easily deduced that increasing the percentage of agar in the developing agar based graphite composite, will increase the water holding capacity of the composite films in a fast and continuous manner (Masuzawa and Sterling, 1968).



**Fig. 1.** Water holding capacity of composites (AGCs) sheets and control (A1).

### Thermal Properties

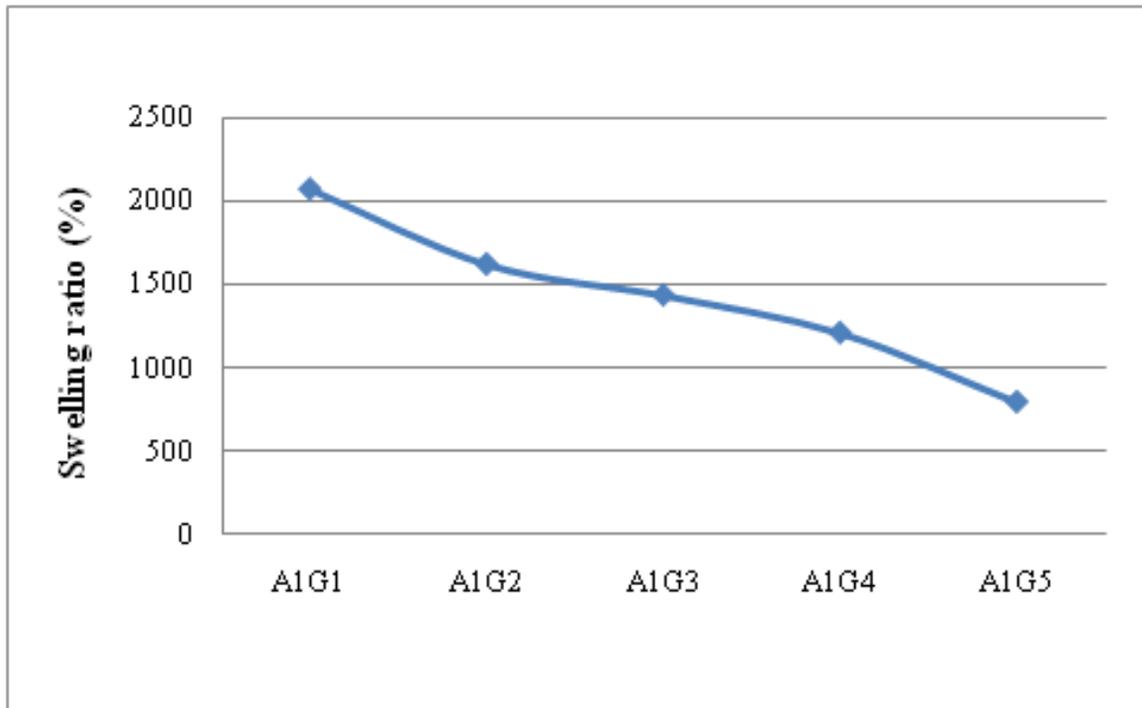
Thermal properties of the developed composite sheets were studied in a pre-heated oven in the temperature range of 20°C to 240°C for specific time intervals. The composite sheets were observed time to time in order to know the effect of any physical change due to thermal treatment. Fig 2 (a-d) clarify that the graphite addition to the composite has enhanced the thermal stability of the AGC. AGC with higher amount of graphite were thermally more stable compared to those with smaller amount and control. It was also observed that all the AGC were stable upto 120°C. However, physically change in the form of folding of the control and A1G1 started above 120°C while other AGC were remained stable. The A1G2, A1G3, A1G4 and A1G5 were all thermally stable upto 200°C whereas started disintegration or breaking beyond this temperature range.



**Fig. 2.** Thermal stability study of AGCs and control at (a) 25 °C (b) 80 °C (c) 160 °C and (d) 240 °C, respectively.

### Swelling Ratio

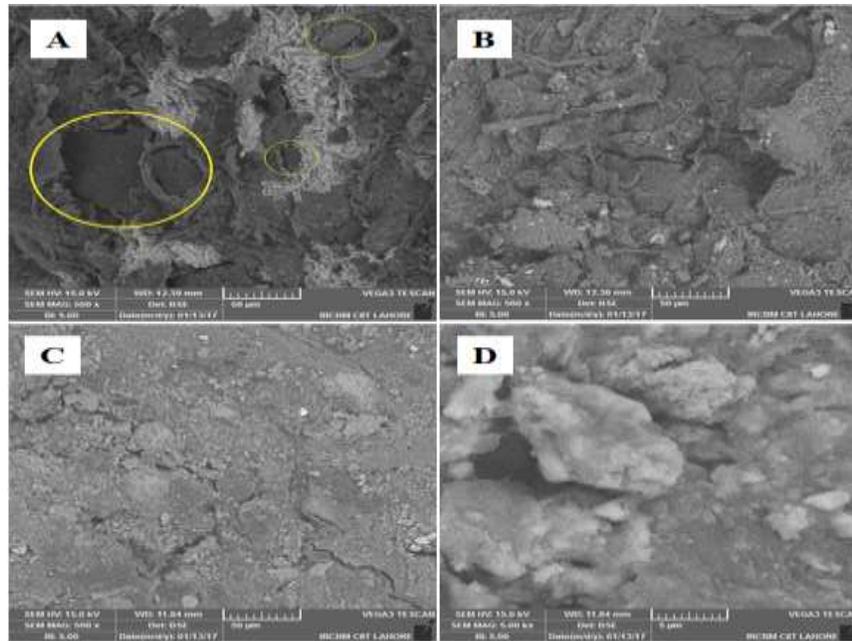
Swelling ratio of a composite shows the ability of a polymer to expand in response of water or some other solvent adsorption. The hydrophilic materials have high swelling ratio compared to less hydrophilic or hydrophobic materials. It can be clearly seen from the Fig 3 for each of the five composite sheets that as the amount of graphite increases in the composite sheets the swelling ratio for the composite sheet decreases. It is because of the hydrophobic nature of graphite. A gradual decrease can be easily noted in the swelling ratio values in case of Fig 3.



**Fig. 3.** Swelling ratio of the composites.

### SEM Analysis

The surface morphology of AGC and distribution of graphite within the AGC was investigated by SEM analysis. In order to observe the surface morphologies of different AGC sheets and control their SEM were investigated. From the SEM images given in Fig 4, it can be observed that the graphite is uniformly distributed within the agar matrix. The yellow circles show the individual graphite particles present in the agar matrix.

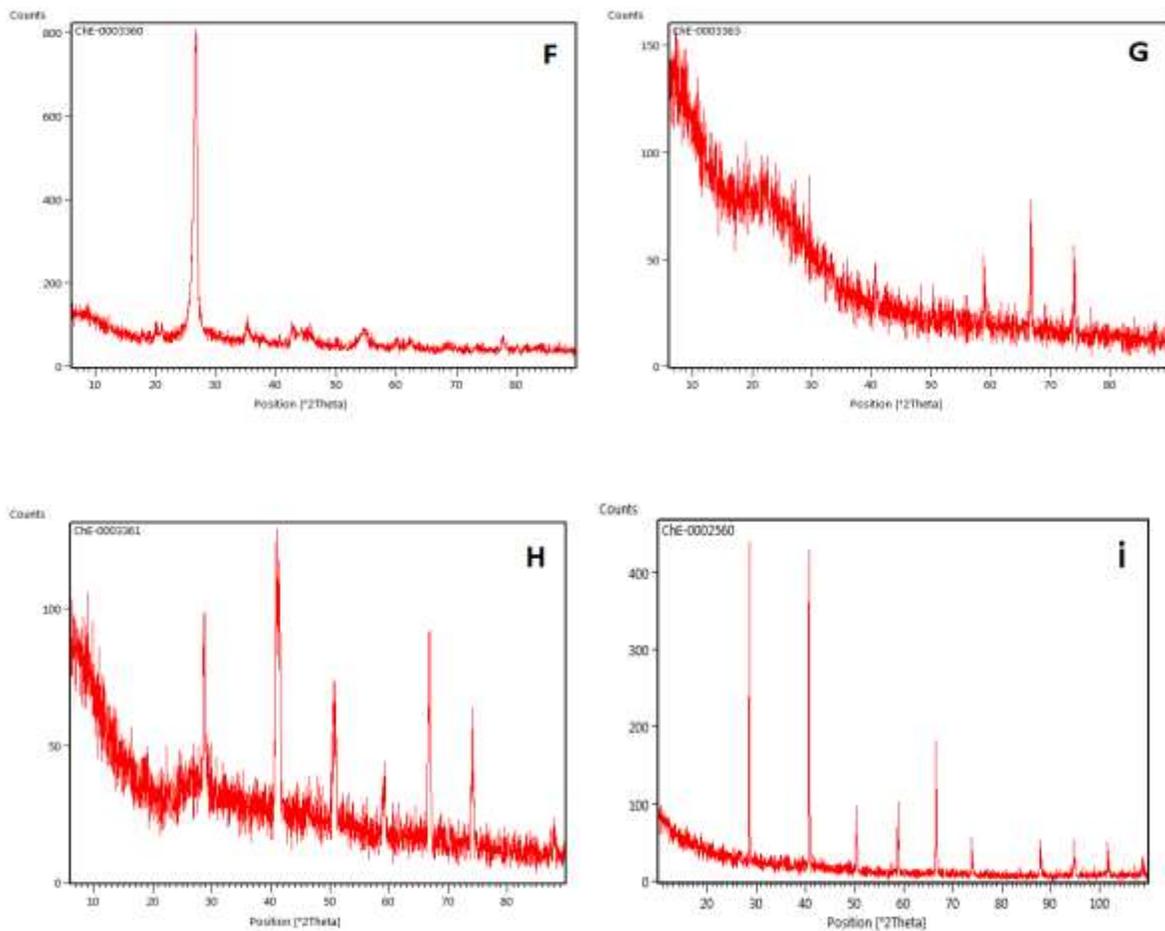


**Fig. 4.** SEM micrographs of A1G5C sheets where (a and b) cross section and (c and d) surface morphology at different magnification.

### XRD Analysis

XRD patterns of AGC sheets containing different amounts of agar and graphite are plotted in the Figure 5 (F to I). A comparison of  $2\theta$  values along with the intensities of XRD peaks are also listed in Table 1. The XRD results confirms the presence and uniform distribution of graphite particles into the agar matrix. Increasing the amount of agar matrix increase the noisy peaks in the agar graphite composite XRD spectra. The peak around  $24\text{-}26^\circ$  in the Fig 5 clearly indicate the decrease in crystalline nature of the graphite in the composite. It shows that increasing the amount of graphite changes the crystallinity of GPC, as it can be seen from the additional noisy peak appearance with an increase in graphite amount. The peaks also indicate an interlayer spacing for graphite of the distance  $0.334\text{ nm}$  ( $002$  crystalline lamella)  $d$ -value with a very good crystalline order of graphitic layers. The above value for  $d$ -spacing and  $2\theta$  indicate that no expansion happened to the gallery of graphitic carbon layers (Zhang et al., 2013). Additional peaks can be observed with increasing amount of agar. The peak around  $26^\circ$  related to the crystalline structure of graphite is slowly shifting towards an increased  $2\theta$  with the decreasing peak intensity. On the other hand it can be clearly seen that gradually increasing the amount of

graphite in the composite mixture increases the crystalline nature of the graphite leading towards sharp and thick peaks in the spectra of composites in question. The incorporation of graphite is confirmed by the appearance of a sharp and thin peak at  $2\theta$  value of  $\sim 26.77^\circ$ . The graphite exhibits a sharp diffraction peak centered at  $2\theta = 26.77^\circ$  corresponding to the 002 reflection plane. A weak but intensive peak appeared at  $2\theta = 55.2^\circ$  is also related to graphite in some cases, as reported by Naebe et al (Naebe et al., 2014).



**Fig. 5.** XRD pattern of Graphite (control) and Agar-based graphite composite sheets. **F** (Graphite), **G**(AIG2), **H**(A1G3), **I**(A1G4).

**Table 1.** XRD analysis of control and AGC sheets.

Graphite		(A1G1)		(A1G3)		(A1G5)	
$2\theta$	Intensity	$2\theta$	Intensity	$2\theta$	Intensity	$2\theta$	Intensity
26.72	811.97	23.34	98.21	27.49	99.01	27.57	437.10
-	-	41.00	82.45	43.11	160.41	43.12	421.12
-	-	51.20	68.65	51.30	80.23	51.90	192.01
		59.0		59.0		59.0	

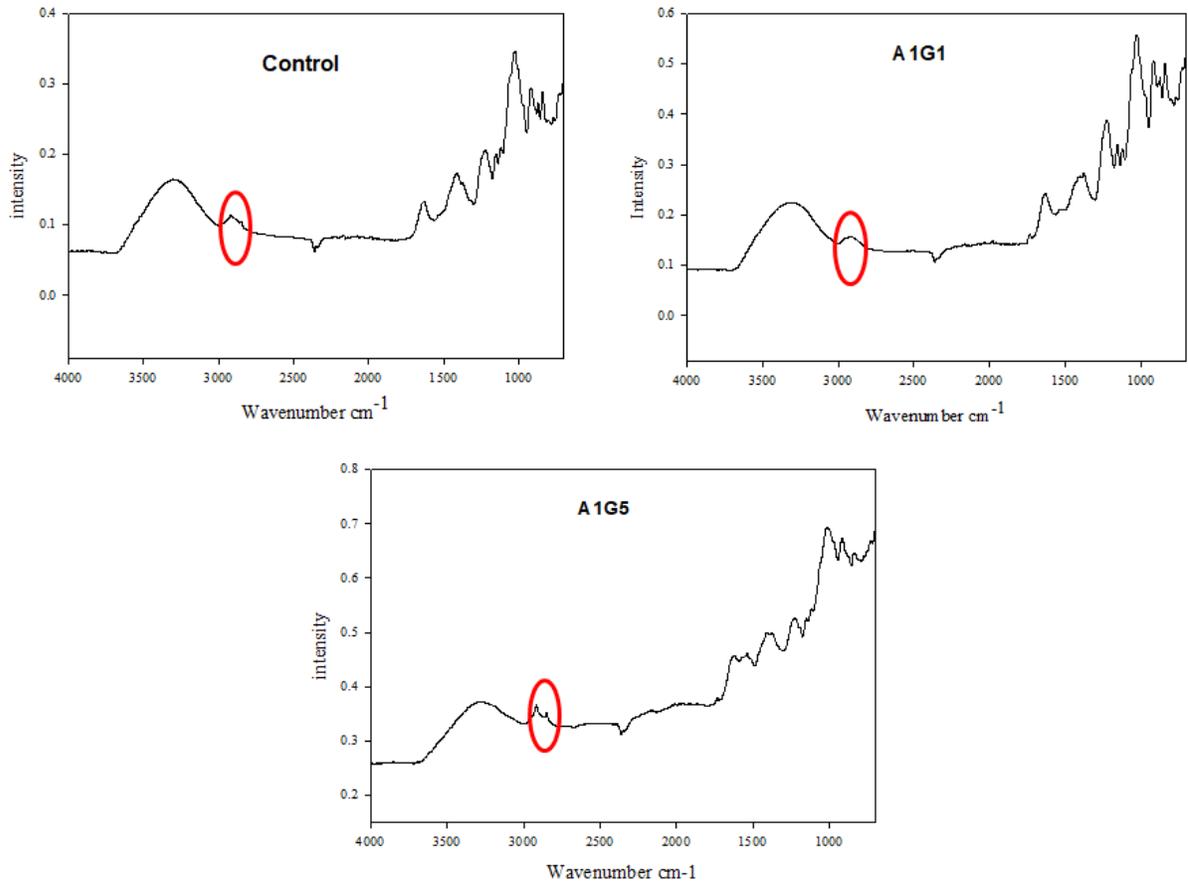
## FTIR Study

The FTIR spectra of control and AGC sheets was measured in the range of  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$  and are given as Fig 6 (a-c). The characteristic bands corresponds to different functional groups were identified. In case of control the characteristic IR peaks were observed at  $3497\text{ cm}^{-1}$  (-OH stretching) and  $1024.85\text{ cm}^{-1}$  (glycosidic bonding). The spectrum also shows that and  $918\text{ cm}^{-1}$  (vibration of C-O-C bridge of 3,6-anhydro-l-galactopyranose). The smaller peak at  $2917.48\text{ cm}^{-1}$  shows the C-H stretch.

In the proceeding spectra of agar AGC (A1G1 and A1G4) sheets the characteristic absorption peak of agar at  $3497\text{ cm}^{-1}$  (-OH stretching) was shifted to  $3301.62\text{ cm}^{-1}$  which confirms interaction between agar and graphite. The peak at  $871$  corresponds 3, 6-anhydro- $\beta$ -galactose skeletal bending in agar. All the peaks clearly illustrates that the graphite particles are present in the agar matrix. The decrease in intensities of the peaks were observed as an increase in the amount of graphite in the AGC composite which confirm the interaction between agar and graphite (Mahmoud Nasef et al., 2011). Similarly, compared an evident sharpness of C-H peak at  $2900\text{ cm}^{-1}$  can be seen in case of A1G1 and A1G4 which is possibly due to the incorporated graphite.

The FTIR spectrum of control film (agar) is shown in the Figure 6. The absorption band around  $3301\text{ cm}^{-1}$  is related with O-H stretching while the peak  $2917\text{ cm}^{-1}$  is attributed to methoxyl groups. The band at around  $1633\text{ cm}^{-1}$  is due to the stretching vibrations of the conjugated peptide bond formed by amine (NH) and acetone (CO) groups. The peak at  $1372\text{ cm}^{-1}$  is assigned to ester sulfate group which is usually not shown in the general chemical structure of agar, their presence can be because of their method of extraction of agar and due to variation in

agar species. The bands at  $1016\text{ cm}^{-1}$  and  $917\text{ cm}^{-1}$  are associated with the 3,6-anhydro-galactose bridges.



**Fig. 6.** FTIR spectra of control (only agar) (b) A1G1C and (c) A1G4C.

## Conclusion

In the present study, thermally and mechanically strong AGC were fabricated by simple thermo-physico-mechanical method. Thermal treatment of the synthesized composite sheets showed the thermal stability up to  $180^{\circ}\text{C}$ , suggesting that the developed composite sheets are much more stable than the controlled film of agar alone with small thermal stability range. The successful incorporation of graphite into the agar matrix was confirmed through the applications of various characterizing techniques such as SEM, FTIR and XRD. Swelling Ratio and WHC showed that increase in the graphite content brought hydrophobic character to the synthesized composite sheets.

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