The influence of graphite on conductivity, crystallinity and tensile properties of hydroxyethyl cellulose (hec) / graphite composite films

Mohd Pisal Mohd Hanif1,*, Abd. Jalil Jalilah1,2,*, Farah Badrul1 and Syed Mahamud Syarifah Nuraqmar1

1School of Materials Engineering, Universiti Malaysia Perlis (UniMAP), Kompleks Taman Muhibbah, Jejawi 2, 02600 Arau Perlis, Malaysia.
2Centre of Excellence Frontier Materials Research, Universiti Malaysia Perlis (UniMAP), Jalan Kangar - Alor Setar, Kampung Seriab, 01000 Kangar, Perlis, Malaysia.

Abstract. Conductive films based on natural polymers may find potential in food packaging and biomedical applications owing to their advantages of biodegradability and biocompatibility. This work demonstrated conductive composite films from hydroxyethyl cellulose (HEC) incorporated with graphite prepared by solution casting. Fourier Transform Infrared (FTIR) spectra confirmed the absence of covalent bond between the HEC matrix and graphite. The electrical conductivity of the composite films with various concentrations of graphite was investigated by a four-point probe. We observed that the conductivity of the HEC film increased remarkably from $10^{-8}$ S/cm to $10^{-5}$ S/cm upon addition of graphite. The highest conductivity of $9.44 \times 10^{-5}$ S/cm was obtained for the film with 30 wt% of filler and further addition of filler reduced the conductivity. The correlation between conductivity and crystallinity was elucidated by X-ray diffraction (XRD) patterns. The difference in $d$-spacing values between HEC and HEC/Graphite films and the decrement of crystallinity percentage suggest that the rearrangement of ordered HEC crystalline structure was perturbed by the filler resulting in reduction of crystallinity phase. The tensile properties results clearly show that the incorporation of graphite into HEC films has reduced the tensile strength which is in agreement with the obtained electrical conductivity and crystallinity percentage.

1 Introduction

The development of conductive polymer composites (CPCs) based on natural polymers has generated considerable interest due to their advantages of renewability resources, biocompatibility and environmentally friendly. CPCs from non-conjugated polymers are made conductive by the incorporation of conductive fillers such as carbon black, carbon fibre and metallic particles [1]. With the advent of biosimilars in biomedical engineering, the

* Corresponding author: 1hanifpisal@unimap.edu.my  2jalilahjalil@unimap.edu.my
biopolymers are becoming an attractive alternative to replace the conventional thermoplastics that have limitation in biocompatibility. Conductive biopolymer composites may find importance in electrically induced drug delivery system, electrode coatings for neural sensing and stimulation, biosensors and etc. [2]. Besides that, conductive biopolymers may also be utilized as antistatic used in packaging films, containers and PET bottles to reduce attraction of dust [3].

Among natural polymers, cellulose is the most abundant and has excellent properties including flexibility and high mechanical strength [4]. Because of its lightweight and high thermal stability and also for being inexpensive, cellulose has also been a potential material for flexible sensors and electronic device applications [5]. Fortunato et al. [6] studied surface modification of a new flexible substrate based on hydroxypropyl cellulose for optoelectronic applications. Recently, carbon-based materials such as graphite, carbon nanotube, carbon fiber, and graphene that have high conductivity are mostly applied in the applications of lightweight and high-performance composite materials. Kim et al. [7] claimed that graphite is good as conductive filler for film because it has good thermal resistance besides its excellent electrical conductivity.

In this present work, we prepared conductive composite films from hydroxyethyl cellulose (HEC) incorporated with graphite as conductive filler by solution casting. The films were characterized by Fourier transform infrared (FTIR) spectroscopy. Electrical conductivity measurement for the composite films was carried out by four-point probe method at various graphite concentrations. The relationship between crystallinity and conductivity was elucidated by the crystallinity percentage obtained from X-ray diffraction (XRD) patterns. The influence of graphite on mechanical properties of the composite films was also investigated.

2 Experimental

2.1 Materials

HEC (cellulose ether = 92 %) was purchased from Merck KGaA (Darmstadt, Germany), graphite (carbon content = 80-98.5 %; particle size = 63 μm or 250 microns), glycerol was supplied by HmbG Chemicals.

2.2 Samples Preparation

2 g of HEC was dissolved in 100 ml of distilled water. 20 wt% of glycerol was added as plasticizer followed by the addition of graphite powder. The mixture was stirred until homogeneous under magnetic stirring at room temperature for about 3 hours. Then, the solution mixture was cast into a glass mould and allowed to dry in oven for 6 hours at 50-60 °C. Thin films of 1 mm were obtained when the water evaporated. The amount of graphite was varied from 15-35 wt%. The formulations of HEC film and HEC/Graphite composite films with different loading of graphite are shown in Table 1.

Table 1. Formulations of HEC film and HEC/Graphite composite films with different loading of graphite.

| Film Code            | HEC (wt%) | Glycerol (wt%) | Graphite (wt%) |
|----------------------|-----------|----------------|----------------|
| HEC Film             | 100       | 20             | -              |
| HEC/Graphite Composite Films | 100       | 20             | 15, 20, 25, 30, 35 |
2.3 Measurements

**FTIR Analysis** Attenuated total reflectance (ATR-FTIR) spectra were recorded using Perkin Elmer Spectrum 400 FTIR with the wavenumber range of 650 – 4000 cm\(^{-1}\).

**Conductivity** Conductivity measurement was carried out at room temperature by standard four-point probe method, using a Keithley Model 4200 Semiconductor Characterization System interfaced with a computer for automatic data collection. The samples were measured with voltage varied from 5 V to 10 V. The electrical resistivity \( \rho \) was determined using Equation 1,

\[
\rho = R \left( \frac{w \times t}{l} \right)
\]

where; \( t \) is the sample thickness, \( R \) is the measured four-point resistance, \( w \) is the width of the sample and \( l \) is the length of the sample. The electrical conductivity \( \sigma \) was obtained by using Equation 2,

\[
\sigma = \frac{1}{\rho}
\]

**Crystallinity** X-ray diffraction (XRD) patterns were performed on a Bruker, D2 Phaser XRD Analyzer equipped with a monochromic CuK\( \alpha \) (\( \lambda = 1.5418 \) Å) radiation. The data were collected at scan rate of 0.1°/min over an angular range from 10° to 60° 2\( \theta \) in a continuous mode. The basal spacing (\( d \)) of the films was calculated based on crystal orientation ratio and the Bragg’s Law formula as given in Equation 3 and 4,

\[
I = \frac{I_2}{I_1}
\]

where \( I \) is the crystal orientation ratio of the crystal planes, \( I_2 \) is the intensity peak number 2, and \( I_1 \) is the intensity peak number 1.

\[
n \lambda = 2d \sin \theta
\]

where \( n \) is the distance between atoms, \( \lambda \) is the wavelength of the incident radiation, and \( \theta \) is the incidence angle.

**Mechanical Properties** Tensile tests were carried out using Instron Universal Testing Machine Model 5569 based on ASTM D882 method to determine the tensile strength, percentage elongation at break and modulus of elasticity of the films. The crosshead speed was set at 5 mm/min. The measurements were replicated at least three times for each type of film.

3 Results and Discussion

**Characterisation by FTIR Spectroscopy** From the spectra of pure HEC shown in Fig. 1 (a), the strong and broad bands that correspond to hydroxyl group in the pyranose unit and C-O-C skeletal vibration appeared at 3334 and 1042 cm\(^{-1}\) [8,9], respectively. The band at 2886 cm\(^{-1}\) belongs to the C-H stretching due to the presence of the CH and CH\(_2\) groups [10]. The absorption peak at 1643 cm\(^{-1}\) can be assigned to the bending mode of naturally absorbed water [8,9] and the peak at 1357 cm\(^{-1}\) is attributed to the O-H bending [8]. For the spectra of HEC film filled with graphite Fig. 1(b), the broad O-H stretching peak slightly shifted to 3341 cm\(^{-1}\) and broadened whereas the C-O-C band shifted to 1039 cm\(^{-1}\). Other peaks were also slightly shifted and there was no any new peaks appeared. This indicates the absence of covalent or strong bond between graphite and the HEC matrix but the incorporation of graphite has somehow altered the environment of the composite films.
Conductivity
The electrical conductivity calculated from the obtained resistivity is plotted in Fig. 2. Pure HEC was obviously insulative with the conductivity of $9.12 \times 10^{-8}$ S/cm. From the graph, it is clearly seen that the conductivity increased two-order magnitude to $2.44 \times 10^{-6}$ S/cm with the incorporation of graphite starting from 15 wt%. The value amplified at 30 wt% to $9.44 \times 10^{-5}$ S/cm. Almost the same value was demonstrated by Hajar et al. from graphite filled polyethylene oxide/polyvinyl chloride polymer film at 25 wt% of graphite content [11]. However, further addition of graphite gave lower values. At lower graphite content, the composite film was dominated by the HEC matrix resulting in low electron mobility due to the absence of conductive interconnected network in the film. The interconnected network was built up as the amount of graphite reached the percolation threshold at 15 wt%. However, the amount of graphite reached saturation at 30 wt% and hence, the conductivity reduced above the saturation point.

X-Ray Diffractogram (XRD)
Fig. 3 represents the XRD patterns of (a) pure HEC film and (b) HEC/graphite composite film with 30 wt% of graphite. The diffraction pattern of pure HEC film exhibits diffraction peaks at $2\theta= 23.2^\circ$, $34.8^\circ$ and $48.5^\circ$. The strong and sharp peak at $2\theta= 23.2^\circ$ depicts the semi-crystalline nature of HEC as reported by Gupta and Varshney [12]. For the XRD pattern of HEC/Graphite-30 film, a high intensity peak around $26.7^\circ$ corresponding to the graphitic structure (002) [13] appeared in between the first and second peak of pure HEC. The shape of the HEC peaks remained unchanged but the intensity was slightly reduced. This explains that there was no strong interaction between the matrix and the filler but suggests that the ordered structure of HEC was slightly perturbed. The calculated $d$-spacing values and crystallinity percentage for pure HEC and HEC/Graphite-30 composite film are shown in Table 2. The change in $d$-spacing value when graphite is incorporated into HEC suggesting a rearrangement occurred in the composite film. Suppiah et al. [14] reported a reduction in $d$-spacing when halloysite nanotube (HNT) filler was increased in carboxymethyl cellulose (CMC). The decrement in crystallinity percentage
shows that the crystallinity reduced by the addition of graphite. The results also confirmed that the graphite filler was insoluble in the matrix.

### Table 2. Crystal orientation ratio, interparticle spacing and crystallinity percentage (%) of HEC film and HEC/Graphite-30 composite film.

| Composite code      | Intensity (counts) | Interparticle spacing, d (nm) | Crystallinity percentage (%) |
|---------------------|-------------------|-------------------------------|------------------------------|
| HEC                 | 13,164            | 606                          | 0.05                         | 4.15                          | 66.8                          |
| HEC/Graphite-30     | 9,424             | 4,747                         | 0.50                         | 3.15                          | 64.7                          |

**Tensile Properties** The tensile properties of the pure HEC and HEC/Graphite films are displayed in Fig 4. It can be seen that the tensile strength of the films were very much affected by the addition of graphite Fig. 4(a). Pure HEC shows tensile strength at around 6 MPa and the value decreased into half upon addition of graphite at 15 wt%. The tensile strength values gradually decreased with the increasing amount of graphite up to 35 wt%. This could be due to the interruption caused by graphite particles on the intermolecular interactions, namely, hydrogen bonding between the polymer chains in the HEC. The excellent mechanical strength in cellulose is attributed to the 3D structure formed by hydrogen bonding between cellulose chains [4]. As demonstrated by the FTIR spectra, there was no evident of covalent bonding formed between HEC and graphite. For the elongation at break as shown in Fig. 4(b), the value increased from 33% to 47% in the presence of graphite at 15 wt%. However, the flexibility of the films filled with graphite reduced with the increment of graphite loading. This is because of the graphite characteristic which has high stiffness with high aspect ratio as compared to HEC matrix [15]. Nonetheless, the modulus of elasticity increased as the amount of graphite was increased. Among the five varied concentrations, the highest tensile modulus was seen for the film with 35 wt% of graphite. The correlation of modulus and crystallinity was not seen probably because the distribution may not be homogeneous as graphite content increases.
4 Conclusions

We have successfully prepared free-standing films of HEC incorporated with graphite powder by solution casting. Strong interaction was not evident between the HEC matrix and graphite as there was no trace of new peak appeared nor any peaks significantly distorted in the FTIR profiles. The conductivity increased three-fold from $10^{-8}$ S/cm to $10^{-5}$ S/cm upon addition of graphite and optimized at 30 wt% of graphite content. The highest conductivity obtained was $9.44 \times 10^{-5}$ S/cm. From the XRD results, we conclude that the incorporation of graphite has slightly altered the arrangement of highly-ordered crystalline structures of the HEC resulting in reduction of the crystallinity which promotes conductivity. The addition of graphite considerably affected the mechanical properties probably because the strong intermolecular interactions in the HEC matrix were destroyed by the graphite filler. Lower in tensile strength upon addition of graphite is associated with reduced crystallinity as proven by the XRD results. This research provides an environment friendly method to prepare conductive composite films. The selection of filler may boost the conductivity and may find applications that crucially require biocompatibility.

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