



Assessment of Mechanical, Water Barrier and Anti-Microbial Properties of Paper Sheets Loaded with Hyperbranched Polyester/Graphene Oxide Composite and Effect of Flaxseed-Gel Coatings



Amal H. Abdel Kader^a, Magda A. Samahy^b, Maysa E. Mohram^c, Mona H. Abdel Rehim^{b*}

^a Cellulose and Paper Department, Chemical Industries Institute, National Research Centre, Giza, Egypt

^b Packing and Packaging Materials Department, Chemical Industries Institute, National Research Centre, Giza, Egypt

^c Departments of Microbial Chemistry, Genetic Engineering and Biotechnology Division, National Research Centre, 33 El-Bohouth St. (formerly El-Tahrir St.), Dokki, P.O. 12622, Giza, Egypt.

Abstract

Hyperbranched polyester/graphene oxide (PES/GO) is prepared by in-situ polymerization technique to ensure complete homogeneity of GO in the formed composite. Chemical structure of the composite is studied using FTIR and its thermal stability is investigated by TGA. The prepared composite is used as active filler for cellulosic paper through additions of different ratios during sheets-making. Physical and mechanical properties beside thermal stability of the paper sheets have been examined. The results showed that both density and thermal stability of loaded paper are increased while porosity is decreased significantly with increasing amount of filler. However, the paper sheets demonstrated very low water permeability when loaded with 20% PES/GO. Paper sheets dipped for 1 min. in flaxseed gel showed improved water vapour permeability compared with uncoated sheets. Moreover, the loaded sheets acquired significant antibacterial activity against different microorganisms. This property is declined upon coating with flaxseed gel but still higher than blank sheets.

Key words: Hyperbranched polyester- Graphene oxide- Paper sheets- Mechanical properties- Water absorption- Antimicrobial activity- Flaxseed gel

Introduction

Hyperbranched polymers (HbP) belong to dendritic macromolecules characterized by their polydispersity, high number of terminal end groups and low solution viscosity compared to their structural analogs. [1-3] Moreover, their 3D spatial form offers them spheroidal structure with degree of branching less than 1. [1] They found applications in many fields such as drug delivery, dye encapsulation and coatings. [4-6] Hyperbranched polymers are synthesized by one-pot approach but with several methodologies among them self polycondensation, proton transfer polymerization and ring opening polymerization techniques. [7,8] Nanocomposites based on HbP are considered as growing field from research and industrial points of views. The fundamental techniques for their preparation varied between sol-gel processes, in-situ polymerization, melt or solution mixing. [9,10] Combination of HbP and nanomaterials yields materials of versatile properties. These nanocomposites with their novel properties can find

applications in many technological fields. For example, TiO₂ nanowires coated with hyperbranched polyester have showed photocatalytic activity and exhibited high potential for water treatment for several runs. [11] The study demonstrated that TiO₂ nanowires coated with hyperbranched polyester are of high potential for water treatment for several runs. This result was attributed to the strong adhesion between the nanowires and the polymer through formation of 2D structure. Preparation of proton exchange membranes for fuel cells using hyperbranched polyester/ sodium titanate nanowires is described by Ghanem et al. [12] lately; hyperbranched polyester is used as capping and reducing agent for the formation of Ag nanoparticles. The formed nanocomposite is used as active material in polyether sulphone matrix as antimicrobial membrane. [13]

Graphene oxide (GO), which is made by oxidizing graphite with strong acids, has a layered structure similar to graphite and nanoclays, but the plane of carbon atoms in GO is heavily decorated with

*Corresponding author e-mail: monaabdrehim23@gmail.com; (Mona H. Abdel Rehim).

Receive Date: 07 July 2021, Revise Date: 13 September 2021, Accept Date: 20 September 2021

DOI: 10.21608/EJCHEM.2021.84381.4132

©2021 National Information and Documentation Center (NIDOC)

oxygen-containing groups, which not only increases the interlayer distance but also makes the atomic-thick layers hydrophilic. [14,15] As a result, GO has great mechanical properties as well as great aqueous solution dispersibility making it suitable for use as a nanofiller in papermaking. Decoration of reduced GO with hyperbranched polyester is described as a route to increase dispersion of the filler in polycaprolactone matrix. [16] The obtained modified films of polycaprolactone showed improved water and gas barrier properties beside antimicrobial activity.

Cellulosic paper has widely and traditionally been utilized in packaging for long time. It is suitable for packing food, glass, precious products and electronic devices, especially for its non-toxic, light, inexpensive and cushioning properties. Compared with plastic materials, cellulosic paper is sustainable, biodegradable and eco-friendly, but its low mechanical and gas barrier properties cannot meet the needs of some perishable foods, prescription medicines or precise instruments. [17,18] Filling pulp with filler during papermaking process is a simple and frequent procedure. Many polymeric films, including polyethylene [19], poly (vinyl alcohol) [20], and regenerated cellulose films [21-23], have been employed to strengthen the barrier properties of impermeable layered and plate-like organic nanoclays. [24] Moreover, improving water vapor permeability of paper sheets besides adding antimicrobial resistance to the formed paper would increase food shelf life and decrease susceptibility of packed staff to microbial attack. It is worth to mention that antimicrobial paper sheets is prepared by several techniques such as coating of paper with chitosan [25], adding silver nanoparticles [26] or oxides of semiconductors during formation of paper. [27]

Commercial brown flaxseed was shown to have 41% fat, 20% protein, 28% total dietary fiber, 7.7% moisture, and 3.4 percent ash. [28] Flaxseed is high in alpha-linolenic acid and bioactive chemicals, among other nutrients. It has been categorized as a functional or bioactive food. [29] Flaxseed gum (FG) is a type of soluble dietary fiber found in the flaxseed husk. [30] When compared to identical solutions made from gum Arabic, guar gum, or xanthan gum at the same concentration, flax gum yields solutions with a larger foam capacity and greater foam stability.

This work presents synthesis of hyperbranched polyester/graphene oxide by in-situ polycondensation reaction. The obtained composite is used as filler for paper sheets that added in different ratios during paper making. The effect of the filler on water vapor permeability and mechanical properties of the formed sheets compared to blank or papers sheets loaded with GO alone is demonstrated. Antimicrobial resistance of the loaded paper sheets against different

microorganisms is investigated. Moreover, paper sheets have been coated with gel extracted from flaxseed by dipping method. The physical, mechanical and water barrier properties of the coated sheets is also investigated and compared with the uncoated paper.

2. Experimental part

2.1. Materials

Graphite (GPH) powder (99.9%) was provided by Fisher Scientific UK. Potassium permanganate (>99%), sulfuric acid (99%) and hydrogen peroxide (30%) were bought from Bio Basic Canada Inc. Tetrahydrofuran was obtained from Fluka. 1,2,4-Benzentricarboxylic anhydride and 1,3- butanediol were supplied by Merck. Chemicals were used without further purification. Bleached kraft bagasse pulp (BBP), delivered by Edfo Paper Mill (Upper Egypt) was used in this work. Flaxseed was purchased from Egyptian market.

2.2 Techniques

Thermal stability of GO, PES/GO and modified paper sheets was studied using a Perkin Elmer thermogravimetric analyzer (TGA), with a heating rang from room temperature to 500°C and heating rate of 10°C/min under N₂ atmosphere. Infrared spectroscopy of the specimen was recorded in the frequency range 4000 to 500 cm⁻¹ by using KBr disc technique using JASCO FT/IR3006 (Fourier Transform Spectrometer). Structural analysis of GO and PES /GO is done by collecting the spectra of the prepared samples at laser wavelength 532 nm and laser power 0.10 MW at 25°C Raman Spectroscopy, Bruker Optics, Rudolf-Plank-Str. 2776275 Ettlingen (Germany). Surface morphology of prepared samples was investigated via Scanning Electron Micrographs (SEM) from JOEL, all samples were coated with gold and the beam energy was 20 KV. Imaging of PES/GO has been carried out using a transmission electron microscope, (JEM-1230; JEOL Ltd., Tokyo, Japan), under acceleration voltage 80 kV. Electronic model of the caliper is used to measure thickness of paper sheet.

2.3 Synthesis of hyperbranched polyester/ graphene oxide composite (HPES/GO)

Graphene oxide was prepared according to Hummer method described elsewhere. [31] Graphene oxide (0.3 g) is dispersed in 50 mL THF, then 24 g of 1,2,4-Benzentricarboxylic anhydride dissolved in another 62.5 g THF and added to the dispersed GO. After stirring for 1 hour 13.15 g of butanediol was added and the reaction proceeded at temperature 70°C for 5 hours then, under vacuum using rotary evaporator to remove water for another 5 hours. A grey paste was formed that is dried under vacuum in oven at 80°C.

2.4 Paper sheets formation and testing

Bleached bagasse pulp (BBP) was beaten to 40 SR using Valley beater according to the Swedish Standard

Method (SCA). Hand sheets of basis weight were around 70 g/m² were made according to the SCAN standard method. [32] The hand paper sheets were formed. Different ratios (2, 5, 10, 15, and 20% by weight) of the hyperbranched polyester/graphene oxide (PES/GO) were added to (BBP). Graphene oxide (GO) (2% GO by weight) was added to BBP in another trial for comparison with HPES/GO. The mixture was disintegrated through electrostatic interaction with stirring velocity around 300 rpm for 5 minutes to ensure homogenous distribution of HPES/GO and BBP fibers. The paper sheets were conditioned at 50 % RH for 48 h before testing.

2.5 Coating of modified paper samples

In another trial, paper sheets of (2, 5% HPES/GO) were prepared according to the SCAN standard method, [32] after that coated for (1min) by 100 ml of 10% flaxseed gel which was extracted by stirring 10g in 100 ml distilled water on a hot plate /magnetic stirrer for 10 min at 80°C then cooled and used). [33] After coating, the paper sheets were pressed between two filter paper sheets to remove the excess gel and then dried on the drum at 105°C for 2 h before testing. Some of coated sheets immersed in water for (1 day) to show the effect of water on the strength. The paper sheets after pressing between two filter paper sheets to remove the excess water were dried to complete the strength test.

2.6 Investigation of physical and mechanical properties of prepared samples

- Thickness measurement

The bending stiffness of a paper sheet is primarily determined by its thickness, and an even thickness profile is ideal in converting processes. The average of three conditioned sheets of blank and modified paper is used to calculate the thickness according to standard ISO 534. [35] Basis weight (grammage) is measured in the metric system. It is the number of grams per square meter of paper (g/m²) (Eq. 1), ISO 536. [36]

Basis weight = Weight of paper sheet (g) / Area of paper sheet (m²) (1)

- Water Vapor Permeability (WVP)

(WVP) was measured in keeping with the ASTM E96 standard method. [36] It was performed by sealing a paper to an open mouth of a test cup containing (CaCl₂ anhydrous) and placing the assembly into a controlled environmental desiccators containing super saturated solution of NaCl at 75% ± 2% relative humidity (RH) and 25°C. The water vapor absorbed by CaCl₂ was detected by weighing the CaCl₂ containing cup periodically at different periods of time, for every measurement, a minimum of three replications were made. WVP was calculated as in (Eq. 2):

$$WVP = WVTR * x / A * \Delta P_v \quad (2)$$

Where WVTR is the water vapor transmission rate (g/h), x is the paper thickness (m), A is the transfer area of the exposed paper surface (m²), ΔP_v is partial pressure difference in kPa, respectively.

- Water absorption

The water absorption was measured using Cobb test according to standard test (ASTM D3285-93(2005)). Typically, a rectangular specimen was used to measure water absorption which was oven-dried for 24 hours at 60°C to achieve a constant weight (M₀), and then submerged in water until saturated using an average of four strips. The specimens were then regularly removed from the water, dried with absorbent paper, and weighed. The weight gain percentage at any time t (M_t) was determined by using (Eq. 3).

$$M_t = M_1 - M_0 / M_0 * 100 \quad \% \quad (3)$$

Where M₀ is the dry initial weight, M₁ is the weight after immersion in water.

- Tensile strength

Tensile strength testing was carried out using a universal testing machine (LR10K; Lloyd Instruments, Fareham, UK) with a 100-N load cell at a constant crosshead speed of 2.5 mm/m, according to TAPPI T494. [37] Strips of 20 cm long and 15 mm width were used in the test and the span was 10 cm.

- Density and porosity

The relationship between paper thickness and grammage is clarified by paper bulk densities; the dimension refers to the volume or compactness of the paper, and the correct meaning is the reciprocal value of density. The density of the paper (ρ_m) was obtained, then the porosity (ε) of the paper was calculated using equation (4) where (ρ_{cellulose}) is the density of the cellulose (1.5 g cm⁻³). [39]

$$\epsilon (\%) = (1 - (\rho_m / \rho_{cellulose}) \times 100) \quad (4)$$

2.7 Studying of biological activity

The antimicrobial activities were carried via measuring the reduction of the optical density (OD) at λ= 600 nm. The method is as follows: The bacterial and yeast cultures maintained on nutrient agar slants were aseptically inoculated into 5 ml of sterile nutrient broth. The samples were thoroughly shaken and then incubated at 30°C for 24h. This was designated as the working stock that was used for antimicrobial studies. 5 ml of nutrient broth medium were taken in different test tubes and autoclaved. Each tube was inoculated with 50 μl of the microbial suspension and 100 μl of the tested specimen then incubated at 30°C for 24 h.

The growth of the selected bacteria and yeast was detected by optical density (OD) at $\lambda = 600$ nm. The antimicrobial activity of the tested compounds were examined with gram positive bacteria, *Staphylococcus aureus* ATCC 6538, and gram negative bacteria *Escherichia coli* NRRN 3008, and yeast pathogen *Candida albicans* EMCC105. The obtained results are compared with the reference antibiotic Cephadrine that was purchased from Egyptian markets.

3. Results and discussion

3.1. Synthesis of HPES/GO

Preparation of the HPES/GO has been carried out by in-situ polymerization technique. The first step includes thorough dispersion of GO in Benzene tricarboxylic anhydride followed by addition of butandiol to start the polycondensation reaction as depicted in (Figure 1-A). The characteristic feature of HbP's is the presence of large number of terminal groups. In our polymer, these terminals are carboxylic and hydroxyl groups which can bond electrostatically with GO nanosheets. However, these bonds results in enhanced dispersion of the sheets in the polymer matrix yielding a very homogenous composite. (Figure 1-B)

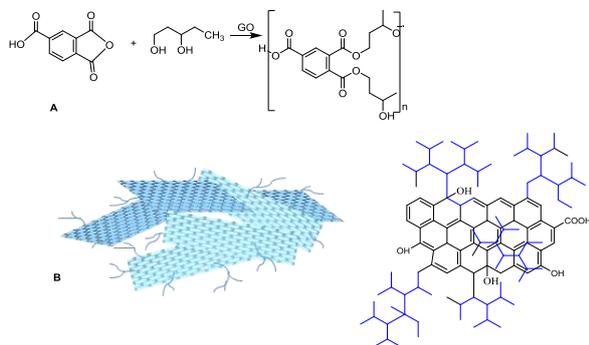


Figure 1: (A) Chemical reaction for synthesis of PES, (B) PES/GO.

The grey coloured-composite (PES/GO) compared to the pure GO and polymer (PES), are characterized by Raman spectroscopy and the spectra are shown in figure 2 (1 and 2). Figure (2-1) depicts the characteristic Raman bands of GO which are G-band at 1582 cm^{-1} corresponding to first order in-plane vibrational mode in Raman and the two bands -2D (2969 cm^{-1}) and D (1349 cm^{-1}).^[31] The intensity ratio between G and D band reflects the quality of the obtained GO. In our case the ratio is near to one which reflects high quality GO. However, the intensity ratio between G and D band for sample PES/Go (figure 2-2) is reduced to about one third indicating the formed

disorder due to presence of PES chains between the GO layers. The shape of the PES/GO can be visualized in the TEM image (figure 2-3) that showed wrinkled GO layers. Also, the image depicted the partial exfoliated structure of GO due to in-situ polymerization process.

Structural analysis of PES/GO composite using FTIR is shown in Figure 2.4. Characteristic bands of PES can be noticed at 3400 cm^{-1} for OH stretching, 2927 cm^{-1} corresponding to aliphatic C-H. The band appeared at 1713 cm^{-1} is due to C=O group while that at 1623 cm^{-1} corresponds to C=C bond showed presence of broad band at $2500\text{--}3400\text{ cm}^{-1}$ corresponding to OH stretching of carboxylic acid and this broadening is a result of presence of water molecules and hydrogen bonding. The carbonyl of ester group can be observed as broad band at $\approx 1730\text{--}1689\text{ cm}^{-1}$ due to presence of ester groups in different environments related to HPES and those near GO sheets. Moreover, this band is overlapped with the band of C=C group which appears as small shoulder at 1611 cm^{-1} . The FTIR spectrum of pure GO is depicted as inset in which the band of C=O and C=C groups can be found at 1780 and 1660 cm^{-1} respectively.

Thermal stability of PES/GO is studied by TGA technique and the obtained thermogram demonstrated in Figure 3 showed that there is no much change in the thermal stability of PES due to inclusion of Go nanosheets. Clearly, only one degradation step started at 300°C at which the polymer or the composite lost about 35% of their initial weights. However, complete decomposition of the materials could be observed at 358°C for the polymer and 366°C for PES/GO.

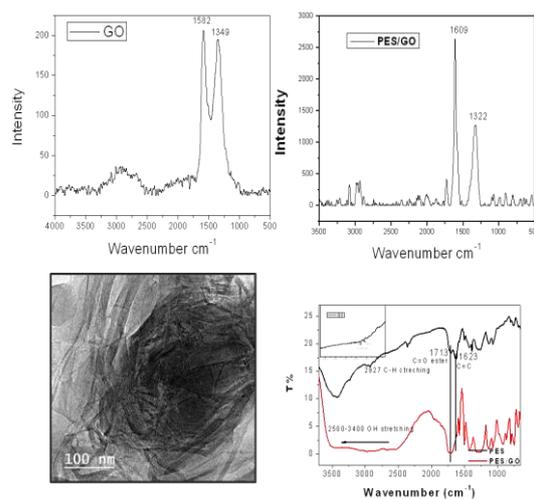


Figure 2: Raman spectra of GO and PES/GO are shown in figures 2.1 and 2.2. TEM image of PES/GO figure 2.3 and 2.4. FTIR spectra of GO (inset), PES and PES/GO.

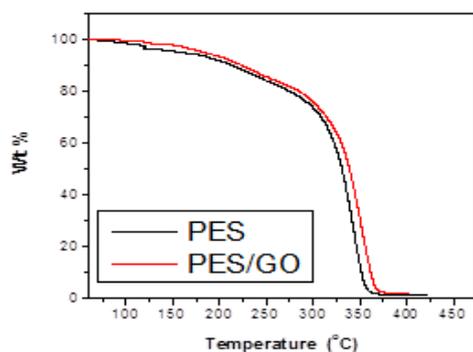


Figure 3: Thermal gravimetric analysis of PES and PES/GO.

3.2. Modification of paper sheets

Thermal stability of modified paper (TGA)

(TGA) is a technique for examining the thermal decomposition of polymers and the kinetic parameters of thermal decomposition, such as activation energy and reaction order, which can aid in understanding polymer thermal stability. It gives powerful tools for studying the behaviour of cellulose materials during thermal degradation, as well as the mass loss of the samples under investigation. Figure (4) describes the decomposition curves of paper sheets treated with (2, 10%, and 20% PES/GO). When lignocellulosic fibers are subjected to TGA, an initial weight loss (10%) is observed between 25 and 150°C due to moisture evaporation.^[39-41] The thermal depolymerization of hemicellulose and the breakdown of the glycosidic linkages of cellulose cause the second weight loss of fiber to occur between 256 and 353°C.^[39, 42] Then, between 353 and 500°C, cellulose begins to decompose. The decomposition temperature of the blank BBP sample was (256°C), which was slightly lower than that of the PES/GO, GO (289°C), i.e. a low decomposition temperature. At the third stage (353–550 °C), loaded paper starts to decompose at 384 °C.^[43] This increase in the decomposition temperature of cellulose' fibers may be attributed to the presence of PES/GO. This result can be attributed to the existence of OH end groups in the PES backbone similar to cellulosic structure that increases hydrogen bonding between the filler and cellulosic fibers and consequently led to higher thermal stability of the loaded paper.

-Thickness of formed paper sheets

The system of thickness measurement can be used on single sheets as well as a stack of multiple sheets. It was found that the average thickness for all specimens of the modified paper sheets loaded with PES/GO in the range of 0.115 and 0.251 mm.^[44, 45]

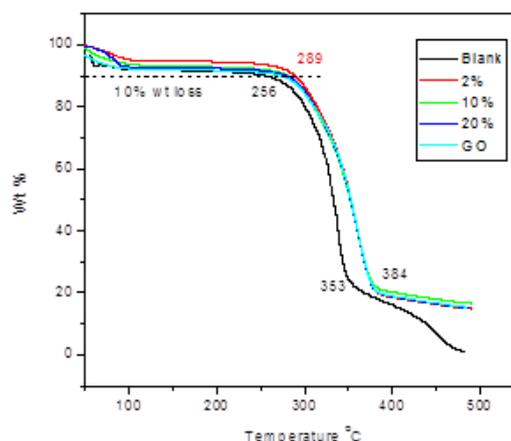


Figure 4: TGA thermogram of modified paper sheets compared with the blank.

- Morphology of modified paper

Morphology of sheets either blank or loaded is studied by SEM and the images are shown in figure 5. The blank sheet showed clear entangled 2D cellulosic fibers with smooth edges and there is no difference between blank sheet illustrated in figure 5a and that loaded with 2% pure GO shown in Figure 5c. However, GO particles can be seen clearly on the surface of latter sheet in the form of small and large aggregates unlike the clean surface of blank paper sheet. (Figures 5b and 5d) Huang e al., described preparation of paper sheets loaded with different amounts of GO up to 16% in presence of polyacrylamide.^[46] The role of the polymer is coating of cellulosic fibers and trapping of the negatively charged GO nanosheets in the pores of coated fibers. However, paper sheet loaded with 10% PES/GO revealed smooth and clear surface with no invoice surface colouring. (Figure 5f) But deep looking in the fibers' shape one can notice that the fibers have got a more protruding form due to the dense coating layer of PES/GO on their surface through hydrogen bonding. (Figure 5).

-Mechanical properties of loaded and paper sheets compared with paper coated with gel.

The ability of paper to resist breaking under stress is measured by tensile strength, which is considered the most fundamental property of packaging materials. The degree to which the fibres are bonded to each other and their distribution within the sheet determine the paper's strength. The formation of hydrogen bonds between fibres is the first step, and the strength of these bonds is determined by the fibre contact area and intrinsic strength per unit area. The addition of modified graphene oxide (2-20% PES/GO) to paper sheets reduces the paper's strength slightly as shown in table (1), see Figure (6).

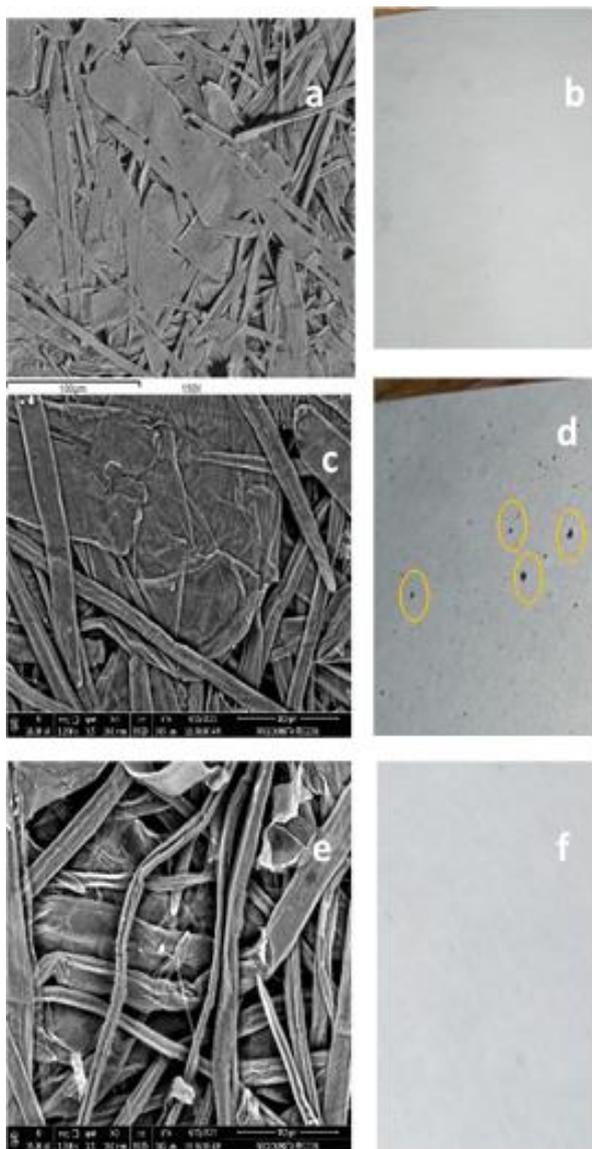


Figure 5: SEM images of paper sheets, (a) blank, loaded with 2% GO (c) and loaded with 10% PES/GO (e). Photos b, d and f are surface imaging for the same samples.

This decrease in strength may be because the addition of additives will interfere with fiber-to-fiber bonding due to additive matrices' weak bonding abilities. While in case of coated samples of (2 and 5% PES/GO/gel) there is a large decrease in the mechanical strength. (Figure 7) The loss in tensile strength of coated paper sheets is due to coating materials being impregnated into the cellulose structure of the paper, interfering with fiber-to-fiber interaction, resulting in a reduced interaction force between the fibers of coated papers, and hence a reduction in tensile strength.^[47] Moreover, table (1) shows that there is observed increase in the density of paper sheets after the addition of fillers from (2%-20%), also the porosity of paper sheets is highly

decreased. This can be attributed to the effect of the loaded filler since (PES/GO) converts porous paper with low density to paper with less porosity and higher density. It tends to open distances between fibers that are tightly bonded and occupies the pores between fibers, so density increased and porosity decreased.^[47] From the results, the difference in porosity (%) shows a pronounced decrease in the porosity of paper sheets with increasing the PES/GO content, that the reduction in porosity of the 20% PES/GO paper by about 22.4% compared to the blank. Moreover, the increase in the paper densities reflects that there is an increase in the weight of paper sheets after addition of fillers. As seen in the previous table, there is an increase in the weight percentage of the samples due to water absorption after the immersion of modified paper sheets in water for 24hs compared with the blank. However, coating of modified paper with a layer of flaxseed gel led to notable decrease of water absorption for samples 2% and 5% PES/GO/flaxseed gel that gave water absorption percentage of 165 and 148 respectively. This result confirms formation of a thick layer of the gel that closed the paper pores and hindered water absorption to a large extent.

- Investigation of water vapour permeability

Figure 8 shows the water vapour permeability (WVP) of paper sheets made from BBP and BBP fibres containing various amounts of PES/GO. WVP of paper sheets at atmospheric pressure is determined by the paper sheet's hydrophilic properties as well as its porosity.^[48] Paper sheets made from BBP fibres had lower WVP than those made from 2% GO and 2-10% PES/GO, as shown in the figures. This indicated that the stronger bonding in the case of BBP fibers produced more compact structure, which affected the permeation of water vapour more than their higher hydrophilic and porous nature as compared to 2% GO. This sample demonstrated increase in WVP more than three times due to low interaction between GO and fibers since both of them carry negative charges.^[49]

However, samples loaded with ratios 2-20% PES/GO showed decreased porosity as illustrated in table 1, the value of WVP also lowered significantly by increasing amount of PES/GO. Which means that PES/GO composite firstly coated the fibers then filled the pores between the cellulosic fibers forming a more compact structure leading to WVP value one third that of blank paper.

Paper sheets were coated with flaxseed gel by immersing in the extract for 1 min then in water for one day. Surprisingly, the coated sheets showed noticeable decrease in WVP value which can be attributed to the presence of dense layer of gel formed

on the paper surface which hindered mobility of water vapour. (Figure 9)

Table (1): Physical and mechanical properties of modified paper sheets.

Samples	Density (Kg/m ³)	*Difference in Porosity (%)	**Increase in weight %	Tensile Strength (kN/m)
blank	610.6± 3	---	215	40.14±3.8
2% GO	624.6 ± 2.5	1.59	201	41.39±2.9
2% PES/GO	658.7±7	5.4	221	38.09±1.5
5% PES/GO	692.6±4	9.2	230	35.97±4.4
10 % PES/GO	730.9±4	13.5	218	35.24±4.5
15% PES/GO	750.7±2	15.8	247	32.49±5.6
20% PES/GO	809.8±3	22.4	219	33.57±2.4
blank / flaxseed gel	615.6±2	0.57	162	26.06±0.9
2% PES/GO/ flaxseed gel	619.9±1	1.1	---	34.19±1.3
2% PES/GO/ flaxseed gel (1d H ₂ O)	624.9±3	1.6	165	28.33±2.9
5% PES/GO/ flaxseed gel	632.9±3	2.5	---	35.72±1.5
5% PES/GO/ flaxseed gel (1d H ₂ O)	640.3±4	3.4	148	24.15±1.3

*The values are related to the porosity % of the blank sheet.

** Increase in weight (%) due to water absorption after immersion in water for 24 hour.

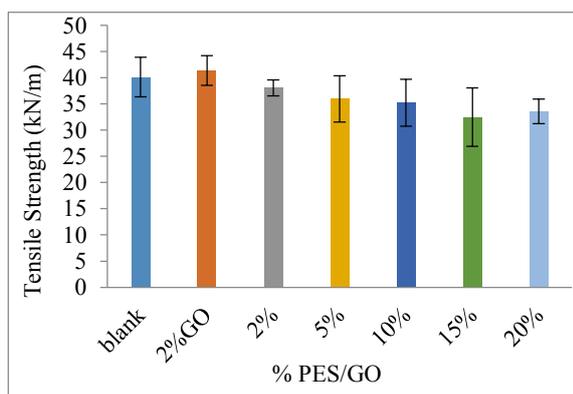


Figure 6: Tensile strength of paper sheets made from BBP loaded with PES/GO.

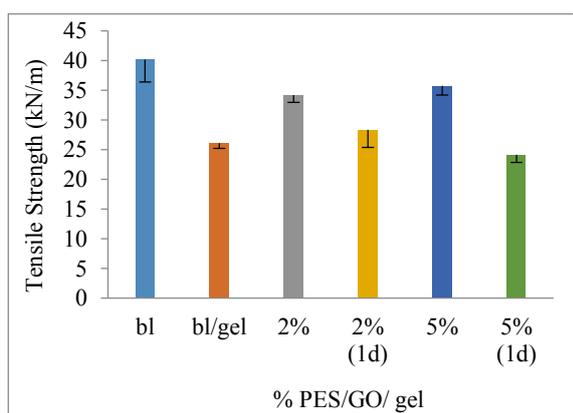


Figure 7: Tensile strength of paper sheets made from BBP loaded with PES/GO, coated with flax gel and immersed in water for 1day.

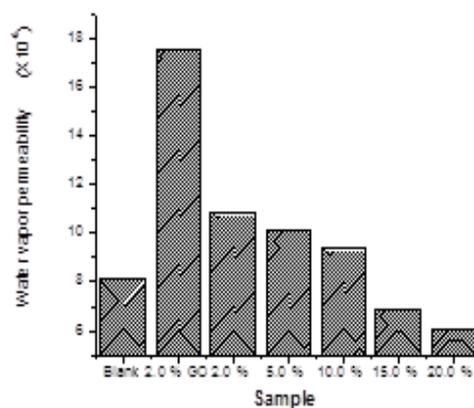


Figure 8: Water vapour permeability of loaded paper sheets compared with the blank one.

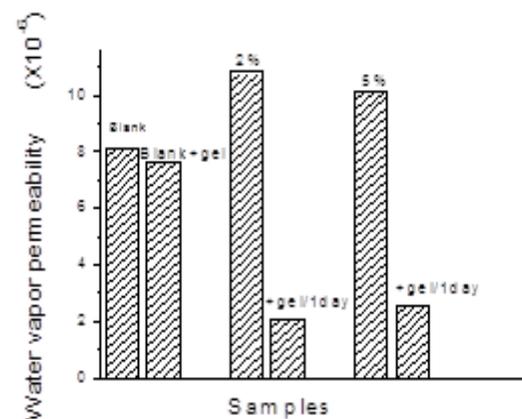


Figure (9): Comparison of water vapour permeability for uncoated and coated loaded paper.

-Antimicrobial activity

Antimicrobial behaviour of both uncoated and coated loaded paper sheets has been investigated. Firstly, the uncoated paper sheets showed high microbial resistance as can be observed in table (2). The antimicrobial activity increased by increasing amount of PES/GO in the sheet compared also to the value obtained by the reference antibiotic. This result can be attributed to the fact that PES has plenty of OH terminal groups and phenyl rings which interact electrostatically with GO sheets causing enhancement in the interaction between GO sheet and bacteria and consequently facilitates trapping of bacteria and rupture of bacterial membrane by cutting edges of GO. [16, 50] It can be also noted that the antimicrobial activity against *Staphylococcus aureus* is lower than

Escherichia coli and yeast. Investigation of antimicrobial activity of coated paper has been performed and the results showed that the coating layer decreased antimicrobial resistance of paper against different microorganisms including *Candida albicans*, so that only two samples were studied (2 and 5% PES/GO). (Table 3) Overall, the results demonstrated superior antimicrobial activity against the gram negative bacteria *E.coli*, the pathogen yeast *Candida albicans* and gram positive bacteria *Staphylococcus aureus* compared to the reference antibiotic. Yet, *Staphylococcus aureus* can be strongly inhibited by the paper sheets upon loading by 20% PES/GO which makes this sample is highly promising and can serve as active food packaging.

Table (2): Antimicrobial activity of modified paper sheets.

Optical Density at 600 nm							
Microorganism	Gram stain	Blank	5%	10%	15%	20%	Reference antibiotic
<i>Staphylococcus aureus</i>	Positive	0.90	0.29	0.24	0.21	0.07	0.19
<i>Escherichia coli</i>	Negative	0.57	0.09	0.12	0.17	0.12	0.25
<i>Candida albicans</i>	Yeast	0.81	0.07	0.08	0.10	0.08	0.15

Table (3): Antimicrobial activity of sheets coated by gel.

Microorganism	Gram Stain	Growth	2% PES/GO + gel	5%PES/GO +gel	Ref. Antibiotic
<i>Staphylococcus aureus</i>	Positive	0.90	0.33	0.40	0.19
<i>Escherichia coli</i>	Negative	0.57	0.44	0.29	0.25
<i>Candida albicans</i>	Yeast	0.81	0.22	0.20	0.15

Conclusion

Hyperbranched polyester/graphene oxide nanocomposites have been prepared by in-situ polymerization technique. Characterization of the GO using Raman spectroscopy confirmed successful synthesis of the material while confirming of structure of the formed nanocomposite was carried out using Raman, TEM, FTIR and its thermal stability is studied by thermal gravimetric analysis. The nanocomposite is used as filler to paper sheets by adding different ratios during paper making. Addition of 2% of pure GO to paper sheet showed inhomogeneous distribution of the filler in the sheet while mixing up to 20% of PES/GO with cellulosic material yielded sheets with no aggregates. This is because of the hyperbranched polymer contains hydroxyl end functionalities as those found on the cellulosic chains. Investigation of mechanical properties of the obtained sheets showed

that the filler particles (PES/GO) transformed porous paper with low density to paper with less porosity and higher density in addition to slight reduction in the paper's strength. On the other hand, paper sheet loaded with 20% PES/GO demonstrated the lowest water vapour permeability compared with the unloaded paper. Paper samples contains 2 or 5% of the filler depicted. Although coating of paper sheets with flaxseed gel obviously decreased their mechanical properties but lowered water vapour permeability to about one third of the uncoated sheet loaded with the same amount of filler. Antimicrobial testing of the coated and uncoated loaded paper showed that loaded sheets acquired antimicrobial resistance against different pathogens. Additionally, coated paper exhibited limited antimicrobial activity compared to uncoated one but still better than blank paper.

References:

1. J. Frechet, and D. Tomalia, Dendrimers and other Dendritic Polymers, John Wiley & Sons Ltd, 2001.
2. G.R. Newkome, Moorefield, C.N. and F. Vogtle, Dendritic Molecules: Concepts. Synthesis. Perspectives, VCH Publishers, 1996.
3. M.K. Mishra, and S. Kobayashi, (Eds) Star and Hyperbranched Polymers, Marcel Dekker, 1999.

4. C. Gao, Y. Xu, D. Yan, and W. Chen, *Biomacromolecules*, 2003, 4, 704.
5. C. Liu, C. Gao, and D. Yan, *Macromolecules*, 2006, 39, 8102.
6. B. Voit, *J. Polym. Sci. Part A: Polym. Chem.*, 2000, 38, 2505.
7. K.C. Cheng, Y.Y. Su, T.H. Chuang, W. Guo, W. F. Su, *Macromolecules*, 2010, 43, 8965.
8. D. amou, K. Twibanire, T.B. Grindley, *Polyester dendrimers Polymers (Basel)* 2012, 4, 794.
9. M.S. Belgaonkar, B. Kandasubramanian, *Eur. Polym. J.* 2021, 147, 110301.
10. Mona H. Abdel Rehim, Ahmad A. Yousef, Hisham A. Essawy, *Mater. Chem. and Physc.* 2009, 119, 546.
11. A.F. Ghanem, A.A. Badawy, N. Ismail, Z. Rayn Tian, M.H. Abdel Rehim, A. Rabia, *Applied Catalysis A: General, Applied Catalysis A: General* 2014, 472 191.
12. A.F. Ghanem, A. El-Gendi, M.H. Abdel Rehim and K.M. El-Khatib, *RSC Adv.*, 2016, 6, 32245.
13. A. El-Gendi, A.F Ghanem, Mohamed A. Yassin, Mona H Abdel Rehim, *RSC Adv.* 2020, 10, 24169.
14. W. Cai, R.D. Piner, F.J. Stadermann, S. Park, M.A. Shaibat, Y. Ishii, D. Yang, A. Velamakanni, S.J. An, M. Stoller, J. An, D. Chen, R.S. Ruoff, *Science*, 2008, 321, 1815.
15. Lerf, A., He, H.Y., Forster, M., Klinowski, J., 1998. Structure of graphite oxiderevisited. *J. Phys. Chem. B* 102, 4477.
16. A.F. Ghanem, M.A. Yassin, A.M. Rabie, F. Gouanvé, E. Espuche & Mona H. Abdel Rehim, *J. Mater. Sci.* 2021, issue 1, DOI: 10.1007/s10853-020-05329-4
17. R.J. Hernandez, S.E. Selke, J.D. Culter, J. Culter, 2000. *Plastics Packaging: Properties, Processing, Applications, and Regulations*. Hanser, Munich.
18. J. Lange, Y. Wyser, Recent innovations in barrier technologies for plastic packaging- a review. *Packag. Technol. Sci.* 2003, 16, 149.
19. A. Durmus, M. Woo, A. Kasgoz, C.W. Macosko, M. Tsapatsis, *Eur. Polym. J.* 2007, 43, 3737.
20. K.E. Strawhecker, E. Manias, *Chem. Mater.* 2000, 12, 2943.
21. M. Farmahini- Farahani, A.H. Bedane, Y. Pan, H. Xiao, M. Eic, F. Chibante, *Cellulose* 2015, 22, 3941.
22. T.T.T. Ho, T., Zimmermann, S. Ohr, W.R. Caseri, *ACS Appl. Mater. Interfaces* 2012, 4, 4832.
23. Q.L. Yang, C.N. Wu, T. Saito, A. Isogai, *Carbohydr. Polym.* 2014, 100, 179.
24. H.D. Huang, C.Y. Liu, D. Li, Y.H. Chen, G.J. Zhong, Z.M. Li, *J. Mater. Chem. A*, 2014, 2, 15853.
25. M.A. El-Samahy, Salah A.A. Mohamed, Mona H. Abdel Rehim, Maysa E. Mohram, *Carbohydr. Polym.* 2017, 168, 212.
26. E. Amini, M. Azadfallah, M. Layeghi, R. Talaei-Hassanloui, *Cellulose*, 2016, 23, 557.
27. S. Baruah, M. Jaisai, R. Imani, M.M. Nazhad, J. Dutta, *Sci. Technol. Adv. Mater.*, 2010, 11, 055002.
28. D.H. Morris, *Flax: A Health and Nutrition Primer*, 3rd ed.; Flax Council of Canada: Winnipeg, MB, Canada, 2003; p. 11.
29. Y.Y. Shim, B. Gui, P.G. Arnison, Y. Wang, M.J.T. Reaney, *Trends Food Sci. Technol.* 2014, 38, 5.
30. J. Liu, Y.Y. Shim, T.J. Tse, Y. Wang, M.J.T. Reaney, *Trends Food Sci. Technol.* 2018, 75, 146.
31. Ahmed F. Ghanem and Mona H. Abdel Rehim, *Biomedicines*, 2018, 6 (2) 63.
32. SCAN CM-64, 2000. Forming sheets for testing physical properties of pulp.
33. Y. B. Tee, J. Wong, M. C. Tan, and R. A. Talib, *Edible film from flax mucilage*, *Bio Resources* , 2016, 11(4), 10286.
34. ISO 536 (E): Paper and board-Determination of grammage, 2012.
35. EN ISO 13934-1: Determination of maximum force and elongation at maximum force using the strip method, 2013.
36. ASTM 1989. Standard test methods for water vapor transmission of materials. E 96-80. In *Annual Book of ASTM Standards*, Vol. 15. American Society for Testing and Materials, Philadelphia, PA, USA, pp. 745-54.
37. Tappi standard, 2006 T494. Om-06, Tensile properties of paper and paperboard (using constant rate of elongation apparatus).
38. S. Tanpichai, W.W. Sampson, S.J. Eichhorn, *Compos Pt A: Appl. Sci. Manuf.* 2012, 43(7):1145.
39. A. Karakoti, S. Biswas, J.R. Aseer, N. Sindhu, M.R. Sanjay, *J. Nat. Fibers* 2018, 1.
40. P. Khawas, S.C. Deka, *Carbohydr. Polym.* 2016, 137, 608.
41. W.A. Laftah, W.A.W. Abdul Rahaman, *J. Mater. Res. Technol.* 2015, 4(3):254.
42. D. Das, M. Mukherjee, A.K. Pal, A.K. Ghosh, *Fiber Polym.* 2017, 18(11), 2225.
43. J.J. Chew, M. Soh, J. Sunarso, S.T. Yong, V. Doshi, S. Bhattacharya, *J. Energy Inst.* 2020, 93 (2), 711.
44. C. Fellers, and B. Norman, 1998: *Pappers teknik. Avdelningen för Pappersoch Massateknik, Kungliga Tekniska Högskolan, Stockholm, Sweden.*
45. O. Schultz-Eklund, C. Fellers, P-Å. Johansson, *International Paper Physics Conference*, 22-26 Sept, Kona, Hawaii, USA, Book 2, 1991, pp. 511.

46. Q. Huang, M. Xua, R. Suna, X. Wang, *Ind. Crops Prod.* 2016, 85, 198.
47. R. Bown, *Paper Technology.* 1998, 39, 44.
48. N.M. Ahmed, H.T.M. Abdel-Fatah, E.A. Youssef, *Prog. Org. Coat.* 2012, 73, 76.
49. S. Tanpichai, W.W. Sampson, S.J. Eichhorn, *Compos Pt A: Appl. Sci. Manuf.* 2012, 43(7):1145.
50. X. Zou, L. Zhang, Z. Wang, Y. Luo, *J. Am. chem. Soc.* 2016, 138(7), 2064.