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**Evaluation of the Functionality of Nanographene Oxide
for Food Packaging Applications**

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Evaluation of the Functionality of Nanographene Oxide for Food Packaging Applications

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Al-Quds University
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Dedication

At the end of my research, I would like to dedicate it firstly to my beloved land "Palestine". As well as to Al-Quds University; University of Creativity and Excellence and Hebron University; my first incubator at the Bachelor's level.

Also I dedicate it to my supervisor Dr. Ibrahim Afaneh and co-supervisor Dr. Sami Makharza who provided me a continuous support whenever I was in need. I will never forget to dedicate this achievement to Mrs. Maryam Faroun; the researcher at Nano lab who did not hesitate a moment to help me.

To my beloved husband who, whatever I said, I will not be able to thank him, my husband who was my first fan to go in this way and did not hesitate for a moment for giving me a financial and moral support.

My little child, Hassan, who is bearing my absence, one a day he will grow up and be proud of his mother and forgive me for negligence towards him.

Mom, Dad and all my family who gave me a bigger support and always encouraging me to complete my education.

My second family, my husband's family and particularly my mother in law who supported me in various ways.

My best friends Fatima Ghnemate , Fatima Hamida, Hayat Atawneh and all my friends.

To all people in my life who love me and remember me.

I dedicate my research.

Declaration

I certify that this thesis submitted for the degree of master, is the result of my own research, except where otherwise acknowledged, and this thesis has not been submitted for the higher degree to any other university or institution.

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Signed:

Date:

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Abstract:

Graphene oxide (GO) produced by oxidation reduction reaction (Hummers' method). GO was used to be incorporated in polyvinyl alcohol (PVA) and methyl cellulose (MC) to study the thermal properties, mechanical properties, as well as the swelling and solubility tests.

Different concentrations of PVA (5,10, and 15%) with different concentrations of GO (0.05, 0.1, 0.25 and 0.5%) were used to prepare PVA/GO nanocomposite by simple casting method. A 2% of MC with different concentrations of GO (0.01, 0.025, 0.05, 0.125 and 0.25%) were used to prepare MC/GO nanocomposite by simple casting method as well.

Thermal properties were studied by using Differential Scanning Calorimetry (DSC), the results show that the thermal properties enhanced and improved by incorporation of GO to PVA matrix. The glass transition temperature (T_g) was increased from 79.6 of neat PVA to 86.6 °C at 0.5% GO. Degradation temperature was also increased from 231.5 °C and reached to 242.7 at 0.5% GO. The crystallinity temperature was increased to a certain extent.

The tensile strength was increased at 15% PVA as GO content increased to 0.25%, but the elongation decreased. At 10% PVA, the elongation increased as the GO content increased.

The swelling of 5 and 15% PVA reduced by adding GO nanoparticles which explains the barrier properties of GO in the molecular level of polymer matrix. However the solubility increased at 5% with increasing GO contents but decreased rapidly at 15% PVA with increasing GO contents.

FT-IR spectra of PVA/GO nanocomposites confirm the strong hydrogen bonding between polymer and nanoparticles.

Briefly, the incorporation of GO into PVA polymer matrix improves the thermal, mechanical and barrier properties of polymer due to strong hydrogen interaction between polymer and GO particles.

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LIST OF ABBREVIATIONS

LDPE	Low density polyethylene
HDPE	High density polyethylene
LLDPE	Linear low density polyethylene
VLDPE	Very low density polyethylene
OPP	Oriented polypropylene
PET	Polyethylene terephthalate
MJ	Mega joule
PP	Polypropylene
PE	Polyethylene
PVC	Polyvinylchloride
PA	Polyamide
PS	Polystyrene
PHB	Polyhydroxybutyrate
PVA	Polyvinyl alcohol
MC	Methyl cellulose
GPa	Gega pascal
BCG	Boston Consulting Group
USD	United States dollar
NNI	National Nanotechnology Initiative
PNC	Polymer nanocomposite
MAP	Modified atmosphere packaging
BHT	Butylated hydroxytoluene
BHA	Butylated hydroxyanisol
EOs	Essential oils
BCE	Before the Common Era
SiO ₂	Silicon dioxide
CNT	Carbon nanotube
2D	Two dimensional
TiO ₂	Titanium dioxide
GRAS	Generally recognized as safe
IFST	Institute of food science and technology
FDA	Food and drug administration
TEM	Transmission electron microscope
SEM	Scanning electron microscope
AFM	Atomic force microscope
XRD	X-ray diffraction
UV-Vis	Ultra violet visible light
ICP-MS	Inductively coupled plasma mass spectrometry
Ppm	Part per million
AAS	Atomic absorbtion spectrometry
STA	Thermal analysis instrument
TGA	Thermogravimetric analysis
r GO	Reduced graphene oxide
PLA	Polylactic acid
PEI	Polyethyleneimine
EVOH	Ethylene vinyl alcohol
Tg	Glass transition temperature
TPa	Tera pascal

PAMPS	Poly-2-acrylamido-2- methyl- propanesulfonic acide
PLGA	Poly (D,L- lactide-co-glycolide)
WAXS	wide-angle X-ray scattering
FESEM	Field emission scanning electron microscope
T _m	Melting temperature
T _c	Crystallization temperature
T _d	Degradation temperature
ΔH _m	Melting enthalpy
R&D	Research and development

Chapter One: Introduction

Food, is all substances that people eat for body growth, providing energy, and sustains life. It contains essential nutrients as carbohydrate, fat, protein, vitamins and minerals. Food exposed progressive deterioration may be very slow or so rapid depending to type of food. Food divided into three categories according to the rate of changes occur during storage: perishable, semi perishable, and nonperishable or shelf stable (Goyena, 2019). The deterioration affects nutritional value, sensory evaluation, safety and aesthetic appeal. In ancient time, food was produced and consumed locally without need to packaging. But later, the need to contain, transport and protect the food became very important and packaging is potentially an important way to deliver these requirements. Hence, the packaging innovations began.

1.1 The Need for Packaging: History

In 1800s, Primitive man used containers made from natural materials as grasses, leaves, wood, bamboo, gourds, clay pots and animal skins. The Industrial Revolution brought and developed many new materials. Metal cans are an example of these materials; it was developed by Nicholas Appert to preserve food for French Emperor Napoleon Bonaparte army. Appert used glass bottles with cork that replaced with metal cans due to fragile nature of glass. In the early 1800s, paperboard was used to manufacturing folding cartons and then in 1850s, corrugated shipping boxes that used to hold smaller packages were developed. Plastics including cellulose nitrate, styrene, and vinyl chloride were discovered in the 1800s but used in the 20th century (Risch, 2009).

In 1892s, William Painter obtained a patent of crown cork, which is a metal cap with a layer of cork inside, it provides a good seal against ingress of oxygen. This invention played a significant role in the development of beverage industry. By developing of plastic and

synthetic material, they have replaced a cork that provides tighter seal. Now the line in the crown have oxygen- absorbing ability to remove oxygen from headspace (Risch, 2009).

The first individually packaged product was a Biscuits packaged and were first sold in the 1890s. At first it was packed in open large barrels and people pick up and put it in a paper bag. But the needed to protect the product from moisture and light helped to developed individual package with an inner liner to provide that protection (Risch, 2009)

After world II, the focus in food packaging was on food quality. The major improvement was occurring for plastics. The most widely used plastic is a polyethylene with their types which include low-density (LDPE), high-density (HDPE), linear low-density (LLDPE), and very low density (VLDPE). Low-density polyethylene (LDPE) was the first to be developed by Imperial Chemical Industries in 1933 (Risch, 2009).

Professor Giulio Natta discovered Isotactic polypropylene in 1954, this film was produced by casting the material and stretching at the same direction of machine and then at opposite direction to give oriented polypropylene (OPP). This method produces more stiffness and more moisture vapor barrier films that used as an overwrap for snack food.

In 1957, plastic sandwich bag was introduced, and by 1966 plastic bags made from LDPE was used to package 25% of bread sold. In 1964, Hercules developed co-extrusion plastic films. These type of films made from two or more layers of different type of plastic in one step (Risch, 2009).

There are some improvement were made to materials that changed the deliver way of product to consumer. Metal cans, which have been used since the early 1800s, now become made from tin-plated steel. Also today aluminum cans are very widely used especially for carbonated beverage. The first aluminum cans were opened with a can opener, and then in 1963 the first ring pull was introduced, but this ring pulls were not attached to cans. In 1975 a stay tab was introduced which is a ring tab stays attached to the can (Risch, 2009).

In 1970, Pepsi introduced the concept of bottle, with a patent on the bottle issued in 1973. The bottle made from polyethylene terephthalate (PET). The challenges in using PET is that must not contaminated the product with component of PET, and must provide gas and flavor barrier. Today most of these bottles made either from multilayer material or have a coating to provide the barrier properties. (Risch, 2009) The development of packaging materials still continuing to this day in order to achieve the packaging functions.

1.2 Packaging Material Functions

Packaging materials have four primary tasks that make our lives easier: containment, convenience, protection and communication. Containment function of package facilitates moving the product from one place to another; also protect the environment from pollution due to product loss. Evolution and great changes in lifestyle created demand for more convenience product to be easy to hold, easy to open and so on. In addition, packaging material make it convenience for handling during transport as permitting primary packages to be assembled in secondary package, and secondary packages to be assembled in tertiary package and so on (Goyena, 2019).

The primary function of Packaging materials is protection the food from external environment as gases, odors, water, water vapor, dust, microorganisms, and compressive forces. But "Once the integrity of the package is breached, the product is no longer preserved" (Goyena, 2019). So the package must provide a suitable barrier around the food. Some microorganisms become active if the package permits the transfer of, for example, O₂ or humidity. On the other hand, packaging can conserve the energy which expended during production of the product. For example, total energy consumed to produce 1Kg of bread is 15.8MJ, and the energy consumed to produce polyethylene bag to package 1Kg of loaf bread is 1.4MJ. By eliminating the package might save 1.4MJ of energy but lead to bread spoilage

and loss of 15.8MJ of energy. But using the package means each unit of energy in the package can protect 11 unit of energy in the product (Goyena, 2019).

Most consumer make purchasing decisions depending on the clues providing by packaging, so packaging communicate with consumer about the food inside the package. There is old saying that “A package must protect what it sells and sell what it protects”(Goyena, 2019), this explain the concept of communication. Other attribute for packaging material: it must contain a minimal adverse environmental impact, and must not transport any adverse contaminates to the food (Goyena, 2019). These functions which performed by packaging regardless of the type of packaging materials, there are many materials used in food packaging.

1.3 Types of Packaging Material

Materials used in food packaging including metal, glass, plastic, paper and cartons(Goyena, 2019).

The FAO in 2014 stated that plastic is the second most used material in packaging, due to desired properties as lightness, softness, and transparency. Polymers which use in food packaging divided into two groups: synthetic polymer or petroleum based polymer as polyethylene terephthalate (PET), polypropylene (PP), polyethylene (PE), polyvinylchloride (PVC), polyamide (PA) and polystyrene (PS). The second group is a biopolymer which are biodegradable by enzymatic action of microorganisms. Biopolymer divided into three categories: (I) biopolymer produce from biomass as proteins such as soy protein isolate, wheat protein isolate, corn zein, wheat gluten, and gelatin, whereas carbohydrates include starch cellulose, chitosan, and agar.(II) synthetic biopolymer produce from bio-derived monomer as polylactic acid, polycaprolactone, and polyvinyl alcohol, or (III) Microbial polyester biopolymers include polyhydroxybutyrate (PHB) and carbohydrates include pullulan and curdlan (Talegaonkar, et al., 2017). Petroleum-based polymer are not

biodegradable, nonrenewable, and noncompostable. It also consumes 65% more energy and emits (30_80%) higher greenhouse gases than biopolymer (Mangaraj, et al., 2019). Therefore cause significant serious environmental issues worldwide. So drive the search for biodegradable polymer alternative to petroleum-based polymers. Although biodegradable polymers have poor mechanical and barrier properties when compared with synthetic polymers, but the incorporation of reinforcing components to polymer has recently proposed to improve the poor properties of biopolymers. According to global market data, using of biodegradable polymers in 2009 only 1%, but may reach 20% in 2020 (Abdullah, et al., 2017). Polyvinyl alcohol (PVA) and methylcellulose (MC) are polymers used in this study and will be discussed.

PVA is one of the most popular synthetic biopolymer used for packaging. It has been used in different field such as commercial, medical, industrial and food field as food packaging materials that are often in contact with food. It made from polyvinyl acetate through hydrolysis. It is thermoplastic, water soluble, odorless, harmless and nontoxic polymer. Also has acceptable thermal and mechanical properties (strength (1.6 ± 0.1 GPa), elastic modulus (48 ± 3 GPa), strain ($6.5\% \pm 1.4\%$), and toughness (40 ± 6 J.g⁻¹)), good processibility, biodegradability and compatibility. But its cost is high and has poor barrier properties. PVA is synthesized by saponification process from polyvinyl acetate. The solubility of PVA in water occurs at temperature above 80°C with a holding time of 30min. The hydrophilic nature of PVA depends on molecular weight, particle crystal structure and element dimension of distribution. Molecular weight of PVA vary from (20,000_400,000) depending on several factors as follow: (I) The rate of hydrolysis to eliminate acetate groups. (II) The medium of reaction if it is acidic or alkaline. (III) The length of initial polyvinyl acetate polymer. Therefore, Hydrogels of PVA exhibit swelling properties in water with ability to

retaining water within matrix without dissolving (Gaaz et al., 2015) and (Abdullah et al., 2017).

Chemical structure of PVA divided according to rate of hydrolysis into partial and fully hydrolyzed (Figure 1.1).

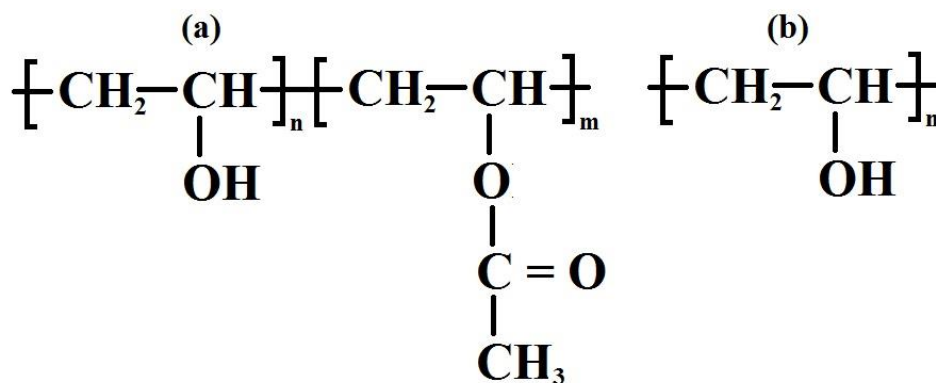


Fig 1.1 Chemical structure of PVA according to the rate of hydrolysis, a) Partially hydrolyzed PVA; b) Fully hydrolyzed PVA.

Methyl cellulose (MC) is cellulose-derived polymer used for polymers coating or films. Cellulose is a linear complex polymer composed of 3000 or more repeating glucose units. Cellulose derivatives formed by fully or partially reacting of three hydroxyl group present on the anhydrous unit with different reagents. Cellulose-derived polymer exhibit moderate flexibility, strength, transparency, and moderate barrier to oxygen as well as resistant to oils and fats, colorless, flavorless, and tasteless. Methyl cellulose formed when one or more of hydroxyl group are replaced with a methoxide group (-OCH₃) (Figure1.2) (Abdul Khalil et al., 2017), (Keshwani & Kharkwal, 2015)

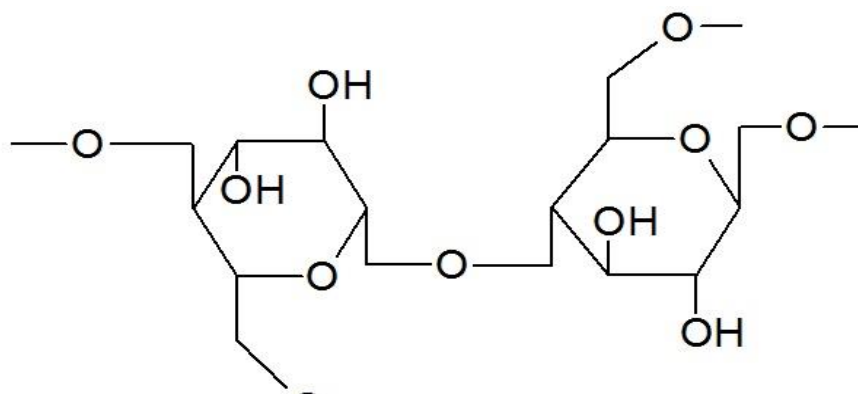


Fig 1.2: Chemical formula of methyl cellulose.

MC is soluble in cold water if the degree of substitution within the range 1.4 to 2. MC films are flexible, transparent, safe, tasteless with good oxygen barrier properties, relatively high tensile strength and young's modulus, but has poor water vapor properties (Keshwani & Kharkwal, 2015).

Each type of packaging materials has certain physical properties that make it suitable for certain type of food not for other. Food packaging material must have sufficient strength to withstand the external pressure during handling, or internal pressure that raise under the influence of temperature occurring within the product. Packaging materials also must be forms a barrier against external environment to agree with requirement of the packaging purpose. For example, if the product sensitive to O₂, the packaging material should be gas-tight. Metal and glass regarded as impermeable materials to gases, water vapors and odors, paper-based packaging materials regarded as permeable material and usually coated with plastic polymer to provide adequate barrier properties. But plastic-based packaging materials are providing varying degree of permeability depending in the nature of the polymer. In the past prior to the advent of nanotechnology, the problem was solved by using thin layer of metal on the top of the polymer, but this process prevent the consumer from see through the package in order to inspect the contents, and these problem affect more on the fresh product that the consumer prefer to see the product to make visual assessment on quality. Other

problem is a small size of oxygen and carbon dioxide that make using polymer without additives, to act as barrier, difficult. This problem affects the product that sensitive to oxidation. Because O_2 is smaller than CO_2 , it is more difficult to prevent oxygen diffusion through the package than keep carbon dioxide from diffusing out. For example, it is not possible to package the beer into PET bottle because these material cannot act as a barrier for oxygen diffusion (Kampers, 2011). In general polymers with good gas barrier often has bad water vapor barrier. For example, polyvinyl alcohol that contain hydroxyl group has good gas barrier but become less useful if it hydrated (Cruz, et al., 2018). These problems have created other problems that have led to heavy losses in the food-processing sector.

1.4 Food Waste and Loss

The amount of food wasted is shameful. Each year 30% of total food production is lost or go to waste, equivalent 1.6 billion ton of food worth \$1.2 trillion. BCG believes that food lost will reach 2.1 billion tons worth \$1.5 trillion in 2030. In addition to waste problem, world population increasing rapidly, we are now 7.5 billion and will reach close to ten in 2050. Only 6 from 7.5 billion people are feed, and there are 870 million people undernourished and get to beds hungry. The scale of the problem is terrible, BCG expect that from 2015 to 2030, the volume of food waste will rise 1.9% annually and the dollar value will rise 1.8% (Esben Hegnsholt, et al., 2018).

The solution requires great efforts from all relevant organizations and companies in addition to consumers and farmers. The most critical solution for this big problem is from companies that operate in food value chain. Food waste occurs at all steps of the value chain but it most clearly in the production and consumption steps. In developing countries, food loss and waste occur largely during production and transportation of food, but in developed countries it occurs largely in the consumption step , among retailers and consumers(Esben Hegnsholt, et al., 2018).

Among the problem that cause food waste and loss in bad packaging, products need packaging and about 99.8% of foods and beverages sold packed (Cruz et al., 2018). Therefore, it is important to conduct research and development of packaging materials to reduce the amount of food waste, thus the food packaging can reduce food by using innovative materials that guarantee safety, quality and developing in process. These innovative materials are active and smart packaging. Active and smart packaging differs from traditional packaging in the adoption of nanotechnology.

1.5 Nanomaterial in Food Science and food technology

Nanotechnology and nanosciences have the potential to impact many aspects of food and agricultural systems, such as efficient food production and security, fresh food, new tastes and flavors, food supplements, new tools for molecular and cellular biology, new materials for pathogen detection, and protection of the environment (Al-Naamani, et al., 2016; Choi et al., 2015; Fang, et al., 2017).

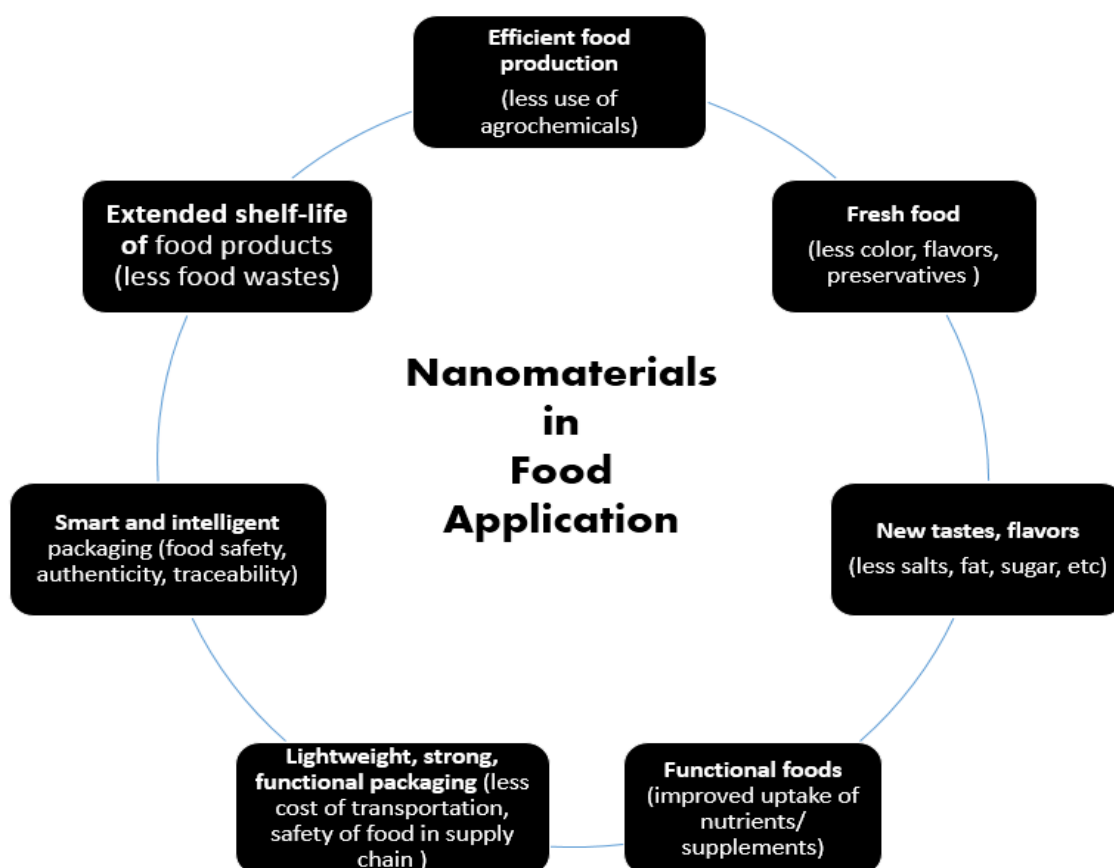


Fig 1.3 Applications of nanomaterials in food sector

Examples of nanotechnology as a tool in the food industry are:

- (I) Development a sensors for pathogen and contaminant detection.
- (II) A particular product and tracking of individual shipments by using specific devices and maintain an environmental records.
- (II) Hybridized systems that provide integration of sensing, localization, reporting, and remote control of food products (smart/intelligent systems) and that can increase efficacy and security of food processing and transportation.
- (III) Carry, protect, and deliver functional food ingredients to their specific site of action through development encapsulation and delivery systems. Nanodispersions and nanocapsules are the functional ingredients of drugs, vitamins, antimicrobials, antioxidants, flavorings, colorants, and preservatives.

Nanotechnology is directed for food applications by two different approaches as “bottom up” and “top down.” The top-down approach depends on a physical processing of the food materials, such as grinding and milling. For example, dry milling of wheat to obtain wheat flour of fine size that has a high water-binding capacity. The bottom-up approach in the food

industry deals with building and growing of larger structures from atoms and molecules, for example, organization of casein micelles or starch and protein folding (Cruz et al., 2018; Díez-Pascual, 2017; and Talegaonkar et al., 2017).

1.6 Nanomaterials in the Food Processing

Food processing is an action of performing a series of mechanical or chemical operations on food in order to change or preserve it. Food processing utilizes nanoparticles for improvement of foods quality, flow properties, flavor, color, and stability or to increase shelf life. Nanotechnology in Food and Food Processing Industry Worldwide predicted that nanofood market will surge from \$10 billion to \$30.4 billion in 2015, because hundreds of companies are conducting research and development on the use of nanotechnology to engineer, process, package, deliver food and nutrients to our shopping baskets and plates.

The global scale of nanofood is approximately 970 billion USD in 2010, and is expected to grow more than 1trillion USD in 2012. The food market for nanotechnology is anticipated to account for about 40% of the global food industry by 2015. At present the USA leads with a 4 years, 3.7 billion USD investment through its National Nanotechnology Initiative (NNI). The USA is followed by Japan and the European Union, which have both committed substantial funds (750 million and 1.2 billion, including individual country contributions, respectively per year). Others such as India, South Korea, Iran, and Thailand are also catching up with a focus on applications specific to the economic growth and needs of their countries (Abdullaeva, 2017).

Nanoencapsulation , nano emulsification and food packaging are the most important applications of using nanomaterials on food packaging.

1.6.1 Nanomaterials in Food Packaging

Packaging can help to slow down deterioration of food by physical, chemical, microbial deterioration, and loss of aroma while retaining the quality of product during shelf life.

Packaging must act as a gaseous barrier to prevent the exchange of moisture, carbon dioxide, oxygen, and aromatics compound.

Polymers, if used alone, have poor tensile, mechanical, and barrier properties, which are hinder to be successful packaging materials. Although traditional packaging providing the basic function of food containment, the consumers demand for packaging that is more

advanced and creative to deliver improved convenience, at the same time, improve sustainability, reduce waste and to fulfill the demands of the modern consumer.

By the advent of nanotechnologies, innovative applications in the area of packaging are being available and developed continuously. Active packaging and smart packaging are the result of innovating thinking in packaging. Figure 1.4 shows a photograph of active packaging and (table 1.1) shows examples of active and smart packaging.

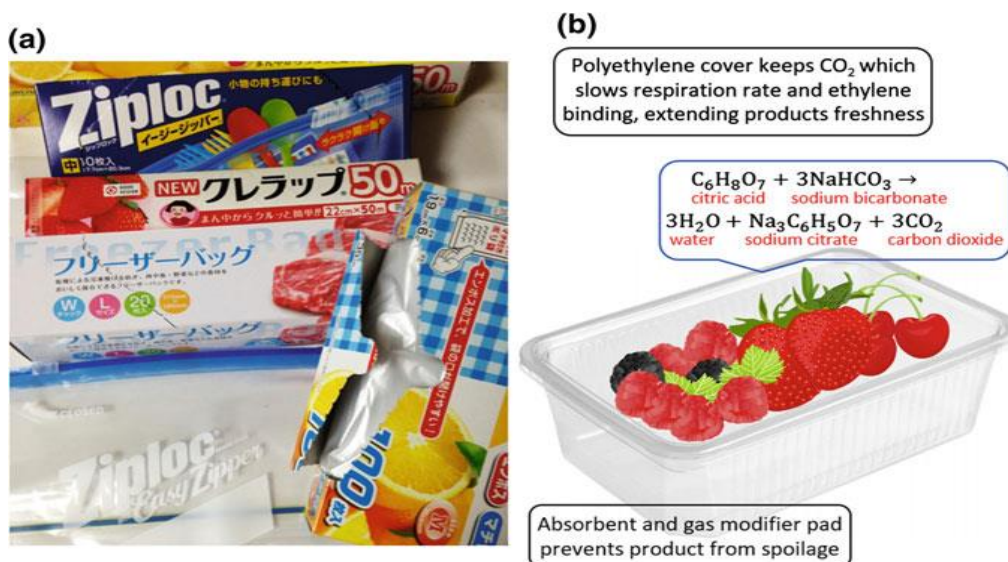


Fig. 1.4: a Photograph of various polyethylene wrapping and packages; b Illustration of the active packaging which extends shelf life of food product by protecting food from spoilage. Chemical reaction will occur inside the package between citric acid released from fruits and the sodium bicarbonate included into absorbent pad.

Table 1.1: Example of active and smart packaging:

❖ Active packaging	❖ smart packaging
Anti-microbial	Time–temperature indicators
Ethylene scavenging	Leakage sensors
Heating/cooling	Allergen sensor
Moisture absorbing	Microbial growth sensors
Odour and flavour absorbing/ releasing	Microbial spoilage sensors/ indicators
Oxygen scavenging	Physical shock indicators
Spoilage retarder	Pathogens and contaminants sensors

1.6.1.1 Active Packaging and its Application

The term “active packaging” was introduced in 1987 by Labuza for improvement of shelf life and nutritional quality. Active packaging materials comprising of bionanocomposites play several roles, including protection of food from external environment, maintaining their quality for a longer period of time, Subsequently increasing the shelf life. These active packaging materials prevent oxidation of the food product, thus delaying its deterioration. They may also act as moisture barriers, antimicrobial agents, freshness indicator, and so on. Components of the active packaging for food include:

(I) Nanocomposites (metal ions of silver, copper, gold and metal oxides of TiO_2 , MgO) (II) Antimicrobial films (antibacterial/antifungal compounds like sodium benzoate, benomyl, Elements like (Si, Na, Al, S, Cl, Ca, Mg, Fe, Pd, and Ti), edible clove, pepper, cinnamon, coffee, chitosan, antimicrobial lysozyme, and bacteriophages).

(III) Gas scavengers, such as TiO_2 , iron powder, silicates, sulfites, chlorides, polymeric scavengers, elements like Fe, Si, Ca, Al, Na, Cl, K, Mg, S, Mn, Ti, Co, V, Cr, and P. Materials and construction of the Tetra Pak™ packaging which have been applied for storage and shelf-life extension of milk products in Switzerland since 1951 are consist of carton board, polyethylene, aluminum sheet, and repeatable polyethylene, carton layers. Examples of various packages utilizing plastic and Tetra Pak for food products shelf-life extension are shown in Figure 1.5.



Fig. 1.5 Photograph of various food packaging items applied for storage of fish, sea food, beverage, and pastry products.

Nanoclay–polymer composites were used for improving of gas barrier properties of food packaging. The most often used one is montmorillonite (also called as bentonite), with natural nanoscalar layered structure that can restrict the permeation of gases when incorporated into a polymer. Barrier improvement mechanism of nanoplate-based composites is based on the well-known “tortuous path” principle depicted in Figure 1.6.

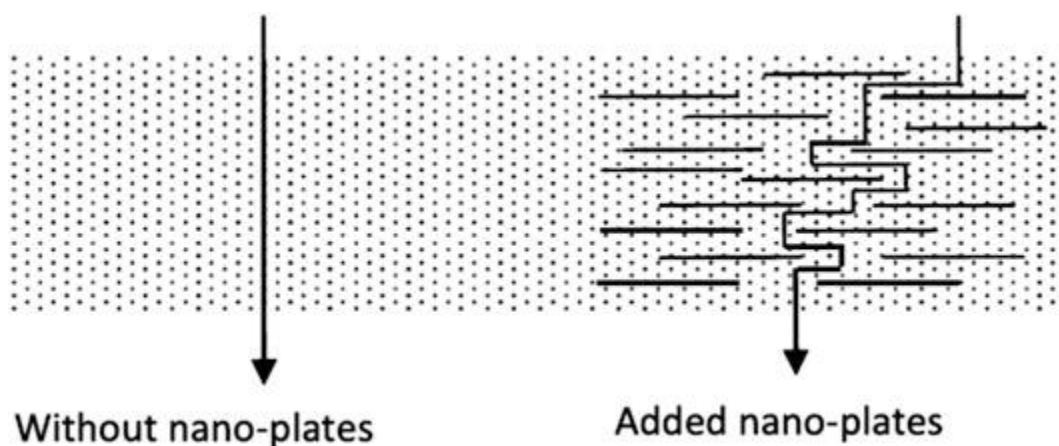


Fig. 1.6 Addition of Nano plates increases tortuosity and decreases permeability

There are three main factors determine the gas barrier performance: (I) filler properties (resistance to gas diffusion, aspect ratio and volume fraction), (II) polymer matrix and their barrier properties, and (III) the 'quality' of dispersion (agglomeration/specific interface, free volume generated by mediocre interface management, and the texture/orientation of filler platelets). The crux of successful development of polymer nanocomposites (PNCs) is coupled with the levels of exfoliation of the layered nanofillers in polymer matrix (Cui, et al., 2016).

Some Application of Active Packaging

a) Oxygen Scavenger:

One of the most important application of food aim to remove any oxygen present in the food package. The presence of oxygen in the headspace of package lead to oxidation and increase the spoilage rate of food by promoting the growth of aerobic microorganisms. Also may cause color modifications, sensory changes and nutritional losses. The most common oxygen scavenger is iron-based scavenger. Some commercially available oxygen-scavenging solutions are SHELFPLUSR O₂, AMOSORBTM ColorMatrix™, etc. (Yildirim et al., 2018).

b) Moisture Scavenger:

Moisture content and water activity have significant role in safety and quality of food. Foods differ from each other in their need for moisture, some of them sensitive to humidity and negatively affected if the moisture rate increased, such as dry products like wheat and parley. Other foods need significantly high rate of relative humidity as fruit, vegetables, meat and fresh fish. Hence there is a need for control moisture in packaging material. Three categories of moisture control are present: moisture reduction by MAP application. Moisture prevention by barrier packaging. The last one is moisture elimination by applying desiccants/absorbers. The first two types are considered passive strategies due to not use active ingredients. The last type considered active. Active moisture scavengers can be also divided into two types: relative humidity controllers, and moisture removers (MAP, vacuum and so on). Humidity controllers applied by use desiccants such as silica gel, clays, and humectant salts. Moisture removers mostly applied as sheet or pads composed of porous materials with superabsorbent polymers/salts/minerals (Yildirim et al., 2018).

c) Ethylene Scavenger:

Ethylene is the hormone responsible for plants growth, increase the respiration rate of fresh product and accelerate the ripening and softening of fruits and vegetables. thus shortening the shelf life of products.

Ethylene scavengers used to remove these hormones and therefore extended the shelf life. The most commonly active components for this purpose are: potassium permanganate, minerals such as zeolite, active carbon, pumice, nanoparticles such as nano TiO₂, nanosilver, and kaolin (Yildirim et al., 2018).

d) Antioxidant Releasers:

Antioxidant releasers divided into: synthetic antioxidant (as butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA)) and natural antioxidants (as polyphenols, tocopherols, plant extracts, and essential oils (EOs)). It is used to prevent lipid oxidation and therefore increase the shelf life (Yildirim et al., 2018).

e) Carbon Dioxide Emitters:

CO₂ emitter devices implemented in MAP Packaging to maintain high level of CO₂ in headspace and therefore inhibit the growth of spoilage bacteria and prolonged the shelf life. The emitter present as sachet or pads. The liquid that seeped out from products react with active components of pads, causing releasing of CO₂ (Yildirim et al., 2018).

f) Antimicrobial Packaging System:

Antimicrobial packaging systems depend on using active components that inhibit the growth of spoilage and pathogenic microbes. Examples of components that used: essential oils, enzymes and bacteriocins, antimicrobial polymers, organic acids (such as citric acid and sorbic acid), metal oxide (titanium dioxide, zinc oxide, magnesium oxide), and organically modified nanoclays (Yildirim et al., 2018).

1.6.1.2 Nanoreinforcements Used in Active Packaging

Reinforcement is "to make a material stronger, by adding one material to another". The idea of using fillers began since the ancient time, it was started when the straws were used to reinforce mud bricks in about 4000 BCE. Also, the using of the grids, plates or fibers to strengthen concrete. This method was invented in 1849 and patented in 1867. Polymer nanocomposite composed of multi-component in which one material dispersed in another one in nanometer range. Polymer nanocomposites are considered as an important materials due to the wide variety of application (Chatterjee, 2012).

There are various types of nanofillers used for various purpose in food packaging. For example: nanoclays and silicates, nanocellulose, Silicon Dioxide (SiO₂), Silica, Carbon

Fillers, antimicrobial agents such as silver, zinc oxide, and titanium dioxide nanoparticles. Other nanoparticles used as moisture control agent and other used as oxygen scavengers agents such as ferrous oxide (Talegaonkar et al., 2017), (Rhim, Park, & Ha, 2013).

Here I will focus on carbon derivatives (especially graphene oxide) which is the primary focus of this present work.

❖ Carbon Fillers:

Carbon is known for its extraordinary ability of catenation. Catenation is the ability of atoms of the same element to bonding into a series. The property of combination with it self and other chemical elements in various forms is the basis of organic chemistry and life. In nature, carbon is abundantly available as coal, natural graphite, and in small quantity as diamonds. There are another forms of carbons used for various application such as electrodes and electrical contacts, gas adsorption, helium gas barrier, printing inks and shoe polish etc. Carbon nanofillers discovery started with fullerene C₆₀ or buckyball by Hary Kroto in the University of Sussex and Richard Smalley in Rice University, it has unique structural properties. CNTs is another nanostructure of carbon, it is a cylindrical graphene tubes with 1D hybridized structure. CNTs can be single, double or multiwalled. CNTs have a diameter of few nanometers and a length of several centimeters. Graphite also is one of allotrope of carbon having planar, layered structure. The carbon atoms in each layer arranged in hexagonal lattice with 0.142 nm distance between layers. Graphene is a single atomic- thick layer of graphite of 2D sp²-hybridized structure. It is densely packed in a honeycomb crystal lattice. In 1987 the name of graphene was coined. Graphene is a building block of fullerene, graphite, CNTs, and charcoal. A schematic in Figure 1.7 shows how fullerene, graphite and CNTs derived from graphene. It was discovered by Kostya Novoselov and Andre Geim from Manchester University in 2004. They have won the nobel prize in 2010 and succeed in extracting one atom thick layer from graphite by a process called micromechanical cleavage

or the Scotch tape technique. Graphene and CNTs have superior properties which include: high surface area, outstanding thermal and mechanical properties, superior electrical conductivity and chemical stability. These properties make it suitable for various applications, as electronics, sensors, energy storage and conversion devices. (Chatterjee, 2012),(Youssef & El-Sayed, 2018)

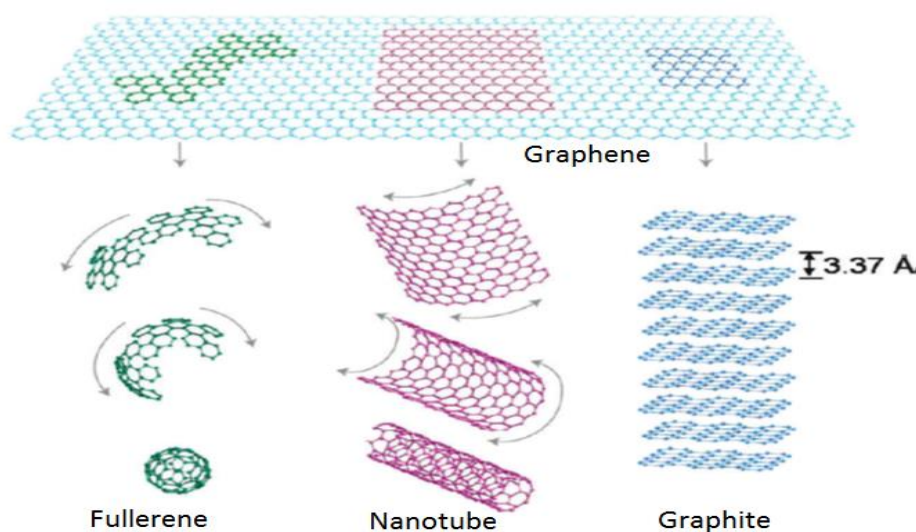


Fig 1.7 Graphene is the building block of all graphitic forms. It can be stacked into 3 dimensional graphite, rolled into 1 dimensional nanotubes, or wrapped up into 0 dimensional buckyballs.

Graphene and CNTs have poor dispersibility in water due to hydrophobicity, also having a restacking problem due to powerful van der Waals. It can be dispersed only in few organic solvents such as o-dichlorobenzene, N-methylpyrrolidone, N,N-dimethylformamide, and N,N-dimethylacetamide which is harmful to environment and living cells. There are two methods used to improve their dispersibility: (1) covalent modifications and (2) non-covalent modifications. Covalent modification performed by chemical reactions on the surface of graphene and CNTs, such as oxidation and coupling with functional group. This method can

improve the dispersibility and can transfer the force when mixed with a polymer matrix. However this method can lead to lose the original properties of graphene and CNTs such as thermal, mechanical properties and electrical conductivity. Non-covalent method depends on adsorbing on the surface by using polymers or surfactants such as poly(sodium 4-styrene sulfonate) and polyvinyl pyrrolidone. This method can maintain the intrinsic properties of graphene and CNTs. However this method may cause deterioration of mechanical properties (Son & Park, 2018).

Graphene has a tendency to agglomerate in a polymer due to Van der Waals forces and its high surface area. So oxidation that followed by chemical functionalization improve stabilization and dispersion of graphene. Graphene oxide (GO) is a result of graphene oxidation, firstly synthesized by Brodie in 1859, then the method was improved in 1898 and 1958 by Staudenmaier and Hummers respectively. Afterwards several improvements and modified Hummer's method was developed. The resultant GO contains a large number of oxygenated functional groups at its edges and on its surface. The oxygenated functional groups such as: hydroxyl, epoxy, and carboxyl as shown in Figure 1.8. These functional groups make it hydrophilic, and enhance its dispersability in water. Also, enhance interfacial bonding between polymer and graphene oxide. (Jinxia Ma, et al., 2017)

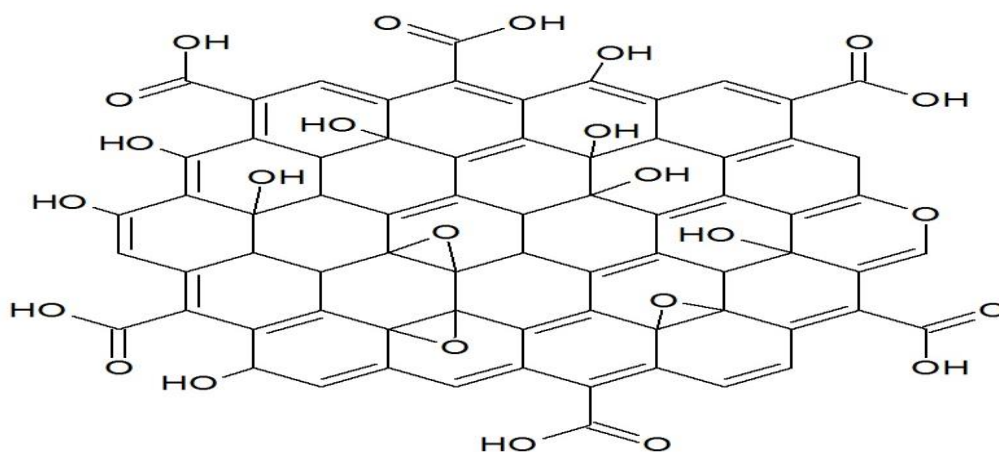


Fig 1.8: structure of graphene oxide.

Polymer/ graphene nanocomposite can be prepared by different route such as solution mixing, polymerization or melt blending. Many studies emphasize that the incorporation of graphene and its derivatives can enhance the properties of conventional polymers.

1.6.1.3 Nanomaterial Migration into Food Matrix

Migration is the unintended transfer of packaging materials into the food. it is a critical issue that may affected food's safety and human health. In addition it may cause undesirable changes in the food. For example, migration of TiO₂ into lipid matrix results in rancidity. Nevertheless, in some cases as the active packaging, nanomaterials are intended to be released deliberately. the possibility of nanomaterials incorporation into food packaging need a Performing migration tests under controlled conditions for assessing the associated safety problems. The analysis condition depends on the type of food matrix or food simulant being tested.

Nanomaterials migration into food depend into Different factors: (I) nanoparticles' properties, such as particle size, molecular weight, concentration, , solubility, and diffusivity into polymer. (II) Environmental conditions like temperature, mechanical stress, (II) food condition like pH value and composition), (IV) packaging properties (polymer structure and viscosity), (V) and contact time. Some sources were considered that there is no any significant risk from nanomaterials that mixed with polymers, this is due to fixed and embedded nature of nanopartiles in polymer matrix. There is a study made by Šimon et al. (2008) about the migration of nanoparticles into food, it predicted that the migration from packaging materials take place only if the size of nanomaterials very small and in the lower nanometer range, if the polymer with low viscosity, or if there is no polymer- nanoparticles binding.

High surface-to-volume ratios of nanomaterials stimulate an active surface chemistry that may cause unwanted chemical reactions. Nanoparticles also can speeding up or slowing

down the migration of other packaging constituents. The complex composition of food makes it difficult to directly estimate the amount of migration into food matrices. the alternative method is by using natural food stimulants that measure the specific and overall migration of different packaging substances into foods. The amount and rate of mass transport in the selected food stimulants should be similar to those that occur in the food matrix.

There are few studies in the safety of nanoparticles that embedded into packaging materials, so more tests will be needed to establish migration patterns for nanomaterial/ polymer composites. (Zohreh Honarvar et al, 2016) and (Ćwiek-Ludwicka, et al. 2017)

1.6.1.4 Concerns About Nanocomposite Packaging

The reduced particles size considered the most challenging concern in using nanoparticles. this is due to chemical and physical properties of tiny materials that may be quite different from thier macroscale counterparts.

This is a very risky problem GRAS (generally recognized as safe) decisions made without any consideration of the size or the related safety evaluations. So present legislation considers that there is no difference between nanomaterials and macromaterials. As a result, nanomaterial for packaging are not considered as new chemicals, and, thus, specific or overall migration limits into food that is in contact with nanomaterials have not been defined. Although it has been reported that some nanomaterials are potentially harmful to human health. The Institute of Food Science and Technology (IFST) recommended that nanomaterials be treated as substances that are dangerous to human health.

One of the responsibilities of the Food and Drug Administration (FDA) is to prove the safety of nanoscale products. The FDA foundation, for nano-based products are being assessed case-by-case according approved standard. Nevertheless, since there is no labeling

prerequisites for such products that state whether nanotechnology has been used in their production, it would be difficult for the FDA to evaluate their safety. (Störmer, et al. 2017)

1.6.1.5 Analyzing Techniques of Nanomaterials

Understanding the potential risks of nanomaterials needs thorough insight about their structures and properties. The detection of nanoparticles that migrate into food materials requires more advanced analytical techniques due to the complexity of the nanomaterials, they represent a tiny portion comparing with packaged food. Microscopic, spectroscopic, and quantitative analytical techniques are considered as promising techniques for this purpose. Microscopic techniques such as: transmission electron microscopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM) which provide structural features of nanomaterials. Spectroscopic technique such as X-ray diffraction (XRD) and UV-vis spectroscopy. XRD is known as a conventional method that used to examine nanocomposite structures and to identify the elemental composition or the crystalline arrangement of nanomaterials, an intercalation, exfoliation, and dispersion.

The UV-vis provides as information about the presence of nanoparticles quantitatively which considered as a vital issue in food packaging because of safety concerns.

The inductively coupled plasma mass spectrometry (ICP-MS) is used to probe the nanomaterials migrate into food quantitatively at very low concentration (0.1 – 10 ppm). Atomic absorption spectrometry (AAS) is used as an alternative method for elemental analysis for the detection of nanomaterial (Shahbazian, Jafari, & Haghnia, 2016) and (Störmer et al., 2017)

Generally speaking, several studies were carried out to study nanographene oxide for different parameters, however, the objectives of this study are the followings:

1. Fabricated polyvinyl alcohol/ graphene oxide nanocomposite films and studying the properties before and after incorporation of graphene oxide

2. Fabricated methyl cellulose/ graphene oxide nanocomposite and studying properties before and after incorporation of graphene oxide.

Chapter Two: Literature Review

2.1 Introduction:

Food packaging is important for keeping food clean and fresh and to slow down food deterioration. So there are a lot of efforts to develop these packages by using nanoparticles to improve properties of polymers as mechanical and thermal properties. It can also be using it as barrier on packaging materials to reduce the permeability and extending the shelf life, or using it to design food sensors.

In this chapter we will review the thermal, mechanical and swelling properties of GO/ polymer nanocomposite, and Fourier transform infrared spectroscopy (FTIR).

2.2 Superior properties of Graphene oxide

The incorporation of graphene oxide into polymer can improve several properties of polymer as thermal and mechanical properties and may also enhance the swelling properties

2.2.1 Thermal Properties of polymer/GO Nanocomposite:

Graphene has a unique thermal properties as high thermal conductivity that reached to $\sim 5000 \text{ Wm}^{-1}\text{k}^{-1}$ (Cui et al., 2016). The change in thermal properties is monitored using different devices as Differential Scanning Calorimetry (DSC), Simultaneous Thermal Analysis Instrument (STA), Thermogravimetric Analysis (TGA), and Pyris1 Thermoanalyzer.

Rama Kanta Layek, et al. (2018) studied thermal properties of methyl cellulose/ graphene oxide nanocomposite by using a Simultaneous Thermal Analysis instrument (STA). thermograph show a slight enhancement of the thermal stability of GO/MC compared with pure MC.

Mónica Cobos, et al. (2018) prepared reduced graphene oxide and studied the effect of incorporation of GO on the thermal properties of PVA polymer. The melting and crystallization

temperature decreased with increasing content of GO, however, the glass transition temperature increased as the GO contents increased.

Vijay Kumar (2018) improved the thermal properties of PET by adding of reduced graphene, the results of TGA showed that PET tends to degrade at faster rate compared with that of the composite, which means the thermal stability of the composite improved by means of adding rGO filler to the PET matrix.

In the same manner, **S. Montes, et al. (2018)** studied the effect of combining graphene nanoplatelets (GR) and cellulose nanocrystals (CNC) in two different ratios on the properties of poly (lactic acid) films by melt blending technique, at a total loading level of 1 wt. The thermal properties by TGA for both nanofillers were also positively influenced (T_d increased with increasing of GO), and the film containing 50/50 of CNC and GR nanofillers possessed the highest thermal stability, showing that the combination of both nanofillers resulted in the highest improvement of the thermal properties of the film.

Meryem Goumri et al. (2017) investigated two Nanofillers; GO/PVA and rGO/PVA nanocomposite by using Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TGA). The results showed an improvement in the tunable thermal properties and thermal stability. The degradation temperature, which measured using TGA, was increased with respect to pure polymer, the glass transition temperature which was measured by DSC was decreased up to 1% GO, and started to increased at concentration above 1% GO, and its higher for GO nanocomposite than those of reduced GO. Melting temperature exhibited no change by addition of GO, the degree of crystallization decreased with an addition of GO and rGO. In general, reduced GO nanocomposite has much better thermal properties than those of GO.

Vorrada Loryuenyong, et al. (2015) used the PVA/ Graphite oxide and PVA/ Graphene oxide nanosystem, it was found that a slight shift of TGA curve toward high temperature by addition

of graphene to polymer, but there is no obvious change by addition graphite oxide.

Xia He, et al. (2015) prepared GO/ poly lactic acid and rGO/ PLA (reduced) by using layer by layer method with the incorporation of positively charged polyethyleneimine (PEI). A thermal property of nanocomposite was studied by using thermo analyzer. In that report it was concluded that the thermal properties enhanced and the degradation temperature was increased from 328.8°C of pure PLA to 337.23 °C for multilayer (PEI/GO).

Hye Min Kim and Heon Sang Lee, (2014) prepared ethylene vinyl alcohol (EVOH)/graphene oxide (GO) and rGO membrane prepared by solution mixing method. It was found that glass transition temperature that measured by DSC increased about 1.6 for GO/EVOH or rGO at 0.3 wt% concentration. The melting temperature of GO/EVOH composites decreased from 456.8 for pure EVOH to 448.4 at 0.3wt % GO and to 455.6 for rGO at 0.01wt%. However, the equilibrium melting temperatures of EVOH was not changed by adding GO into EVOH

Chengpeng Li, et al. (2013) prepared PVA/GO for dye removal and studied the glass transition temperature and crystallinity by using DSC. An addition of GO leads to a slight increasing in the glass transition temperature from 79.2 °C for pure hydrogel to 80.6 at 0.3% GO concentration, and 81.4 °C at 0.6% GO. The melting point of the composite hydrogels decreased from 226.5 °C for pure hydrogel to 226.1°C at 0.3% GO and to 225.8 °C at 0.6%. Furthermore, degree of crystallization decreased with addition GO.

Jin Joo Parka, et al. (2013) studied the thermal properties of PLGA/ GO nanocomposite by using TGA. The results confirmed that GO improved the thermal stability of PLGA polymer. The degradation temperature shifted to higher value with increasing the contents of GO

Another research was done by **Seira Morimune, et al. (2012)**, studied the PVA/GO nanocomposites, the glass transition temperature measured by DSC increased from 62°C for pure

PVA to 65°C, 68°C, and 76°C at 0.1wt%, 0.5wt% and 1wt% GO/ PVA respectively. The melting temperature appeared without a significant change at 0.5wt% and 1wt% GO/PVA concentrations. The temperature of degradation measured by using TGA increased with increasing GO concentration from 263°C for pure PVA to 265°C, 269°C and 271°C for 0.1wt%, 0.5wt% and 1wt% GO/PVA respectively.

2.2.2 Mechanical Properties of Polymer/GO Nanocomposite

Graphene is believed to be the basic unit of graphite and carbon nanotubes (CNTs). It has a similar tensile modulus (1.01 TPa) and ultimate strength (116 GPa) to CNTs" (Zhang et al., 2011). Many researches are studying the mechanical properties of graphene oxide with different type of polymer.

Yibo Zhao et al. (2018) studied PVA/GO nanocomposite hydrogel as an artificial cartilage material. The Young's modulus for PVA/GO has a higher value than PVA, it was improved with increasing GO concentration.

Mónica Cobos, et al. (2018) prepared reduced graphene oxide and studied the effect of incorporation it in mechanical properties of PVA polymer. It was found that the elastic modulus was not affect by addition GO, this result was ascribed to experimental error. Tensile strength was increased from 47 to 56 MPa. However, the elongations at break decreased with adding GO.

Rama Kanta Layek, et al. (2018) studied the mechanical properties of graphene oxide/ methyl cellulose. The composite produced by simple solvent evaporation assisted assembly. 1%, 3% and 5% of GO was added with respect to MC. The mechanical results show that the addition of GO increased the stress at break and young's modulus. The stress at break and young's modulus of nanocomposite with 5% GO reached to (104 ± 3) MPa and (3.8 ± 0.2) GPa respectively, whereas pure MC only reached to values of 56 ± 4 MPa and 1.27 ± 0.2 GPa. The elongation decreased from (22 ± 4) to (11.6 ± 3) .

In addition **Vijay Kumar, (2018)** intends to improve the mechanical of PET by adding reduced graphene. The results show that Tensile strength of PET/ Graphene nanocomposite was observed to be greatly increased, and it higher than that of virgin PET. Also it was observed that tensile modulus was not changed very much but decreased slightly to a maximum of 9% for PET+0.5wt% and decreased gradually up to 5% for PET+5wt%, and for PET+10% it was 4% increased with comparison to that of virgin PET.

S. Montes, et al. (2018) studied the Effect of combining cellulose nanocrystals (CNC) and graphene nanoplatelets (GR) in two different ratios on the properties of poly(lactic acid) based films by melt blending technique, at a total loading level of 1 wt. Young's modulus, slightly higher in the formulations containing CNC/GR combination, and especially in the 50/50 ratio in which the Young's modulus was 8% higher than the reference formulation PLA-T. Similarly, the PLA-CNC50/GR50 showed the highest tensile strength, 11% higher than the reference, without a significant variation in the elongation at break.

The mechanical properties were studied also by **Yeong-Rae Son & Soo-Jin Park (2018)** on graphene oxide (GO)/carbon nanotube (CNT) loaded carboxymethyl cellulose (CMC/GCC) by simple solution mixing-evaporation method. The addition of GO to CMC caused increasing in tensile strength from 37.28 MPa to 39.72 MPa. Young's modulus also increased from 1.89GPa to 2.14GPa, but the strain was decreased from 11.85% to 11.44%. The addition of CNT to form CMC/GCC nanocomposite films also caused further increasing on tensile strength and young's modulus, and decreasing on strain.

Meryem Goumri et al. (2017) studied mechanical properties of GO/PVA and CRGO/PVA (reduced GO). For the addition of GO, the Young's modulus (E) and yield stress (σ_y) increased,

and a loading of 1wt% results in an increase of the Young's modulus from 4.52 to 4.93 GPa and of the yield stress from 53.7 to 66.8 MPa. The yield strain (ϵ_y) of the GO nanocomposites also was slightly increased as compared to pure PVA. On the other hand, when the loading of CRGO (reduced GO) reach 2wt%, the yield stress and Young's modulus dramatically decreased from 53.7 to 18.9 MPa and from 4.52 to 0.56 GPa respectively. Moreover, the yield strain did not evolve comparing to pure PVA.

R. Mahendran, et al. (2016) studied the effect of incorporation of GO to poly(vinyl alcohol) (PVA) and poly-2-acrylamido-2-methyl-1-propanesulfonic acid (PAMPS) matrix . The results show that comparing with the PVA/PAMPS composite, Young's modulus of PVA/PAMPS/GO nanocomposite was enhanced and increased with increasing GO content.

Xie Rui-Hong¹, et al. (2015) studied mechanical properties of graphene oxide reinforced regenerated cellulose/polyvinyl alcohol (GORCE/ PVA) ternary hydrogels, an addition of GO improved the mechanical properties. A 1wt% of GO, the tensile strength increased by 40.4% from 0.52MPa to 0.73MPa. However, increasing GO content to 1.5wt%, the tensile strength suffered a little decrease. Almost 130% increases in elongation at break (from 103% to 238%) of ternary hydrogel was obtained when add 1.0 wt% GO. (Rui-Hong et al., 2015).

Jin Joo Parka, et al. (2013) studied the mechanical porperties of Poly (D,L-lactide-co-glycolide) 50:50 (PLGA)/graphene oxide (GO) nanocomposite film. They found an enhancement in the mechanical properties of PLGA with addition of GO compared to pure PLGA. Tensile strength of PLGA/GO nanocomposite was increased from 4.3 ± 0.9 MPa to 10.9 ± 0.2 MPa as the GO content increases up to 5 wt%, and the same trend was found to that of young's modulus which increased from 203 ± 50 to 960 ± 85 MPa.

The same previous tests were done and the same results were obtained by **Seira Morimune, et al. (2012)** on PVA/GO nanocomposites. Young's modulus (E) dramatically increased by the incorporation of GO. It was reached to 176% for PVA with only 0.1 wt% GO compared with the Young's modulus of free PVA. Conversely, the elongation at the break (ϵ_{\max}) of the nanocomposites decreased with an increasing GO content. For the nanocomposites with 0.1wt% GO loading, the high ϵ_{\max} close to that of the PVA film remained. The K value (toughness) drastically decreases with increasing of GO. Film with 0.1% GO loading was increased 33% higher than that of PVA film

Lu Zhang, et al. (2011) studied the mechanical properties of PVA/GO for using as biomaterial in biomedical and tissue engineering. The Tensile strength was increased by 132% and 36% improvements of compressive strength were achieved with an addition of 0.8wt% of GO, compared with pure PVA.

2.2.3 Swelling and Solubility Ratio of Polymer/GO Nanocomposite

Swelling properties of polymer affect the barrier properties and the ability of polymer to trap chemicals that reach the packaging material during storage.

Xie Rui-Hong¹, et al. (2015) studied swelling ratio of graphene oxide reinforced regenerated cellulose/ 25% polyvinyl alcohol (GORCE/ PVA) ternary hydrogels. Swelling ratio of ternary hydrogels gradually increase with the increase of GO loading from 0.5, 0.8, 1, 1.5%. It is also increase with the increase of PH value.

Chengpeng Li, et al. (2013) studied PVA/GO for dye removal. PVA used was with a concentration of 14%, and GO was with 0.3 and 0.6%. The swelling ratio which determined by gravimetric method increased and improved with increasing of GO from 0 to 0.3 to 0.6%.

Hossein Hosseinzadeh (2013) studied the swelling rate of PVA that prepared by a crosslinking technique using glutaraldehyde as a crosslinker. It was found that with increasing amount of

crosslinker the swelling rate decreased. also it was found that the swelling rate increase with increasing concentration of PVA from 1.2 to 2.4 % then it was decreased at higher concentration.

Seira Morimune, et al. (2012) studied swelling ratio of PVA/GO nanocomposites. PVA was used with a concentration of 5%, and GO with 0.1, 0.5, and 1%. Swelling ratio decreased with the increase of GO. It was decreased by 45% for 0.1 wt% GO loading compared with that of PVA film.

Lu Zhang, et al. (2011) studied swelling properties of PVA/GO nanosheet for using as biomaterial in biomedical and tissue engineering. PVA used was with 16% and GO was with 0.2, 0.4, 0.6, 0.8 and 1% concentration. Swelling ratio was fast at the beginning and reached the highest maximum swelling ratio at 0.6% GO (exceed 180%), and then gradually decrease.

2.3 Quality Assurance (FT-IR of polymer with graphene oxide)

There is a need to rapid, reliable feedback on structure and quality in addition to interaction between graphene/polymer. Infrared spectroscopy is one of the spectronic techniques used to identify polymer structure.

Rama Kanta Layek, et al., (2018) prepared MC/GO nanocomposite. The ATR-FTIR, WAXS, and STA analysis was performed. It was indicated a successful incorporation of GO into the MC matrix. FESEM analysis also supported the good dispersion of GO sheets in the MC matrix. FT-IR spectra of GO show the typical C-O stretching vibration appear at ca.1722 cm^{-1} . O-H stretching vibration peak and intercalated water molecule present in GO appear at 3415 cm^{-1} . The absorption bands at 1212 cm^{-1} and 1044 cm^{-1} are assigned to the C-OH stretching vibrations of the hydroxyl group and C-O stretching vibrations of epoxy groups,

respectively. Oxidized graphitic zone is visible at 1620 cm^{-1} . $2924/2852\text{ cm}^{-1}$ proves the existence of fewer CH_2/CH in the GO.

FT-IR Spectra of pure MC show characteristic broad bands at 3451 cm^{-1} and 1055 cm^{-1} for O–H stretching vibration of the hydroxyl group and C–O–C stretching vibration of glucosidic units of MC. The C–H stretching of pyranose unit appears at 2929 cm^{-1} . C–H bending vibration appears at 1644 , and OCH_3 appears at 941 cm^{-1} .

H-bonding that occur between MC and GO was examined by the shift of O–H stretching band to a lower frequency from 3444 cm^{-1} at 1% GO and to 3440 at 5% GO. Also C–O–C peak shifted from 1055 to 1050 cm^{-1} .

In the same year, **Yeong-Rae Son & Soo-Jin Park, (2018)** studied the effect of incorporation graphene oxide (GO)/carbon nanotube (CNT) complexes to carboxyl methyl cellulose (CMC). UV-Vis spectrophotometry was confirmed uniformly dispersion of GCCs in the CMC matrix. Transmission electron microscopy, scanning electron microscopy, and X-ray diffraction were used to study the morphological and crystalline structures of the samples. FT-IR spectra for GO was as follow: O–H stretching vibration at 3420 cm^{-1} , C=O at 1730 cm^{-1} , C=C at 1630 cm^{-1} , C–O at 1230 cm^{-1} and C–O–C at 1057 cm^{-1} ; and bending vibrations corresponding to O–H in the carboxylic group at 1400 cm^{-1} . The FT-IR spectra for GCC show the presence of a shoulder peak at 1570 cm^{-1} , which could be related to the π – π interactions between GO sheets and the CNTs.

Compared with reduced GO, **Meryem Goumri, et al. (2017)** studied the effect of addition of GO and reduced GO to PVA. By XRD analysis, it was confirmed that GO can form more hydrogen bonds with PVA matrix than reduced GO.

Also, **R. Mahendran, et al., (2016)** studied the properties of GO that incorporated into poly (vinyl alcohol) (PVA) and poly-2-acrylamido-2-methyl-1-propanesulfonic acid (PAMPS).

The dispersion of the GO in the polymer matrix were analyzed by XRD, FE-SEM, and AFM. It was revealed a homogeneous dispersion of GO in the polymer matrix. The physiochemical properties of polymer was enhanced by addition of GO and it was confirmed by Ionic exchange capacity, proton conductivity, and tensile texture results.

The cross linking between polymers and GO was validated by using FT-IR. In PVA spectra, there is a stretching O-H vibration between 3000 and 3400 cm^{-1} . The stretching band of C-H alkyl groups appeared between 2900 and 2700 cm^{-1} . The GO spectra show peaks around 3450 cm^{-1} for O-H stretching vibrations. C=O stretching vibrations appear at 720 cm^{-1} , the peak at 1250 cm^{-1} is for OH stretching vibrations, and peak at 1050 cm^{-1} is for C-O stretching vibrations.

The spectra of PVA/PAMPS/GO show signals around 1700 cm^{-1} that correspond to the vibrational mode of amide groups (C=O and N-H) of PAMPS, and the sharp peak at 1100 cm^{-1} correspond to asymmetric S-O stretching of sulfonate groups. These result indicate an interaction occur between polymers and GO.

Vorrada Loryuenyong, et al., 2015 investigated the suitability of PVA/GO for packaging. Fourier transform infrared spectroscopy, X-ray diffraction and scanning electron microscope revealed the strong hydrogen-bonding interactions between graphene oxide and PVA matrix. The FTIR graphs of graphite oxide and graphene oxide show the stretching and bending of hydroxyl groups at 3428–3432 cm^{-1} and 1630–1631 cm^{-1} , respectively. C–OH vibration show at 1384–1392 cm^{-1} and the C–O stretching at 1048 cm^{-1} . Hydroxyl group of PVA showed at 3312 cm^{-1} . The FTIR spectra of graphite oxide or graphene oxide and PVA matrix show a shift of hydroxyl vibration peaks around 3200–3300 cm^{-1} which indicate to the presence of hydrogen bonding between PVA and oxygen-functional groups in graphene and graphite oxide. The largest shift occurs in PVA-2.0% graphene oxide which could be ascribed to the strongest hydrogen bonds.

K. Sundar, et al., (2014) studied the properties of chitosan/ GO nanocomposite. UV-visible spectra used to determine the interaction between CS and GO and revealed successful formation of CS-GO nanocomposite. FTIR peaks of GO appear at 3444.26 cm^{-1} for hydrogen bonds, 1637.60 cm^{-1} for deformation of O–H bonds, 1091.45 cm^{-1} for C–O–C stretching, 2926.57 cm^{-1} for C–H stretching and 1759.09 cm^{-1} for C=O stretching. The FTIR peaks of CS-GO nanocomposite were recorded at 1555.86 cm^{-1} for N–H bending amide-I band, 1113.65 cm^{-1} for C–O–C stretching, 2922.69 cm^{-1} for C–O–C stretching and 3449 cm^{-1} for OH-hydrogen. The peak at 1759.09 cm^{-1} on GO spectra was completely disappeared in CS/GO. Moreover the band corresponding to C–O–C stretching shifts to higher wave number.

According to **Hye Min Kim and Heon Sang Lee (2014)** who prepared EVOH/GO membranes by solution casting method, the XRD analysis showed GOs were fully exfoliated in the EVOH/GO membrane.

By using different methods, **Jin Joo Park, et al. 2013** studied the properties of Poly (D,L-lactide-co-glycolide) 50:50 (PLGA)/graphene oxide (GO) nanocomposite films. UV–vis spectra of PLGA/ GO indicate that the GO sheets were well dispersed in the PLGA matrix. X-ray diffraction pattern of PLGA/1 wt% GO indicating that GO sheets were well exfoliated and uniformly dispersed in PLGA matrix.

Different from **Jin Joo Park, Seira Morimune¹, et al. 2012** studied the properties of PVA/ GO nanocomposite. The FT-IR spectra of GO show the presence of C=C at 1622 cm^{-1} , C–H stretching and deformational vibration show as 2915 and 1352 cm^{-1} respectively. In addition, the bands at 1733 cm^{-1} , 1225 cm^{-1} and 1075 cm^{-1} can be assigned as C=O stretching, C–OH bending and C–O stretching, respectively. At 975 cm^{-1} the symmetric epoxy ring deformation as well as the out- of- planer wagging of O–H–O. The hydroxyl group (O–H) stretching appeared at 3404 cm^{-1} and O–H bending vibration appeared at 1622 cm^{-1} . The

XPS analysis was performed for GO powder, it was revealed that GO contains 27.8% oxygen which can be related to the oxygen-containing groups. X-ray diffraction revealed that GO was well exfoliated and homogeneously dispersed in the PVA matrix.

For the same polymer, **Lu Zhang, et al., 2011** prepared GO/PVA hydrogel. Raman mapping study was used to evaluate the dispersion of GO nanosheets in the PVA matrix. It was prove the well dispersion of GO in PVA matrix. XRD was used to get information about the degree of crystallinity of PVA after the GO nanosheets were incorporated. The results suggests that the GO nanosheets do not have a noticeable effect on the degree of crystallinity of the PVA.

Chapter Three: Materials and Methods

3.1 Introduction

In general, there are a lot of research has been done to improve packaging materials by different methods. Active and smart packaging are types of improved material used to increase the shelf life and facilitate the communication between packaged food and consumer.

The purpose in this research is to go through the use of nanoparticles in food packaging. These nanoparticles provide super properties to polymer to turn toward active packaging.

This chapter will be providing the experimental procedure including materials, methods and methodology that used to prepare and study food packaging materials.

3.2 Materials and Equipment:

Materials were purchased from Sigma Aldrich: Polyvinyl Alcohol (PVA) powder, 99+%, M.wt = 89000-98000g/mol and density of 1.269 g/l. GO stock solution (5g/l) with size distribution ca. 200 nm (prepared at Hebron university). Methyl Cellulose, viscosity of 3000-5500 mPa.

The following equipment were used at Nano lab: Spin coater with timer reaches to 30sec and speed reaches to 1000rpm, Analytical Balance, Bath Sonicator (type T 490DH), model 37600 Mixer, Digital Caliper (STAINLESS HARDENED) 0-150mm. DSC analysis was performed using DSC Perkin Elmer 4000 (heated for 450 °C) with a heating rate of 10 C/min and under nitrogen atmosphere, Universal Mechanical Test Machine, Sinowon Testing Mchines ST series. The Fourier transform infrared (FTIR) spectrometer of Bruker IFS 66/S, that equipped with liquid nitrogen- cooled MCT detector and aKBr beam splitter, this equipment refers to physics lab at Al-Quds university. The tip Sonicator, MODEL VCX750

with 750 watts was used at Hebron University to produce nanographene oxide particles and Methyl cellulose/ GO nanocomposite. Figure (3.1) show the photograph of equipments used.

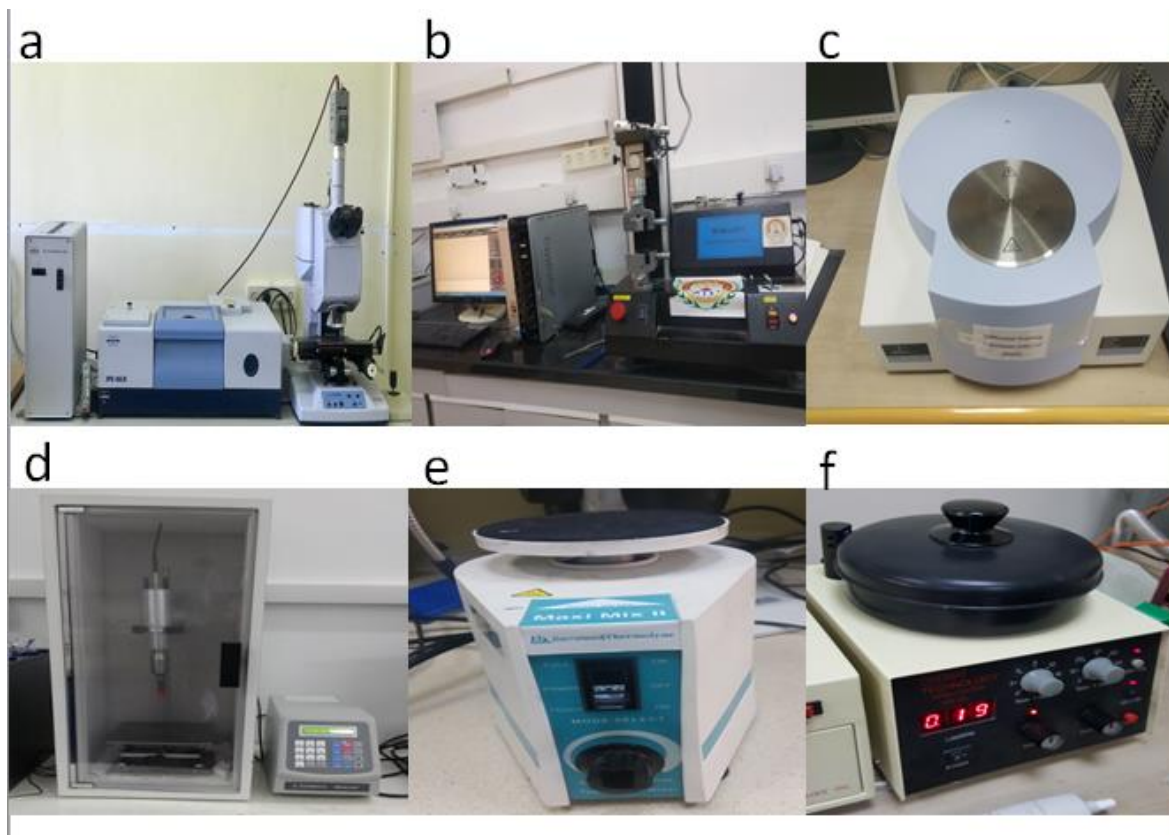


Fig 3.1: photograph of equipment used. a) FT-IR, b) Universal testing machine, c) DSC, d) Tip sonicator, e) Mixer, and f) Spin coater.

3.3 Methods

This approach includes methods of preparation: PVA thin films, PVA/GO nanocomposite, methyl cellulose (MC), MC/GO nanocomposite and their analytical methods.

3.3.1 Preparation of PVA Thin Films

A 5, 10, 15 wt. % of PVA solutions were prepared under continuous stirring for 30 min at 80°C. Afterwards, the PVA solutions were casted on Petri dishes and then spin coated at different speed (200- 550 rpm) with different times (5, 15, 30, 60s), different volumes (2, 3, 4 ml) as shown in table 3.1, which show the matrix of PVA casting.

For low concentration of PVA 5%, spin coater shows hard process of preparation due to loss of material during spinning at any speed and any time interval, for 10 and 15%, almost sample also lost during spin coater especially for the volume of 3 and 4ml. other samples were not distributed uniformly due to high viscosity. In addition to opaque appearance that produced from 3 and 4 ml of 15% PVA. As a result, samples using casting method were prepared and allowed to dry in an incubator at room temperature for 3 days to be ready for characterization.

Table 3.1: Matrix of 5%PVA thin film preparation.

N o.	Code	Conc. (%)			Volume			Note
		5	10	15	2	3	4	
	C _{0.05} V ₂	x			x			No need for rpm as the conc. is very low thus samples will be lost at any rotation
2	C _{0.05} V ₂	x			x			
3	C _{0.05} V ₃	x				X		
4	C _{0.05} V ₃	x				X		
5	C _{0.05} V ₄	x					x	
6	C _{0.05} V ₄	x					x	

(Table 3.2): Matrix of 10% PVA thin film preparation using spin coater.

No.	code	Conc.					Volume			Rpm				Time				Note
		5	10	15	0.2	2	3	4	200	300	400	550	5	15	30	60		
	C ₁₀ V ₂ R ₂₀₀ T ₅		×			×			×				×				A large part of the sample has been lost during spin coating as spill over the cover of spinner	
2	C ₁₀ V ₂ R ₂₀₀ T ₁		×			×			×					×				
3	C ₁₀ V ₂ R ₃₀₀ T ₅		×			×				×			×					
4	C ₁₀ V ₂ R ₃₀₀ T ₁₅		×			×				×				×				
5	C ₁₀ V ₂ R ₄₀₀ T ₅		×			×					×		×					
6	C ₁₀ V ₂ R ₄₀₀ T ₁₅		×			×					×			×				
7	C ₁₀ V ₂ R ₅₅₀ T ₅		×			×						×	×					
8	C ₁₀ V ₂ R ₅₅₀ T ₁₅		×			×						×		×				
9	C _{0.1} V ₂ R ₅₅₀ T ₃₀		×			×						×			×			
10	C ₁₀ V ₂ R ₅₅₀ T ₆₀		×			×						×				×		
11	C ₁₀ V ₃ R ₂₀₀ T ₅		×				×		×				×				A small part of the sample has been lost during spin coating as spill over the cover of spinner	

12	C ₁₀ V ₃ R ₂₀₀ T ₁₅		×				×	×					×			A large part of the sample has been lost during spin coating as spill over the cover of spinner
13	C ₁₀ V ₃ R ₃₀₀ T ₅		×				×		×			×				
14	C ₁₀ V ₃ R ₃₀₀ T ₁₅		×				×		×				×			A small part of the sample has been lost during spin coating as spill over the cover of spinner
15	C ₁₀ V ₃ R ₄₀₀ T ₅		×				×			×		×				
16	C ₁₀ V ₃ R ₄₀₀ T ₁₅		×				×			×			×			A large part of the sample has been lost during spin coating as spill over the cover of spinner
17	C ₁₀ V ₃ R ₅₅₀ T ₅		×				×				×	×				
18	C ₁₀ V ₃ R ₅₅₀ T ₁₅		×				×				×		×			
19	C ₁₀ V ₃ R ₅₅₀ T ₃₀		×				×				×			×		
20	C ₁₀ V ₃ R ₅₅₀ T ₆₀		×				×				×				×	
21	C ₁₀ V ₄ R ₂₀₀ T ₅		×					×	×				×			A large part of the sample has been lost during spin coating as spill over the cover of spinner
22	C ₁₀ V ₄ R ₂₀₀ T ₁₅		×					×	×					×		
23	C ₁₀ V ₄ R ₃₀₀ T ₅		×					×		×			×			
24	C ₁₀ V ₄ R ₃₀₀ T ₁₅		×					×		×				×		
25	C ₁₀ V ₄ R ₄₀₀ T ₅		×					×			×		×			

26	C ₁₀ V ₄ R ₄₀₀ T ₁₅		x					x			x			x			
27	C ₁₀ V ₄ R ₅₅₀ T ₅		x					x				x	x				
28	C ₁₀ V ₄ R ₅₅₀ T ₁₅		x					x				x		x			
29	C ₁₀ V ₄ R ₅₅₀ T ₃₀		x					x				x				x	
30	C ₁₀ V ₄ R ₅₅₀ T ₆₀		x					x				x					x

(Table 3.3): matrix of 15% PVA thin film preparation using spin coater.

No.	Code	Conc.				Volume			Rpm				Time				
		0.05	0.1	0.15	0.2	2	3	4	200	300	400	550	5	15	30	60	
	C _{0.15} V ₂ R ₂₀₀ T ₅			x		x			x				x				
2	C _{0.15} V ₂ R ₂₀₀ T ₁₅			x		x			x					x			
3	C _{0.15} V ₂ R ₃₀₀ T ₅			x		x				x			x				
4	C _{0.15} V ₂ R ₃₀₀ T ₁₅			x		x				x				x			
5	C _{0.15} V ₂ R ₄₀₀ T ₅			x		x					x		x				
6	C _{0.15} V ₂ R ₄₀₀ T ₁₅			x		x					x			x			A small part of the sample has been lost during spin coating as spill over the cover of spinner
7	C _{0.15} V ₂ R ₅₅₀ T ₅			x		x						x	x				A large part of the sample has been lost during spin coating as spill over the cover of spinner
8	C _{0.15} V ₂ R ₅₅₀ T ₁₅			x		x						x		x			
9	C _{0.15} V ₂ R ₅₅₀ T ₃₀			x		x						x			x		
10	C _{0.15} V ₂ R ₅₅₀ T ₆₀			x		x						x				x	

11	$C_{0.15}V_3R_{200}T_5$			x			x	x				x				
12	$C_{0.15}V_3R_{200}T_{15}$			x			x	x					x			
13	$C_{0.15}V_3R_{300}T_5$			x			x		x			x				
14	$C_{0.15}V_3R_{300}T_{60}$			x			x		x						x	
15	$C_{0.15}V_3R_{400}T_5$			x			x			x		x				
16	$C_{0.15}V_3R_{400}T_{15}$			x			x			x			x			
17	$C_{0.15}V_3R_{550}T_5$			x			x				x	x				A small part of the sample has been lost during spin coating as spill over the cover of spinner
18	$C_{0.15}V_3R_{550}T_{15}$			x			x				x		x			A large part of the sample has been lost during spin coating as spill over the cover of spinner
19	$C_{0.15}V_3R_{550}T_{30}$			x			x				x			x		
20	$C_{0.15}V_3R_{550}T_{60}$			x			x				x				x	
21	$C_{0.15}V_4R_{200}T_5$			x			x	x				x				A large part of the sample has been lost during spin coating as spill over the cover of spinner
22	$C_{0.15}V_4R_{200}T_{15}$			x			x	x					x			
23	$C_{0.15}V_4R_{300}T_5$			x			x		x			x				
24	$C_{0.15}V_4R_{300}T_{15}$			x			x		x				x			
25	$C_{0.15}V_4R_{400}T_5$			x			x			x		x				
26	$C_{0.15}V_4R_{400}T_{15}$			x			x			x			x			
27	$C_{0.15}V_4R_{550}T_5$			x			x				x	x				
28	$C_{0.15}V_4R_{550}T_{15}$			x			x				x		x			
29	$C_{0.15}V_4R_{550}T_{30}$			x			x				x			x		
30	$C_{0.15}V_4R_{550}T_{60}$			x			x				x				x	

3.3.2 Preparation of PVA/GO Nanocomposite Films

Different concentrations of GO were prepared using dilution factor from stock solution of GO (5g/l). The diluted solution was divided into 3 parts to add PVA and prepare PVA/GO nanocomposite solutions with 5, 10, 15 wt.% PVA, then the solution was heated on hot plate at 80 °C for 30min. These three concentrations of PVA/GO nanocomposite were sonicated using bath sonication at 80 °C for 30 min and ultrasonicated for two minutes in order to obtain homogeneous solution. These solutions were labeled as G_{2.5} P₅, G_{2.5} P₁₀, G_{2.5} P₁₅. A 1, 0.5, 5g/l of GO with different concentrations of PVA (5, 10, 15%) were prepared using the same previous manner. (Figure 3.2) show some picture of preparing PVA/GO solutions.

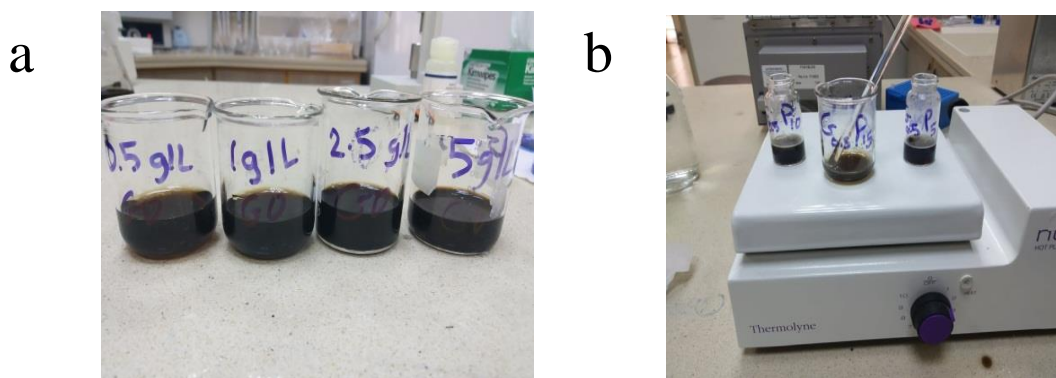


Fig 3.2: Images of PVA/GO nanocomposite solutions, a) A picture of four concentration that diluted from stock solution, b) the PVA/GO nanocomposite using hot plate at temperature 80 °C for 30 min.

All Solutions were adopted to casting method, which is a casting method with different volumes (2,3 and 4 ml) on plastic petri dishes and left to dry at ambient condition for 3days to be ready for characterization.

Matrix of PVA/GO nanocomposite is shown in (Table 3.2) and flow chart for PVA/GO nanocomposite films preparation show in flow chart (Figure 3.3)

Table 3.4 :Matrix of PVA/GO nanocomposite preparation.

No.	Code	Conc. Of GO " %"				Conc. Of PVA "%"			Volume		
		0.05	0.1	0.25	0.5	5	10	15	2	3	4
1.	G _{0.5} P ₅ V ₂	x				x			x		
2.	G _{0.5} P ₅ V ₃	x				x				x	
3.	G _{0.5} P ₅ V ₄	x				x					x
4.	G _{0.5} P ₁₀ V ₂	x					x		x		
5.	G _{0.5} P ₁₀ V ₃	x					x			x	
6.	G _{0.5} P ₁₀ V ₄	x					x				x
7.	G _{0.5} P ₁₅ V ₂	x						x	x		
8.	G _{0.5} P ₁₅ V ₃	x						x		x	
9.	G _{0.5} P ₁₅ V ₄	x						x			x
10.	G ₁ P ₅ V ₂		x			x			x		
11.	G ₁ P ₅ V ₃		x			x				x	
12.	G ₁ P ₅ V ₄		x			x					x
13.	G ₁ P ₁₀ V ₂		x				x		x		
14.	G ₁ P ₁₀ V ₃		x				x			x	
15.	G ₁ P ₁₀ V ₄		x				x				x
16.	G ₁ P ₁₅ V ₂		x					x	x		
17.	G ₁ P ₁₅ V ₃		x					x		x	
18.	G ₁ P ₁₅ V ₄		x					x			x
19.	G _{2.5} P ₅ V ₂			x		x			x		
20.	G _{2.5} P ₅ V ₃			x		x				x	
21.	G _{2.5} P ₅ V ₄			x		x					x
22.	G _{2.5} P ₁₀ V ₂			x			x		x		
23.	G _{2.5} P ₁₀ V ₃			x			x			x	
24.	G _{2.5} P ₁₀ V ₄			x			x				x
25.	G _{2.5} P ₁₅ V ₂			x				x	x		
26.	G _{2.5} P ₁₅ V ₃			x				x		x	
27.	G _{2.5} P ₁₅ V ₄			x				x			x
28.	G ₅ P ₅ V ₂				x	x			x		
29.	G ₅ P ₅ V ₃				x	x				x	
30.	G ₅ P ₅ V ₄				x	x					x
31.	G ₅ P ₁₀ V ₂				x		x		x		
32.	G ₅ P ₁₀ V ₃				x		x			x	
33.	G ₅ P ₁₀ V ₄				x		x				x
34.	G ₅ P ₁₅ V ₂				x			x	x		
35.	G ₅ P ₁₅ V ₃				x			x		x	
36.	G ₅ P ₁₅ V ₄				x			x			x

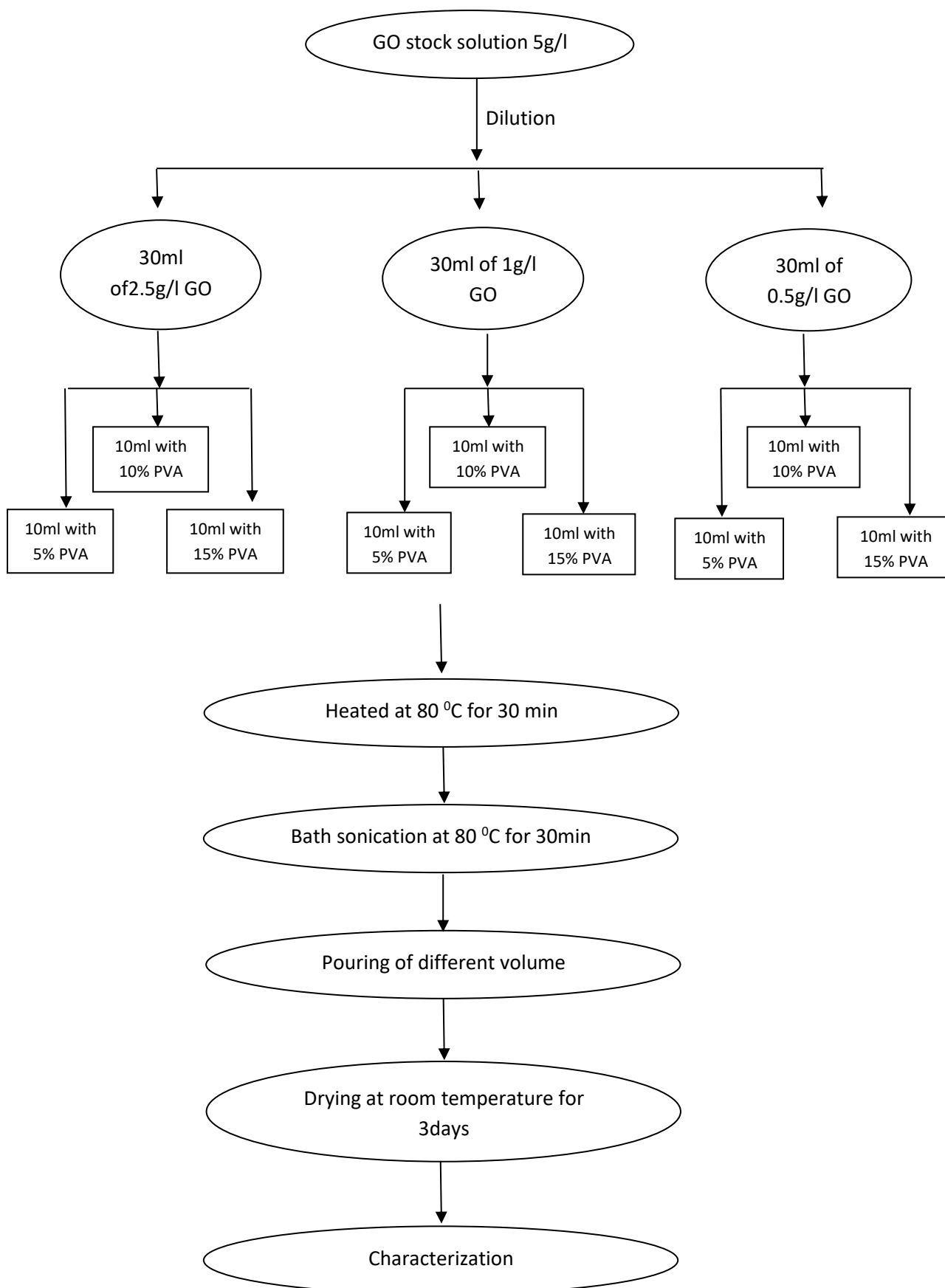


Fig 3.3: Flow chart for PVA/GO nanocomposite films preparation

3.3.3 Preparation of methylcellulose thin film

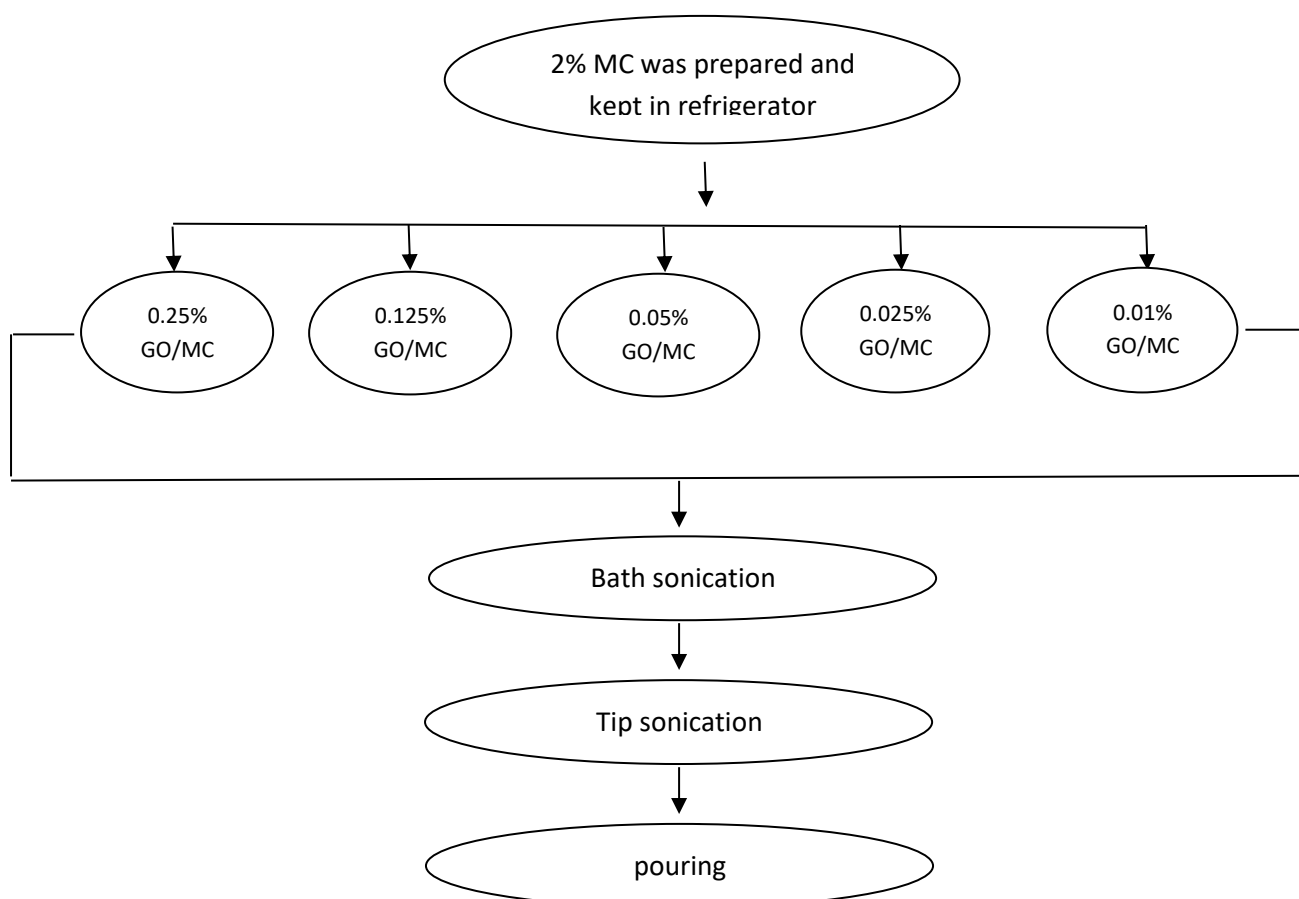
A 1.0 g of methylcellulose was added to 50ml distilled water to prepare solution with 2% concentration. Then the solution was kept in refrigerator at 4°C for overnight followed by stirring at room temperature by using magnetic stirrer. A 3 ml of MC solution was poured in plastic petridish and dried for 3 days at room temperature.

3.3.4 Preparation of MC/GO nanocomposite films

Five different concentrations of GO were prepared in distilled water; these concentrations are 0.25%, 0.125%, 0.05%, 0.025% and 0.01%.

Initially the MC/GO solution was sonicated using bath sonication at 100 watt for 5 min, followed by tip sonication for 2min. A 3ml from each concentration was poured in petridishes and let to dry at room temperature for 3 days.

Flow chart of MC/GO show in (Figure 3.4)



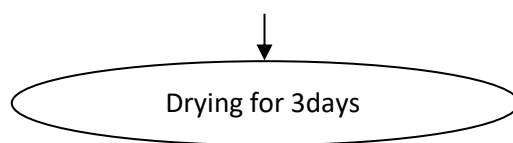


Fig 3.4: Flow chart for MC/GO nanocomposite films preparation.

3.3.5 Analysis and Characterization of PVA/GO Films

a) Measurement of Thickness

The thickness of PVA thin films was measured using digital caliber and calculations that depend on weighing the sample that cut into squares, then measuring the volume according to equation: $\text{Volume} = \text{mass} / \text{density}$. The volume calculation used for thickness calculation according to the following equation: $\text{Volume of cube} = \text{length} * \text{width} * \text{height (thickness)}$. The thickness of PVA/GO films was determined by using the digital caliber, the thickness of each sample was measured at 4 different locations and averaged by using Digital Caliber. The thickness of MC and MC/GO nanocomposite were measured as described with PVA samples.

b) Thermal Properties

DSC was performed for pure 10% PVA, pure 2% MC films and for samples contained different concentration of GO with different concentration of PVA and MC.

A 3.0 mg of each sample was cut using a scissors and weighed on a digital balance, the samples were sealed inside DSC pans, the changes in its heat capacity are tracked as changes in heat flow. This process provides thermal information as glass transition temperature, melting/crystallization behavior, degree of crystallinity, solid-solid transitions,

polymorphism, cross-linking reactions, specific heat, purity determination, oxidative stability, and decomposition behavior.

The heating program was performed in the range from 25 °C to 200°C and then cooled to 25 °C at a rate of 10°C to obtain melting and crystallization temperature. The sample was reheated to 400 °C at the same rate to obtain glass transition temperature and degradation temperature.

c) Mechanical Properties

The tensile properties (TS) and elastic modulus for all films were performed using Universal Mechanical Test Machine. Mechanical properties of material provide information about the mechanical resistance and its suitability to our application.

The films were cut into rectangular strips (2×4cm) with a thickness maintained at (0.01_0.05) mm.

The basic idea of a tensile test is placing a sample between two clamps, which pull the material until it breaks. The force and the elongation are measured and the plot of stress versus strain can be generated.

Mechanical test was performed only for high concentration of PVA.

The MC and 5% PVA are not applicable in this machine.

d) Fourier-Transferred Infrared Spectrometer (FT-IR)

The FTIR is a technique utilized as a fingerprint of the sample depends on IR radiation that passes through the sample, some of the IR radiation absorbed and some of it transmitted. The resulting spectrum represents the molecular absorption and transmission.

FT-IR can provide a qualitative analysis about each kind of sample and determine the unknown material as well as determine the amount of components in a mixture.

The absorption spectra in the mid infrared region (4000-400 cm⁻¹) were taken and discussed.

e) Swelling and Solubility Test

The swelling and solubility tests were calculated by immersing the weighted samples in the distilled water overnight, Thereafter, the film removed, dried and weighted in order to measure the amount of adsorbed water by the film sample. The samples were dried at a temperature of 60 °C in an oven and then weighing them again to calculate swelling and solubility using the following equations:

$$\text{Swelling ratio} = ((M_2 - M_1) / M_1) * 100\%$$

$$\text{Solubility ratio} = ((M_1 - M_3) / M_1) * 100\%$$

M₁: Initial weight of film.

M₂: After immersing in distilled water over night.

M₃: After drying in oven overnight.

Swelling and solubility tests of MC are non-applicable, the entire sample was dissolved in water and the film was disappeared.

3.4 Methodology

The permeability and the real knowledge of food spoilage are play a key role to identify the expired date in food packaging.

So that, the trends now are toward a more sustainable food system that guarantee safety, quality, prolonged shelf life and developing in process. These criteria are being achieved using innovative materials instead of conventional material as nanoparticles.

The purpose of this research is to introduce graphene oxide nanoparticles on polyvinyl alcohol and methyl cellulose polymers material in order to developing active system.

Graphene oxide has superior properties and densely packed regime when properly dispersed in polymer matrix.

This research requires a lot of work and a lot of steps to get the final results. At first step polyvinyl alcohol and MC were chosen due to its availability, good biodegradability, processability and acceptable mechanical and thermal properties. PVA is soluble in water and has hydrophilic nature and this corresponds to the use of graphene because it is also soluble in water and able to form hydrogen bonding with this polymer.

Three concentrations of pure PVA was prepared and casted in plastic petridishes. GO was introduced to PVA and MC to study the effect of GO on swelling ratio. Swelling ratio gives us an indication of the ability of water molecules or any gases to penetrate the polymer. If the addition of GO reduce the swelling ratio of polymer, this means the ability of GO nanoparticles to act as a barrier and reduce the permeability of polymer. In addition, reducing permeability means the ability to trap molecules and gases emitted from spoiled food.

The second analysis was performed for pure PVA, PVA/GO, MC and MC/GO is FT-IR to examine the interaction between the polymer and nanoparticles.

Thermal and mechanical tests were also investigated to study the effect of GO on polymer strength, thermal stability, and suitability for food packaging.

Chapter Four: Results and Discussion

4.1 Introduction

This chapter show the results was obtained and discussion for this results to provide a clear explanation about the purpose of this research. Each result will be linked to what appeared in the literature review and try to find logical solutions to the reasons of difference

The results which obtained divided into: thermal properties of GO with PVA, mechanical properties of GO with PVA, swelling and solubility of GO with polymers (PVA& MC), and FT-IR of GO with polymers (PVA & MC).

4.2 Superior Properties of Graphene Oxide

4.2.1 Thermal Properties of PVA with Graphene Oxide:

The thermal properties of PVA/GO were investigated by using differential scanning calorimeter (Figure 4.1). The glass transition temperature of pure 10% PVA is 79.6 °C, it was increased as the concentration of GO increased to reach the value of 86.6 at 0.5% GO as shown in Table 4.1. This behavior is attributed to strong hydrogen bonding between GO and the polymer matrices. The melting temperature slightly increased by the addition of GO, which also confirm the thermal enhancement that obtained by incorporation GO nanoparticles. In addition, the temperature of degradation was increased by incorporation of GO nanoparticles; it was changed from 231.5 °C for neat PVA to 242.7 °C for 0.5% PVA/GO nanocomposite. This increase in degradation is due to rigid structure of nanocomposite, stability of hydrogen bonding and thermal stability of GO nanoparticles. Also may be due to barrier properties of GO that may hinder the diffusion of volatile decomposition products.

Degree of crystallization(%X_c) was calculated using the following equation (Batista, et al., 2016):

$$X_C = \left[\frac{\Delta H_m}{\Delta H_m^0 \times \left(1 - \frac{\%wt_{filler}}{100}\right)} \right] \times 100$$

ΔH_m is the melting enthalpy of PVA and PVA/GO nanocomposite, ΔH_m^0 is the theoretical melting enthalpy of 100% crystalline PVA (141.932 J/g) and %wt. filler is the weight percentage of GO.

The PVA crystallinity is 3.7% and it was increased at 0.05 and 0.1% to 6.4% and 6.7% respectively. Then it was decreased to 6% and 4.2% when the concentration of GO was increased to 0.25%, and 0.5% respectively. This decrease is might be the formation of a constrained polymer region.

The degree of crystallinity affect the melting temperature. As the degree of crystallinity increased the melting temperature increased. In addition, as the crystallinity increased, the rigidity of polymer increase which affect the tensile strength.

In conclusion, GO can improve the thermal properties of PVA due to strong hydrogen bonding with polymer chains (Seira Morimune, et al. (2012), Chengpeng, et al. (2013), and Meryem Goumri, et al. (2017)).

The results are fully compatible with Seira Morimune, et al. (2012). It is corresponds with Chengpeng, et al. (2013), and Meryem Goumri, et al. (2017) with respect to glass transition and degradation temperature , but differs in the melting and crystallization temperature results. Perhaps because of usage different molecular weight of PVA and different concentration of GO.

Table 4.1 DSC results of Different concentrations of GO with 15% PVA concentration

	First Heating		Cooling	Second Heating	
GO%	T_m (C°)	ΔH_m (J/g)	T_c (C°)	T_g (C°)	Initial Td (C°)
0%	228.1	5.3173	139.4	79.6	231.5
0.05%	229.1	9.0912	209.1	81.2	237.8
0.1%	230.3	9.5767	211.8	84	238
0.25%	229.4	8.4513	211.7	84.2	237.8
0.5%	229.5	5.9637	210.7	86.6	242.7

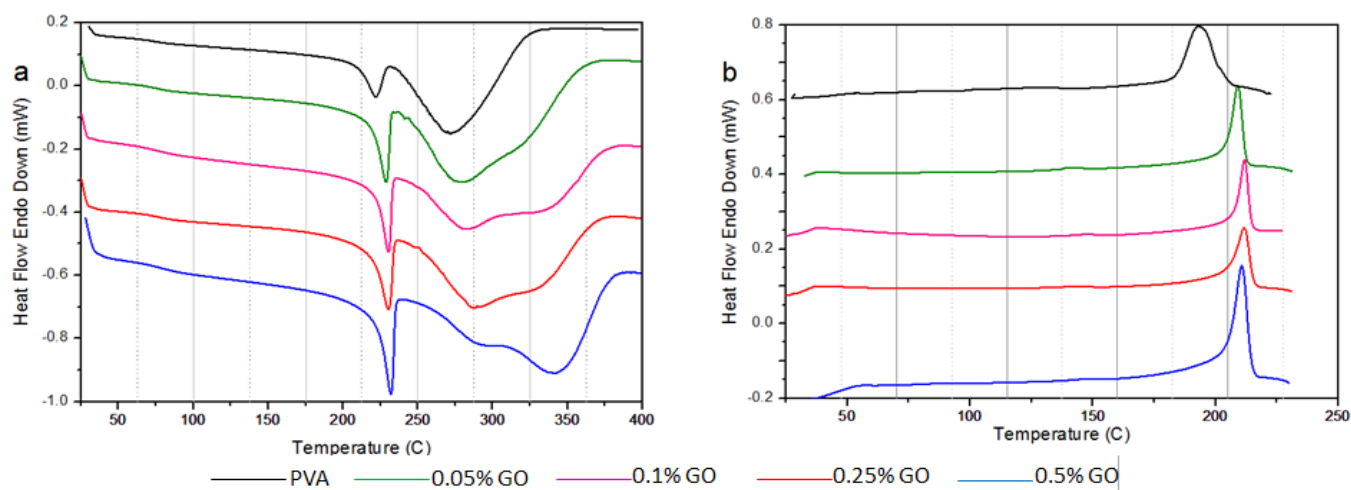


Fig 4.1. Thermal properties of GO/PVA. a) glass transition temperature, melting temperature, and degradation temperature. b) Crystallization temperature induced from cooling step.

4.2.2 Mechanical Properties of Polyvinyl alcohol with Graphene Oxide:

Figure 4.2 shows the stress-strain curve of 10% and 15% PVA with different concentration of GO. By comparing the 10% with 15% neat PVA, the tensile stress of 10% is more than 15%, the reason is due to the higher solubility of 10% PVA in water. At a higher concentration of PVA, the water become unable to absorb all polymer molecules and does not dissolved. In addition, at higher concentration, chains interact by hydronamic interaction. Also begin to agglomerate, form entanglements, and form network by physical crosslinks.

The ductility of 15% is more than 10%, this behavior might be due to rigidity of higher concentration of PVA and a complex network that enhance the ductility of film.

At 10% PVA with different concentration of GO (Fig 4.2 a.), there is no significant effect on tensile strength with addition GO, the reason is that the low concentration of the polymer contains

large voids that the GO was not able to fill it completely, to give a clear effect on the tensile strength at the molecular level.

In the other hand, the elongation was increased as the GO content increased. It is 46% for pure 10% PVA and increased to 132% at 0.5% GO incorporation, this confirmed the significant improvement in mechanical properties that obtained by GO into PVA matrix. The enhanced mechanical properties are increased from a well dispersion of GO on PVA matrix, and a strong hydrogen bonding between PVA and GO. The ductility results correspond with Lu Zhang, et al., 2011, Vorrada Loryuenyong, et al., 2015, and Meryem Goumri, et al. 2017. However, it is Conflicting with Seira Morimure, 2012. Perhaps the reason is the usage lower concentration of PVA (5%). The tensile strength in these researches were affected and increased as the GO concentration increased Contrary to our result. May be is due to usage different concentrations of PVA and GO contrary to what we used.

Fig 4.2b shows the 15% PVA with different concentration of GO, tensile strength increased from 35.4 MPa for PVA to 63.4 MPa for 0.1% GO. After that at 0.5% GO it was decreased to 45.5MPa, but still above neat PVA value. This explains that there is a certain limit of the GO concentration to fill all the voids with the polymer and so increase its strength. Above this concentration, the sheet layers become closer and GO particles begin to agglomerate. Therefore it gives an opposite result, which is reducing the strength.

This result corresponds with Lu Zhang, et al., 2011, Vorrada Loryuenyong, et al., 2015, Seira Morimure, et al. 2012 and Meryem Goumri, et al. 2017.

The ductility result of 15% PVA was in contrary with 10% PVA, it decreased with increasing GO content. It was reduced from 106% for pure PVA to 67.7% for 0.5% GO, this is due to: (I) increasing in brittleness that caused from GO with high concentration of PVA.(II) It indicated the poorer dispersion of GO in PVA matrix. (III) And finally may be to the decrease in the porous

and vacancies in the polymer matrix with the increase in the proportion of GO particles, which leads to the inability of the bonds to expand and move freely, therefore, the ductility decreased as increasing the GO contents.

Ductility results of 15% were correspond with Seira Morimune, et al. 2012. However, it is conflicting with Lu Zhang, et al., 2011, Vorrada Loryuenyong, et al., 2015, and Meryem Goumri, et al. 2017. Perhaps due to the usage higher concentration of GO.

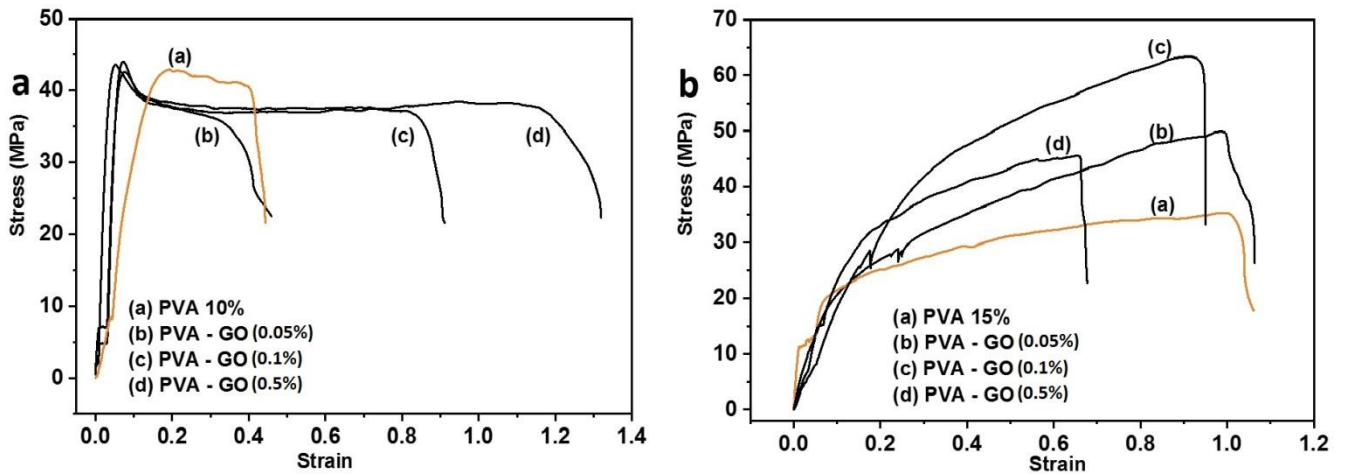


Fig 4.2: mechanical properties of PVA/GO

4.2.3 Swelling and Solubility of Polymers (PVA& MC) with Graphene Oxide

4.2.3.1 Swelling and Solubility of Polyvinyl alcohol with Graphene Oxide

As shown in Figure 4.4, the swelling rate of 5% PVA decreased slowly from 0 to 0.25% GO, but at 0.5% GO swelling increased, that means the swelling rate decreased as the GO content increased. The highest value of swelling was observed at 5% PVA, and the lowest value is at 0.25% GO. The decreasing in swelling is due to effect of GO nanoparticles. PVA chains have a porous in its structure, which can hold large number of water molecules, but an addition of GO decreases the space between the polymer chains, and produce more rigidity which cannot

expanded to hold more water molecules. In conclusion, the graphene oxide acts as a barrier for penetration of water molecules.

The solubility rate is increased slowly with adding GO particles, the highest solubility rate is for PVA with 0.1% GO, and the lowest value is for 0.05% GO. At the concentration of 10%, there is no effect on swelling and solubility rate with adding GO nanoparticles.

A decreasing logarithmic trend of the swelling and solubility rate of 15% PVA were observed. Both are decreasing rapidly with adding GO from 329% to 161% for swelling rate and from 40% to 8% for solubility rate as shown in Table 4.2. The swelling rate is attribute to synergistic effect of both high viscosity of PVA and barrier molecules from GO that obstruct the penetration of water molecules through the matrix.

The difference between the effect of GO on the solubility of 5 and 15% of PVA might be due to the viscosity, at lower concentration of PVA the viscosity is low and thus the porous is large and allows water and GO to bind with groups of polymer and so dissolved easily. At higher concentration the viscosity is high and impedes the movement of water molecules inside the polymer to attached with them, so the solubility decrease.

The difference between the effect of GO on the solubility of 5 and 15% of neat PVA attributed to abundance of binding sites, At higher concentration of PVA, the binding sites for GO interaction with PVA are higher than of 5% PVA. Therefore, the solubility of polymer increased.

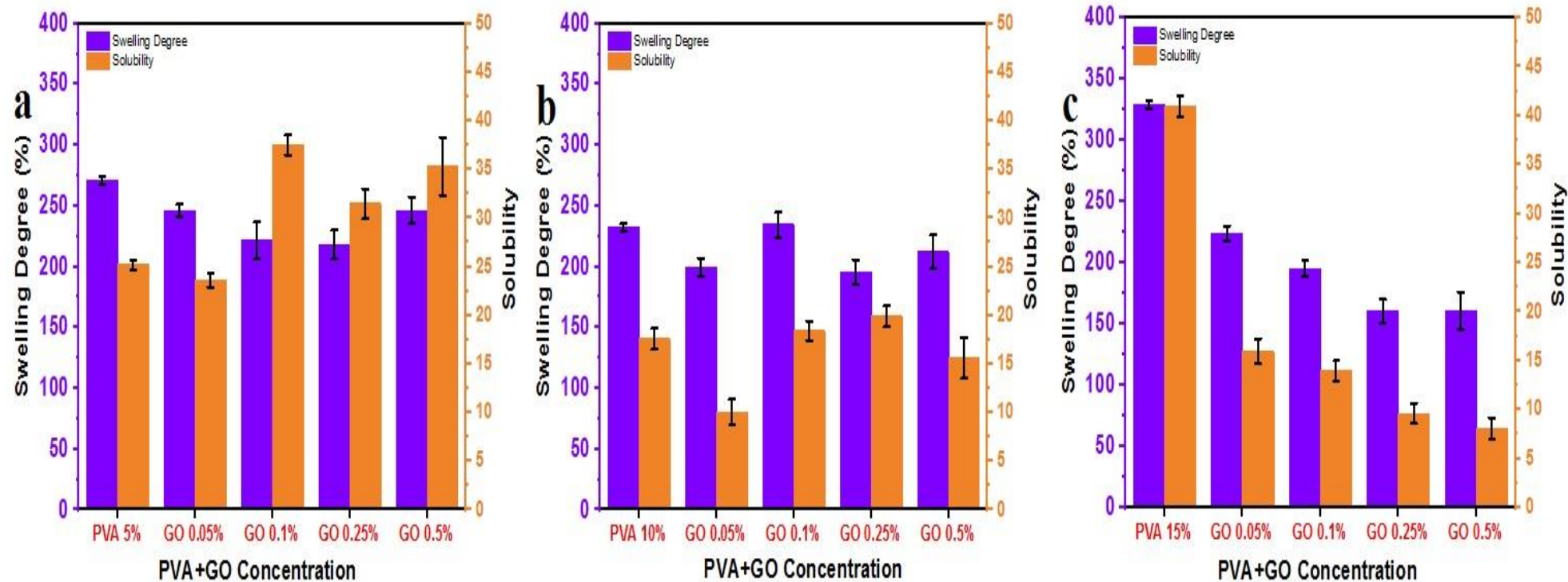


Fig 4.3: swelling and solubility rate of PVA/ GO nanocomposite

Table 4.2: Swelling and Solubility Rate of PVA with Different Concentration of GO

PVA %	GO %	Swelling %	Er±	Solubility %	Er±
5%	0%	271.014	3.5	25.217	0.5
5%	0.05%	246.3483	4.8	23.59551	0.72
5%	0.1%	221.5278	15	37.5	1.01
5%	0.25%	218.1481	12	31.48184	1.53
5%	0.5%	246.1078	10.9	35.32934	3
10%	0%	232.4468	2.9	17.55319	1.08
10%	0.05%	199.8102	7.2	10.05693	1.29
10%	0.1%	234.4173	10.33	18.42818	1.01
10%	0.25%	195.8984	9.92	19.92188	1.09
10%	0.5%	212.4561	13.99	15.61404	2.09
15%	0%	329.227	3.05	40.985	1.08
15%	0.05%	224.1561	5.9	15.92827	1.29
15%	0.1%	194.9535	6.9	13.94422	1.01
15%	0.25%	160.1918	9.5	9.592326	1.05
15%	0.5%	160.7103	15	8.102109	1.09

4.2.3.2 Swelling and Solubility of Methyl cellulose with Graphene Oxide

Swelling test for MC was failed, because MC was disappeared completely and the GO appeared as black dye. The way of MC dissolve is in a pattern of forming slurry rather than real dissolving. This slurry happening when a rich amount of water is been added to MC, this MC particles start to absorb water molecules at micro level. By time of H₂O:MC interaction; more water particles imbedded inside the MC particles causing swelling state for these particles. However, the major component of these particles, namely: amylose and amylopectin were flushed out of the particles. This perfect state of H₂O:MC interaction ended up with forming entanglement state for new network. Thus more water particles were grabed inside MC particles which in turn caused major rupturing to such molecules therefore dye (GO) found to be separated in aggregated state.

4.2.4 Quality Assurance (IR of Graphene Oxide and Polymers (PVA&MC))

4.2.4.1 FT-IR of Polyvinyl alcohol with graphene oxide

a. FT-IR of Pure polyvinyl alcohol and pure Graphene oxide

The FT-IR spectra were used to evaluate the interaction between PVA and GO. The FT-IR spectrum of GO and PVA is shown in (Figure 4.5). For GO spectrum, the oxygen functional group were observed as the following: C=O, C-OH, and C-O can be assigned at the bands of 1727.9 cm⁻¹, 1253.5 and 1039 respectively. The hydroxyl group (O-H) can be noticed at 3441.3 cm⁻¹. C-H, C=C and CH₂ groups appeared at 2965.9 cm⁻¹, 1621.8cm⁻¹ , and 2865.98 cm⁻¹ respectively.

FT-IR spectrum of PVA shows the hydroxyl group (O-H) at 3370.9 and C-H at 2940.9.

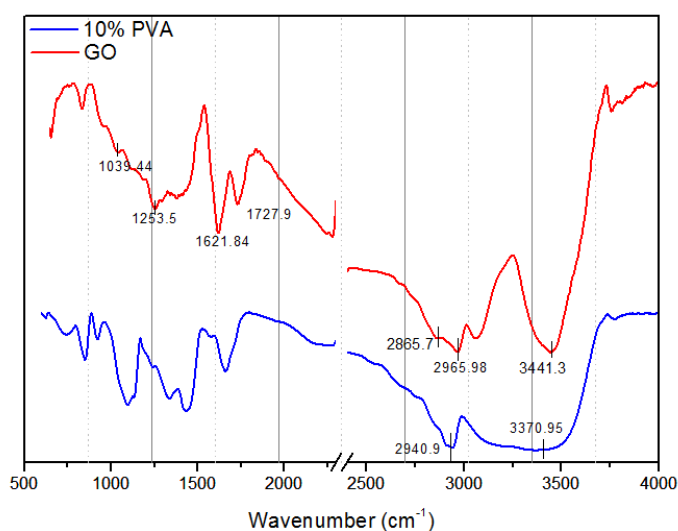


Fig. 4.4: FTIR Spectra of Graphene oxide (GO), Polyvinyl Alcohol (PVA)

a) FT-IR of Polyvinyl alcohol with different concentration of Graphene oxide:

The shift of hydroxyl group can be assigned to the interaction occurred between PVA and GO. At all concentration of PVA the shift is clear whether to lower or higher frequency as shown in (Figure 4.6 a, b and c.)

Figure 4.6a shows the shift of O-H group that occurs in all concentration of GO. Approximately there is a 42 degree of wavenumber shift to left occurs when add 0.05% and 0.5% GO to 5% PVA. It is indicated that the strong hydrogen bonding between polymer and GO occur at 5% PVA with these concentration of GO. For the concentrations of 0.1% and 0.25% of GO into PVA matrix, a clear shift attributed to the interaction between GO and polymer chains.

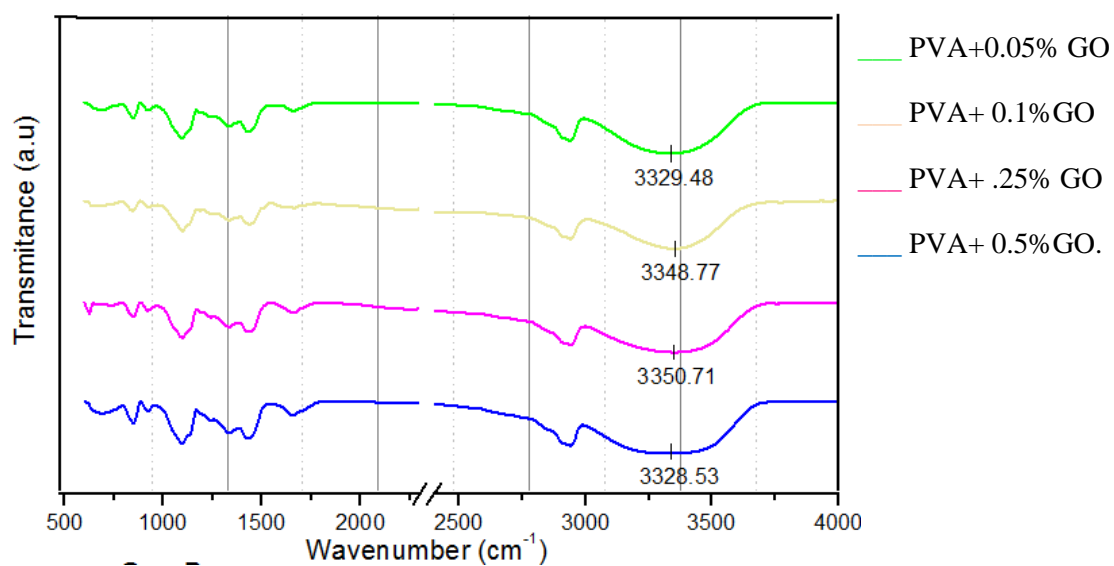


Fig 4.5: FT-IR of 5% PVA with different concentration of GO.

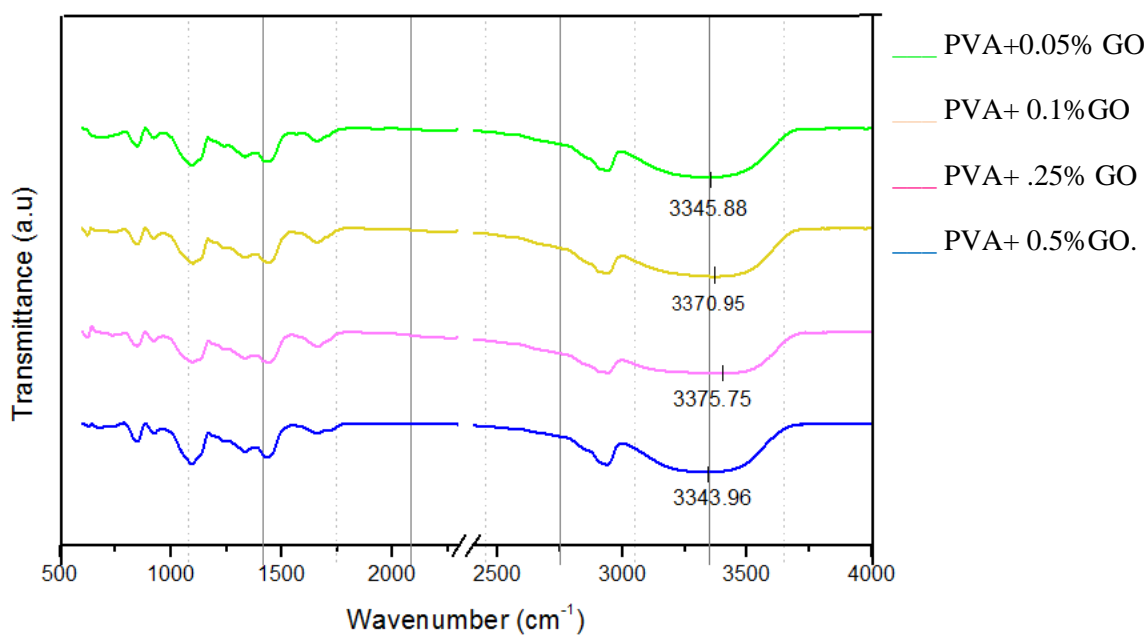


Fig 4.6: FT-IR of 10% PVA with different concentration of GO.

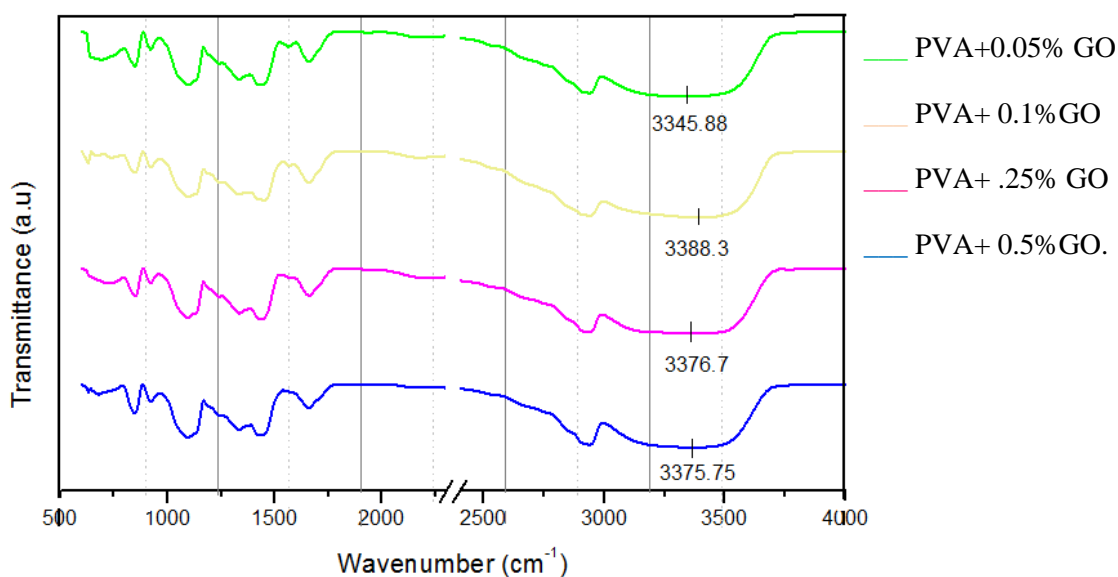


Fig 4.7: FT-IR of 15%PVAwith different concentration of GO.

4.2.4.2 FT-IR of methyl cellulose with Graphene oxide

a) FT-IR of Pure Methyl cellulose and Pure Graphene oxide:

FT-IR spectra of graphene oxide, methylcellulose and a nanocomposite films (MC/GO) were recorded.

Figure 4.9 exhibits the spectra of GO and pure MC. GO spectrum was explained in the previous section of PVA/GO.

MC spectrum shows broad band at 3451.9 cm^{-1} that corresponds to O-H group, C-O-C group (glucosidic unit) appeared at 1070 cm^{-1} . The absorption band at 2933 cm^{-1} attributed to C-H stretching band of pyranose unit. The bands at 1643 cm^{-1} and 948.8 cm^{-1} corresponded to C-H bending vibration and OCH_3 respectively.

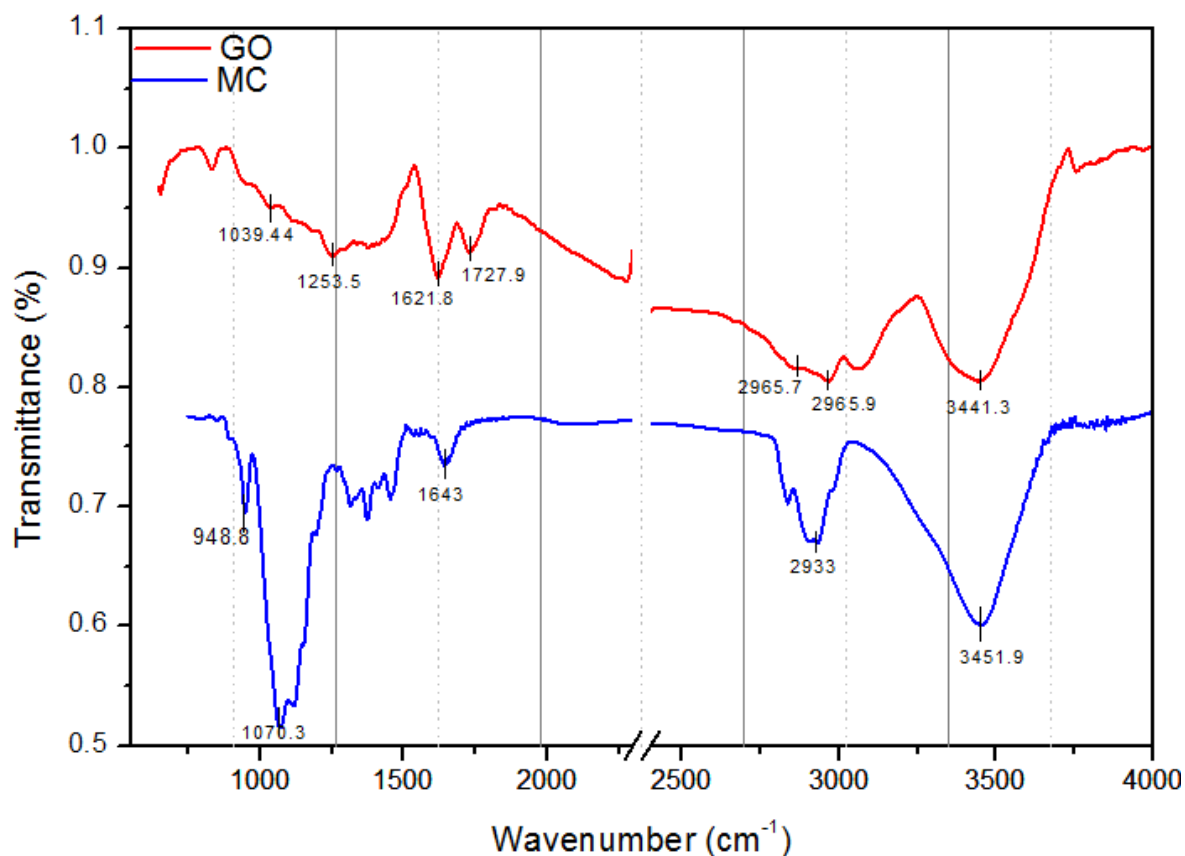


Fig 4.8: FT-IR spectra of graphene oxide, methyl cellulose.

b) FT-IR of Methyl cellulose with different concentration of graphene oxide

Figure 4.10 shows the FT-IR spectra of MC/GO nanocomposite, there is almost no effect occurs with adding GO particles, it may be assigned to that functional groups of MC were more stable and tolerated the effect of the GO limited concentration addition.

The results of MC/GO are conflicting with Rama Kanta Layek, et al., (2018) who finds a shift at O-H group by 11 units for MC with 5% GO and by 6 unit for MC with 1% GO.

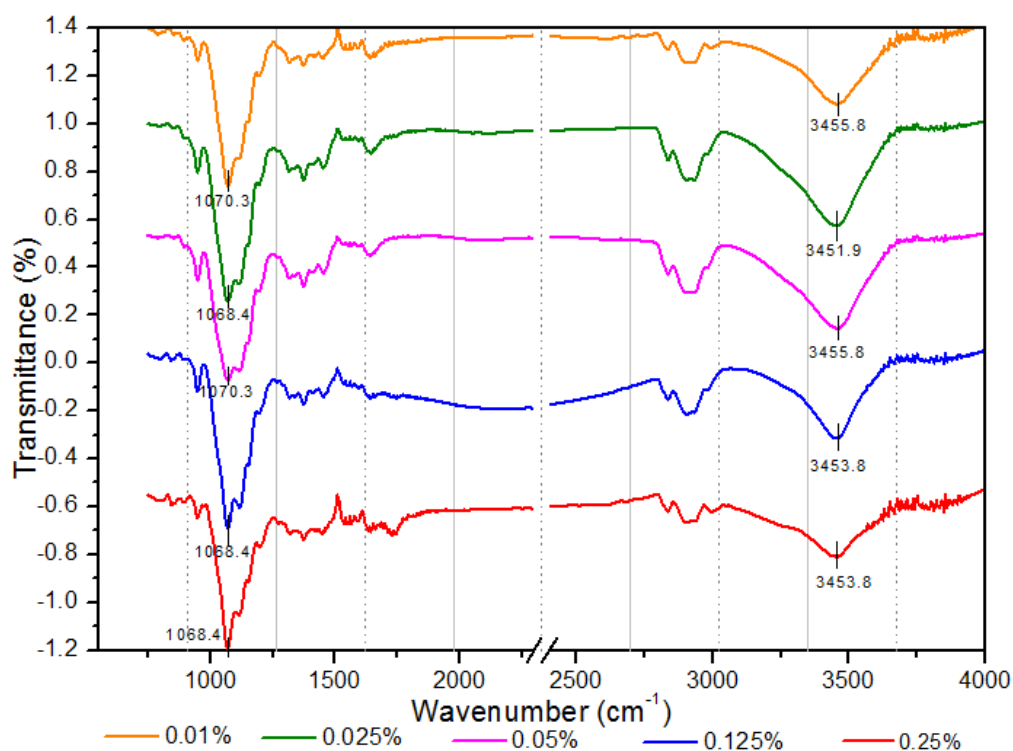


Fig 4.9: FT-IR of methyl cellulose with different concentration of GO.

4.2.5 Thickness test of pure PVA, pure MC, PVA/GO nanocomposite, and MC/GO nanocomposite.

The thickness of PVA films and PVA/GO nanocomposite measured by using caliber was between 0.02mm to 0.05mm according to concentration of polymer, that means as the concentration increased the thickness increased.

Thickness of MC and MC/GO was maintained between 0.01 to 0.03 mm. thickness table of PVA and MC with GO were present in table 4.3 and Table 4.4.

Table 4.3: Thickness table of 5,10 and 15% PVA with Different Concentration of GO

PVA%	GO%	M ₁	M ₂	L ₁	L ₂	Average	Total average
5%	0%	0.02	0.02	0.02	0.02	0.02	0.0172
5%	0.05%	0.01	0.01	0.01	0.01	0.01	
5%	0.1%	0.02	0.02	0.03	0.02	0.0225	
5%	0.25%	0.01	0.01	0.01	0.007	0.00925	
5%	0.5%	0.007	0.01	0.01	0.07	0.02425	
10%	0%	0.04	0.05	0.04	0.04	0.0425	0.0375
10%	0.05%	0.04	0.04	0.05	0.04	0.0425	
10%	0.1%	0.03	0.03	0.04	0.03	0.0325	
10%	0.25%	0.03	0.03	0.04	0.03	0.0325	
10%	0.5%	0.03	0.04	0.04	0.04	0.0375	
15%	0%	0.05	0.05	0.05	0.05	0.05	0.051
15%	0.05%	0.04	0.06	0.04	0.04	0.045	
15%	0.1%	0.04	0.05	0.05	0.05	0.0475	
15%	0.25%	0.05	0.06	0.05	0.06	0.055	
15%	0.5%	0.06	0.07	0.05	0.05	0.0575	

Table 4.4: Thickness Test of MC with Different Concentration of GO

MC%	GO%	M ₁	M ₂	L ₁	L ₂	Average
2%	0%	0.03	0.03	0.02	0.03	0.0275
2%	0.01%	0.01	0.02	0.01	0.01	0.0125
2%	0.025%	0.02	0.01	0.01	0.01	0.0125
2%	0.05%	0.01	0.01	0.01	0.01	0.01
2%	0.125%	0.01	0.02	0.01	0.01	0.0125
2%	0.25%	0.01	0.01	0.01	0.01	0.01

5 Conclusion and future work

- a) PVA/GO and MC/GO nanocomposite were prepared by simple casting method.
- b) The interaction leads to improving the thermal properties. It lead to increased in T_g, melting, degradation, and crystallization temperature.
- c) The tensile strength of 15% PVA was increased with addition GO to 0.1%. the ductility of 10% PVA was increased with adding GO to 0.5%.
- d) Barrier properties of GO was interpreted by decreasing in swelling as the concentration of GO increased especially at 15% PVA.
- e) FT-IR of PVA/GO nanocomposite indicate the strong interaction between polymer and GO particles .
- f) On the basis of these results, the improvement on polymer porperties can be ascribed to a homogenous dispersion of GO in polymer matrix and efficient interaction between both components.
- g) In the future, it will be applied to specific foods that include water-based foods, fatty-based foods, liquid foods and solid foods.

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تقييم وظيفة أكسيد النانوجرافين لتطبيقات تغليف المواد الغذائية.

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ملخص:

تم انتاج أكسيد الجرافين باستخدام تفاعل الاكسدة والاختزال (طريقة هامر). تم استخدام أكسيد الجرافين لتضمينها في بوليمر الكحول متعدد الفايثيل والميثيل سليولوز من أجل دراسة الخواص الحرارية والخواص الميكانيكية، وكذلك اختبارات التورم والذوبان.

تم استخدام تراكيز مختلفة من بوليمر الكحول متعدد الفايثيل (5، 10 و 15%) مع تراكيز مختلفة من اكسيد الجرافين (0.05 ، 0.1 ، 0.25 و 0.5%) لتحضير مركب النانو كحول متعدد الفايثيل/ اكسيد الجرافين باستخدام طريقة الصب البسيطة. تم استخدام 2% من الميثيل سليولوز مع تراكيز مختلفة من اكسيد الجرافين (0.01 ، 0.025 ، 0.05 ، 0.125 و 0.25 %) لتحضير مركب النانو ميثيل سليولوز/ اكسيد الجرافين باستخدام طريقة الصب البسيطة أيضاً.

تمت دراسة الخواص الحرارية باستخدام مسعر المسح التبايني (DSC)، وأظهرت النتائج أن الخواص الحرارية تحسنت من خلال دمج أكسيد الجرافين في مصفوفة الكحول متعدد الفايثيل. درجة الانتقال الحراري (Tg) زادت من 79.6 للكحول متعدد الفايثيل النقي إلى 86.6 درجة مئوية عند اضافة 0.5% من أكسيد الجرافين.

درجة حرارة التحلل زادت أيضاً من 231.5 ووصلت إلى 242.7 درجة مئوية عند 0.5% من اكسيد الجرافين. درجة حرارة البلورة زادت إلى حد ما.

قوة الشد في 15% كحول متعدد الفايثيل زادت بزيادة نسبة أكسيد الجرافين إلى 0.25% ، ولكن الاستطالة انخفضت. عند 10% كحول متعدد الفايثيل زادت الاستطالة بزيادة نسبة الجرافين أكسيد.

نسبة التورم عند 5 و 15% كحول متعدد الفايثيل قلت بزيادة نسبة أكسيد الجرافين والتي تفسر خصائص حاجز اكسيد الجرافين في المستوى الجزيئي لمصفوفة البوليمر. ومع ذلك زادت القابلية للذوبان عند 5% مع زيادة نسبة أكسيد الجرافين، ولكنها انخفضت بسرعة عند 15% مع زيادة نسبة الجرافين أكسيد.

تؤكد أطياف تحويل فورييه الطيفي بالأشعة تحت الحمراء (FT-IR) من مركبات النانو كحول متعدد الفايثيل/ أكسيد الجرافين الترابط الهيدروجيني القوي بين البوليمر والجسيمات النانوية.

باختصار، دمج أكسيد الجرافين في مصفوفة بوليمر كحول متعدد الفاينيل يحسّن الخواص الحرارية والميكانيكية والحاجز للبوليمر، بسبب تفاعل الهيدروجين القوي بين جزيئات البوليمر وأكسيد الجرافين.