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"Prepare Polymeric Nanocomposites for Biomedical Application"

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قال تعالى

» وقُلِ اعْمَلُوا فَسَيَرَى اللَّهُ عَمَلَكُمْ وَرَسُولُهُ وَالْمُؤْمِنُونَ ۖ هَادَةِ فَيُنَبِّئُكُمْ بِمَا كُنْتُمْ تَعْمَلُونَ«

صدق الله العلي العظيم

Abstract

The availability of different types of wound dressings has increased in the last decade. Wound care practitioners have at their disposal an extensive range of dressings. Emerging dressing types include interactive/bioactive dressings and tissue-engineered skin substitutes. There is no one dressing that is suitable for the management of all types of chronic wounds and few are suited for the treatment of a single wound during all stages of the healing cycle. Successful wound management depends on an understanding of the healing process combined with knowledge of the properties of the various dressings available.

The current study interested with prepared blend of biodegradable polymers (70% PVA and 30% PEG) reinforced with different weight fraction of magnesium oxide nanoparticles (MgO) (0.2, 0.4 and 0.6)w.t% for biodegradable wound dressing. From FTIR results, the chemical bonds don't create but only the hydrogen bonding between PVA, PEG and MgO. The test of contact angle refers the contact angle of blend is 56.289° which indicate the polymeric blend has hydrophilic nature and the contact angle also decreased with addition MgO that made the film more hydrophilic which increased the biocompatibility of the film and enhance the adhesion of livening cells which accelerate the healing process of the wound and also increased the degradability process after used the wound dressing. The DSC results show The T_m of blend PVA/PEG was 53.16 °C and the T_m of nanocomposite increased with the addition of different weight fraction of MgO nanoparticles due to addition these nanoparticles which improved the thermal stability of the film. Moreover, the tensile strength and elastic modulus increased with increased the weight fraction of MgO nanoparticles due to good adhesion between the blend and reinforcement phase and also due to the nature of particles of MgO that is a ceramic materialhas a high mechanical properties which enhances the tensile strength and elastic modulus of the polymer.

CHAPTER 1

INTODUCTION

A wound is defined as a disruption in the continuity of the epithelial lining of the skin or mucosa resulting from physical or thermal damage. According to the duration and nature of healing process, the wound is categorized as acute and chronic [1] An acute wound is an injury to the skin that occurs suddenly due to accident or surgical injury. It heals at a predictable and expected time frame usually within 8-12 weeks depending on the size, depth and the extent of damage in the epidermis and dermis layer of the skin. Chronic wounds on the other hand fail to progress through the normal stages of healing and cannot be repaired in an orderly and timely manner [2]Chronic wounds generally results from decubitus ulcer, leg ulcer and burns. Wound healing is a dynamic and complex process of tissue regeneration and growth progress through four different phases (i) the coagulation and hemostasis phase (immediately after injury); (ii) the inflammatory phase, (shortly after injury to tissue) during which swelling takes place; (iii) the proliferation period, where new tissues and blood vessels are formed and (iv) the maturation phase, in which remodeling of new tissues takes place. These phases occur in an ordered manner overlapping with each other in a well-connected cascade .Promotion of these phases are largely depends on the wound type [3], and its associated pathological conditions and the type of dressing material. With the advancement in technology, currently, different types of wound dressing materials are available for all types of wounds. But the selection of a material for a particular wound is important to achieve faster healing. In this review, an attempt has been made to consolidate the different types of wound dressing materials and their function on healing process.

The restoration of wounds with variable thickness and intensity is one of the most vital, interactive, and arduous processes occurring during human lifeDifferent parts of human body (i.e., extracellular matrix molecules, mediators, fibroblasts and keratinocytes, and infiltrating leukocyte subtypes) are involved in a complex interaction to repair the integrity of the damaged tissue and regenerate the lost one.[4] For this purpose, wound healing includes three continuous stages of inflammation, proliferation, and maturation.
Figure **1** presents a schematic of the wound healing process.

Fig: Main stages of the wound healing process, adapted with permission from ref. [5]

Wound, whether it is a minor cut or a major incision, it is important to care for it properly, part of this process includes wound dressing. Dressing is designed to be in contact with the wound, which is different from a bandage that holds the dressing in place. Historically, wet-to-dry dressings have been used extensively for wounds requiring debridement. In 1600 BC, Linen strips soaked in oil or grease covered with plasters was used to occlude wounds. Clay tablets were used for the treatment of wounds by Mesopotamian origin from about 2500 BCE. They cleaned wounds with water or milk prior to dressing with honey or resin. Wine or vinegar usage for cleaning the wounds with honey, oil and wine as further treatment was followed by Hippocrates of ancient Greece in 460- 370 BCE. They used wool boiled in water or wine as a bandage [6]. There was a major breakthrough in the antiseptic technique during the 19th century, antibiotics were introduced to control infections and decrease mortality. Modern wound dressing arrival was in 20th century [7].

When the wound is closed with dressing they are continuously exposed to proteinases, chemotactic, complement & growth factors, which is lost in the wound exposed. So during late 20th century, production of occlusive dressing began to protect and provide moist environment to wound. These dressings helps in faster re-epithelialization, collagen synthesis, promotes angiogenesis by creating hypoxia to the wound bed and

decreases wound bed pH which leads to decrease in the wound infection [8]. Woven absorbent cotton gauze was used in 1891. Until the mid-1900's, it was firmly believed that wounds healed more quickly if kept dry and uncovered whereas 'closed wounds heal more quickly than open wound' written in an Egyptian medical text -Edwin smith surgical papyrus in 1615 BC. Oscar Gilje in 1948 describes moist chamber effect for healing ulcers. In the mid 1980's, the first modern wound dressing were introduced which delivered important characteristics providing moisture and absorbing fluids (e.g. polyurethane foams, hydrocolloids, iodine-containing gels). During the mid 1990's, synthetic wound dressings expanded into various group of products which includes hydrogels, hydrocolloids, alginates, synthetic foam dressing, silicone meshes, tissue adhesives, vapor-permeable adhesive films and silver/collagen containing dressing.

Types of wound dressings

Knowing different kinds of wound dressings can dramatically increase the wound healing process and prevent infection. Follow along to learn more about which types of wound dressing best promote healing.[9]

1. Gauze

Gauze, or cloth, dressings are made of woven cotton fabric in various sizes and shapes. Most common are gauze sponges and rolls of gauze. You can use gauze sponges and gauze rolls depending on the type, size, or location of the wound that needs to be dressed. Gauze sponges absorb excess fluid that injuries can produce from damage.

Rolls of gauze bandages are generally all-purpose regarding wound care dressing types and are usually inexpensive and widely available.

❖ **when to use a gauze wound dressing:**

- On an infected wound
- On wounds that require wrapping or extra packing
- On injuries that require frequent dressing changes
- Injuries that are draining or will have excess discharge

2. Foam

Foam dressings are soft and gentle wound dressings made of polyurethane foam. This dressing will keep moisture in the wound area while protecting the wound from harmful bacteria. The foam dressing's design will ensure that it will not stick to the wound area.

Foam dressings can be purchased in either adhesive or non-adhesive forms. By keeping the wound area moist, foam dressings can promote faster healing of the wound area.

❖ **when to use a foam wound dressing:**

- Pressure ulcers
- Minor burns
- Skin grafts
- Diabetic ulcers

3. Transparent film

Transparent film wound dressings are thin films composed of polymer membranes. These film dressings come in several thickness variations and will have an adhesive on one side of the film dressing.

The essential function of transparent film dressings is to allow a doctor or physician to actively see and monitor a wound without being exposed to the elements. Additionally, these surgical wound dressing types of bandages protect against liquid, water, and bacteria from entering the damage.

Patients that have received transparent film wound dressings have claimed that the thin and flexible material is comfortable on the wound and can aid in mobility.

❖ **when to use a transparent film wound dressing:**

- On IV sites
- Lacerations
- Abrasions
- Second-degree burns
- On a surgical incision site

4. Hydrocolloid

Hydrocolloid dressings are absorbent pads that are incredibly flexible. The pads consist of particles like methylcellulose, gelatine, or

pectin. When these colloidal particles mix with moisture, they create a gel-like substance that sits in the wound area. [10] The gel made by hydrocolloid wound dressings keeps the wound's surface moist and promotes faster healing.

❖ **when to use a hydrocolloid wound dressing:**

- On wounds with light to moderate draining
- Burn wounds
- Necrotic wounds
- Pressure ulcers
- Venous ulcers

5. Hydrogel

A hydrogel wound dressing treats wounds that are too dry or need some extra help healing. Hydrogel acts as a wound dressing that will intentionally add moisture to an injury. The healing rate of a wound is increased when additional moisture is introduced.

Some hydrogel wound dressings include an additional cooling gel that can add comfort to the patient as their injuries heal. Hydrogel dressings are helpful for various types and sizes of wounds, and their application can be multitudinous.

❖ **when to use a hydrogel wound dressing:**

- On excessive dry wound areas
- Wounds with dead tissue
- Painful or necrotic wounds

Fig 2: Traditional wound dressings: gauzes, transparent films, foam dressings, hydrogels, hydrocolloids and hydroconductive dressings [11].

Advanced wound dressings

Advanced wound dressings refer to a class of smart systems able to release their payload in response to external stimuli, such as

temperature, pH, oxygen and moisture composition, with the aim to further increase their therapeutic efficacy while reducing the released dosages (Fig.3). Based on their mode of operation, stimuli-responsive wound dressings can be classified in: (i) self-responsive wound dressings, (ii) externally-triggered wound dressings, and (iii) automated wound dressings. Specifically, in the case of self-responsive systems, the diffusive payload release is enhanced by structural changes in the wound dressing.

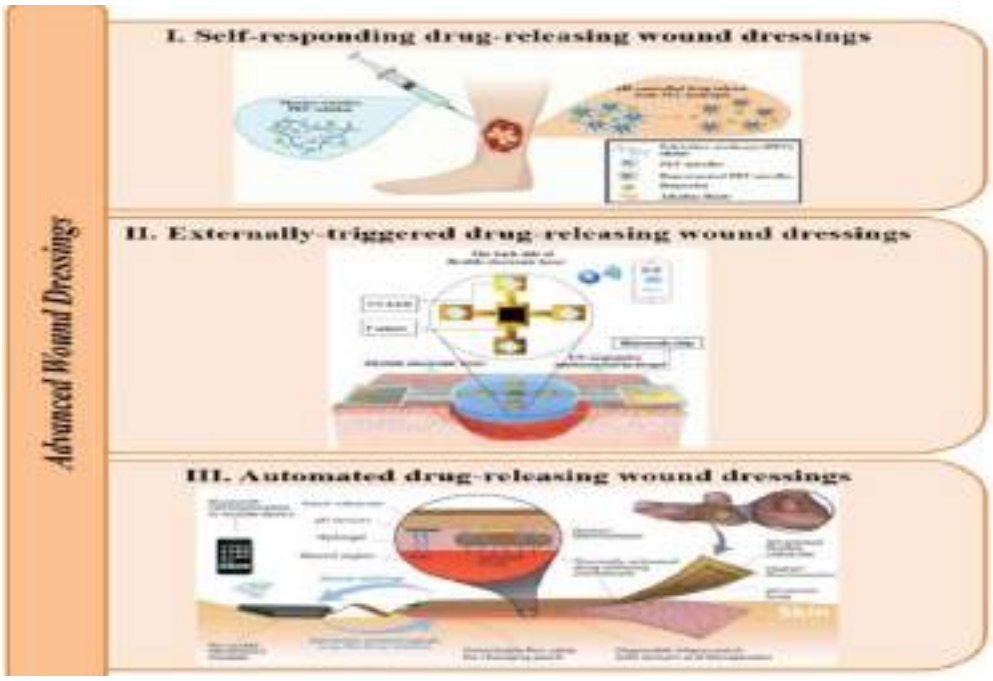


Fig4: Examples of advanced wound care products. (I) Self-responding wound dressing: the release of drug from a multi-responsive poly(ether urethane)-based hydrogel dressing is triggered by the alkalinity of wound exudate. Reproduced from [12]. Copyright 2021, Publisher KeAi Communications Co. Ltd. (II) Externally triggered wound dressing: the on-demand release of therapeutic agents is activated through UV irradiation of an UV-responsive anti-bacterial hydrogel. Reproduced from [13]. Copyright 2020, Publisher John Wiley and Sons. (III) Automated wound dressing: smart patch composed by pH sensors, thermo-responsive drug-loaded microbeads, heating activators, electronics to monitor measured parameters and on-request triggered drug release. Reproduced with permission from [14]. Copyright 2018, Publisher John Wiley and Sons.

Relationship between wound dressing and polymers

Wound dressing materials based on polymers have attracted much attention in the management of chronic wounds, especially diabetic injuries. These dressings demonstrate several interesting properties that can be beneficial for the management of chronic injuries. The properties of ideal polymeric dressings include high porosity and swelling ability, adequate water vapour transmission rate (WVTR), ability to offer moisture and

warm environment to accelerate the wound healing process, gaseous permeation, excellent antimicrobial properties, excellent mechanical performance, and capability to deliver bioactive agents [15,16,17]. Various polymers can be utilized for the formulation of ideal wound dressing materials. They are categorized as biopolymers and synthetic polymers. Examples of biopolymers (natural polymers) include alginate, dextran, hyaluronic acid (HA), chitosan, cellulose, gelatin, chitin, etc. [18]. These polymers present excellent biomedical properties such as good biocompatibility, non-immunogenicity, non-toxicity, hemostatic effects, excellent biodegradability, antibacterial features, and wound healing properties [19]. However, natural polymers also suffer from poor mechanical properties.

Fig5: The skin cells are cultured on the polymeric scaffold for typically several weeks and then removed from cultured, and can be applied to a patient as a customized, autologous skin graft using their own cells. The graft is thought to work via a number of mechanisms, including coverage and protection of the wound [20].

Phases of Wound Healing

Wound passes by different phases, as shown in figure 6:

1. Wound occurring distribution of the healthy tissues in the site.
2. Hemostasis stage: the creation of a clot to prevent any further bleeding.
3. Inflammation stage: penetration of neutrophils to the injured site.
4. Proliferation stage: infiltration of fibroblasts to the injured site and keratinocytes, and granulation tissue appears.

5. Maturation, the final phase which may last for years. During the final stage, fibroblasts disappear and the ECM matures.

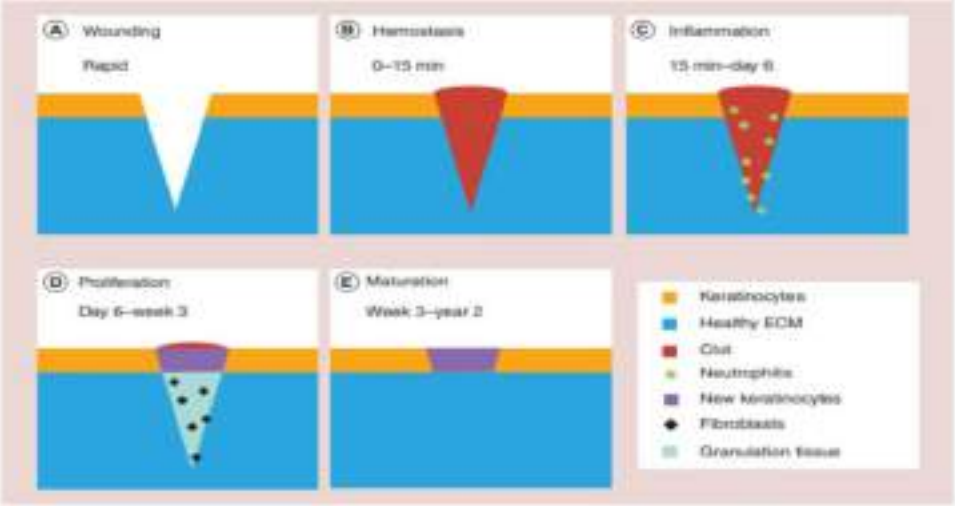


Fig6: Schematic representation of the different phases of wound healing.[21]

Wound healing Requirements:

An ideal wound dressing should absorb excessive exudates; control the moisture in the wound bed; possess good mechanical stability; have great gases transmission; protect from microorganism colonization and infections; be non-toxic, biocompatible, and biodegradable; ensure easy and non- painful removal after completed skin regeneration; and be available at an acceptable cost. The above-mentioned features are summarized in Figure 7 [22]

Fig7: The features of the ideal wound dressing [22]

CHAPTER 2

Previous studies on wound dressings

There are many scientists who have carried out several experiments and analyses recently to examine many products and use them as wound dressings, the most prominent of which are:

1) **In 2022 studied Oh Gun-Woo and others** about wound dressings and they discovered when he fabricated composite polyvinyl alcohol (PVA) and pectin hydrogels with different blend ratios using a freeze–thaw method. Scanning electron microscopy revealed that the PVA/pectin hydrogels had a porous structure, with the porosity increasing from 82.8% ± 0.5% to 93.2% ± 0.3% with an increase in the pectin content. In addition, with the addition of pectin, the gel fraction of the hydrogel decreased and the swelling ability increased compared with PVA. Of the fabricated hydrogels, the hydrogel with the 9:1 PVA/pectin ratio had the highest compressive strength (684 ± 62 kPa) and *G′* value (~1014 kPa). Based on cytotoxicity studies, none of the fabricated hydrogels showed cytotoxicity against HDF or HaCaT cells. These results indicate that varying the pectin content can be used to control the mechanical characterization, porosity, and swelling ability of composite PVA/pectin hydrogels, which are thus promising candidates for use as wound dressings. [23]

2) **in 2023 Zhao Yanan, and others** et al. study Construction of antibacterial photothermal PCL/AgNPs/BP nanofibers for infected wound healing Infected wound healing remains a significant issue in clinical medicine and has attracted wide attention in the field of biomedical engineering. Although a range of bioactive materials have been developed, few provide sufficient antibacterial and pro-angiogenic effects for effective wound healing. Herein, we constructed a series of nanofibers (termed PL-n, n = 0, 1, and 2) based on polycaprolactone (PCL), nanosilvers (AgNPs) and black phosphorus (BP) using electrospinning technology. The water contact angle of PL-n decreased significantly from 144.00 ± 1.00° for PL-0 to 0° for PL-2. The photothermal temperature increased significantly from 27.27 ± 0.25 °C for PL-0 to 40.7 ± 0.15 °C for PL-2. After exposure to near-infrared ray (NIR), the release rate of PL-2 increased from 78.00 ± 2.95 % to 89.46 ± 2.05 %. Biological experiments demonstrated that NIR-assisted PL-2 has excellent antibacterial and biofilm ablation activity with good biocompatibility. Furthermore, *in vivo* studies indicated that the NIR-assisted PL-2 accelerated wound healing by stimulating granulation tissue formation, collagen deposition, and angiogenesis and decreasing expression levels of CD68. The study suggests that this bi-functional

nanofiber is indeed a versatile wound dressing, and is expected to be applied in clinical settings. [24]

3) **In 2019 Kaczmarek Beata and others** they did study about wound dressings and they founds performed assessments of thin films over TA proposed as a cross-linker to be used in combination with polymeric matrix based on chitosan (CTS), i.e. CTS/TA at 80:20 or CTS/TA at 50:50 and poly(ethylene glycol) (PEG) at the concentration of 10% or 20%. We evaluated their mechanical parameters as well as the cytotoxicity assay for human bone marrow mesenchymal stem cells, human melanotic melanoma (MNT-1), and human osteosarcoma (Saos-2). The results revealed significant differences in dose-dependent of PEG regarding the maximum tensile strength (σmax) or impact on the metabolic activity of tissue culture plastic. We observed that PEG improved mechanical parameters prominently, decreased the hemolysis rate, and did not affect cell viability negatively. Enclosed data, confirmed also by our previous reports, will undoubtedly pave the path for the future application of tannic acid-based biomaterials to treat wound healing.[25]

4) **In2023, Samatya Yılmaz and other** discovered novel hollow nanofiber materials were produced by the coaxial electrospinning method from polyurethane (PU)/poly(lactic acid) (PLA) blend nanofibers of different weight ratios (80:20, 60:40, 50:50, 40:60, and 20:80). Thus, the tissue scaffolds as dermal wound dressing materials which can absorb the exudate liquid formed on the wet wound and dry quickly, providing patient comfort with high mechanical properties, showing high biocompatibility, and supporting fibroblast cell growth were developed. Moreover, the characteristics of hollow PU/PLA nanofibers were compared in detail with the characteristics of solid PU/PLA nanofibers in our previous study. Hollow PU/PLA nanofibers were observed 2–4 times thinner than solid PU/PLA nanofibers. The production of hollow nanofibers in the range of 235–518 nm was achieved. It was reported that the hollow PU/PLA (50/50, w/w) nanofiber has the highest tensile strength with a value of 7.19 MPa, and the hollow PU/PLA (60/40) w/w) nanofiber has the highest percentage elongation with a value of 63.78%. It was determined that the biomedical material, which has the highest liquid absorption capacity with a value of 756% and can dry in 10 min, is H5PU5PLA nanofiber. As a result, the highest value of fibroblast cell viability with 92.38% by cytotoxicity test was observed for hollow PU/PLA (20/80, w/w) nanofiber.[26]

5) **in 2022**, **Chen Mingtao and others** founded a fast and reversible adhesive consisting of dynamic boronic ester covalent bonds, formed between poly(vinyl alcohol) (PVA) and boric acid (BA) for potential use as a wound dressing adhesive. Mechanical testing shows that the adhesive film has strength in shear of 61 N/cm2 and transcutaneous adhesive strength of 511 N/cm2, generated within 2 min of application. Yet the film can be effortlessly debonded when exposed to excess water. The mechanical properties of PVA/BA adhesives are tunable by varying the cross-linking density. Within seconds of activation by water, the surface boronic ester bonds in the PVA/BA film undergo fast debonding and instant softening, leading to conformal contact with the adherends and reformation of the boronic ester bonds at the interface. Meanwhile, the bulk film remains dehydrated to offer efficient load transmission, which is important to achieve strong adhesion without delamination at the interface. Whether the substrate surface is smooth (e.g., glass) or rough (e.g., hairy mouse skin), PVA/BA adhesives demonstrate superior adhesion compared to the most widely used topical skin adhesive in clinical medicine, Dermabond. in 2022 Chen, M., Wu, Y., Chen, B., Tucker, A. M., Jagota, A., & Yang, S.and others founded a fast and reversible adhesive consisting of dynamic boronic ester covalent bonds, formed between poly(vinyl alcohol) (PVA) and boric acid (BA) for potential use as a wound dressing adhesive. Mechanical testing shows that the adhesive film has strength in shear of 61 N/cm2 and transcutaneous adhesive strength of 511 N/cm2, generated within 2 min of application. Yet the film can be effortlessly debonded when exposed to excess water. The mechanical properties of PVA/BA adhesives are tunable by varying the cross-linking density. Within seconds of activation by water, the surface boronic ester bonds in the PVA/BA film undergo fast debonding and instant softening, leading to conformal contact with the adherends and reformation of the boronic ester bonds at the interface. Meanwhile, the bulk film remains dehydrated to offer efficient load transmission, which is important to achieve strong adhesion without delamination at the interface. Whether the substrate surface is smooth (e.g., glass) or rough (e.g., hairy mouse skin), PVA/BA adhesives demonstrate superior adhesion compared to the most widely used topical skin adhesive in clinical medicine, Dermabond.[27]

6) **In 2022 D'souza and other** they prepare eco-friendly composite films , were prepared based on poly(vinyl alcohol) (PVA) containing different content of *Basella alba* stem extract (BA) (1.5 mL, 2.5 mL and 3.5 mL) by cost effective solvent casting technique. The physicochemical properties of the prepared films were investigated using different instrumental techniques. The molecular interaction

between PVA and BA was confirmed by FTIR studies. The incorporation of BA at higher content leads to more strengthen and less flexible bio-composite films which was determined by mechanical test. DSC studies confirmed the miscibility of BA with PVA matrix. TGA studies revealed increased thermal stability of PVA/BA composite films in contrast with pristine PVA. The morphological studies disclosed that a uniform distribution of BA at lower content in the bio-composite film. The X-ray Diffraction study illustrated that, increased BA content reduces the semicrystalline structure of PVA. Moreover, Moisture Content, Water Solubility, Water Contact Angle and Water Vapor Transmission Rate results indicated that, bio-composite films had high surface hydrophilicity. Additionally, PVA/BA films exhibited low transparency value compared to control film and improved UV barrier property. Soil degradation rate of PVA/BA films increased as the BA content increased signifying the films are biodegradable in nature. Furthermore, doping of BA into PVA enhanced antibacterial potential of the bio-composite film towards *Staphylococcus aureus* and *Escherichia coli*. These results suggest that PVA/BA composite films can be utilized as promising material for green packaging application.[28]

CHAPTER 3

Polyethylene glycol (PEG): is a biocompatible, synthetic, hydrophilic polyether compound that has many applications, mostly in the medical industry, but also in the chemical and industrial sectors. The structure of the compound is known as $H–(O–CH_2–CH_2)_n–OH$. While varying the molecular weight of PEG can have slight effects on its characteristics, mostly on its shape and physical appearance, many characteristics define PEG. It is non-toxic, colorless, inert, odorless, and non-volatile. Also, it is incredibly soluble in water, and organic solvents such as benzene, carbon tetrachloride, and chloroform. Creating PEG substances of different molecular weights relies on constructing PEG with different length chains. Larger PEG molecules have a greater number of repetitions of their structure compared with smaller ones

Applications in preservation have also found a use for PEG, which is now employed to prevent and slow the damage and shrinkage of wood that has been submerged. It was used to preserve the Vasa warship in Stockholm, replacing the water trapped within the wood to prevent warping and shrinking.

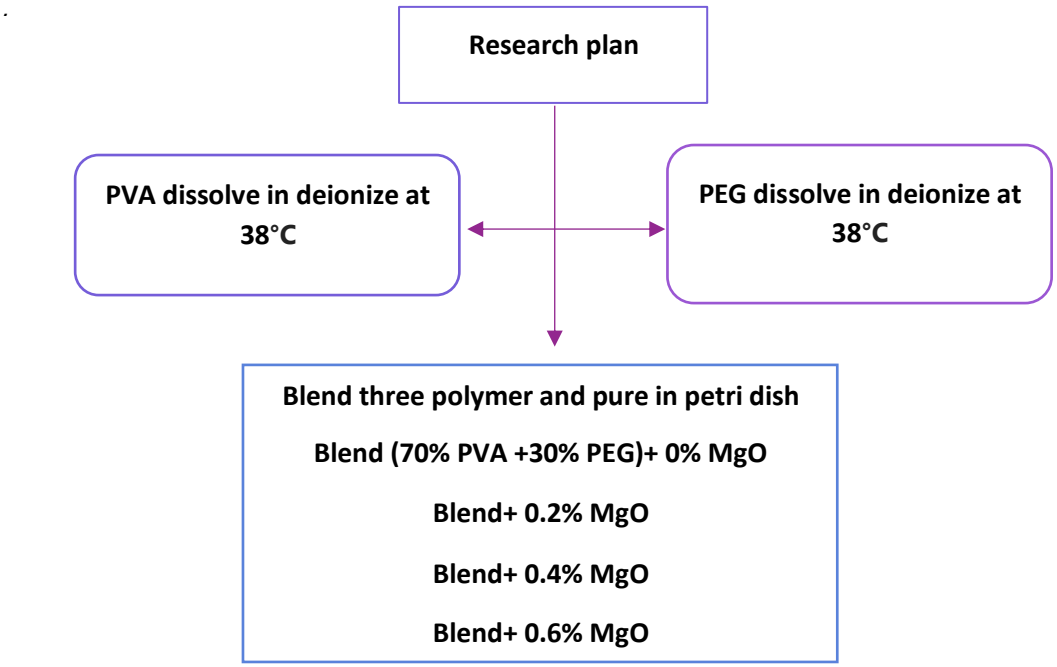
Polyvinyl acetal (PVA): It is prepared by the reaction of aldehydes with polyvinyl alcohol. Polyvinyl Butyral and Polyvinyl Formal are examples of this family of polymers. It is prepared from polyvinyl alcohol by its reaction with butyrate aldehyde and formaldehyde, respectively. The preparation of PVB is the largest use of PVA in the United States and Western Europe. Polyvinyl alcohol is used as an emulsifying coagulant, as a protective colloid, for the preparation of polyvinyl acetate suspensions. And the biggest market for this app is in China. In Japan, its largest use is in the production of vinylon fibers Other uses for polyvinyl alcohol include: Paper adhesive with boric acid in spiral tube winding and rigid sheet production.Thickener and modifier in PVC gluesTextile fumigation agentCover paper and release line Water soluble film is useful for packaging. An example is the envelope containing the washing powder in "liqui-tabs."Biodegradable plastic backing film in feminine hygiene products and adult incontinence products.Carbon dioxide barrier in polyester bottlesFilm in aqueous transfer printing technology It is used in eye drops (such as artificial tears to treat dry eyes) and lubricant solutions for hard contact lensesPVA fibers in concrete reinforcement Raw material for polyvinyl nitrate. It is an ester of nitric acid and polyvinyl alcohol.A surfactant to form encapsulated nanoparticles Manufacturer of chemical resistant protective gloves.

Magnesium oxide (MgO) : is a naturally occurring colorless, crystalline mineral with a high melting point that is used in various industries due to its large-scale production. MgO has a high thermal conductivity coupled with a low electrical conductivity. In recent years, the strong antimicrobial activity of MgO with a high stability, compared with organic antimicrobial agents, has been an interesting field of research. This combination of properties leads to its use as a multifunctional solid material. In the United States and Europe [EU-approved food additive (E number 530)], MgONP-based packaging has replaced many construction materials in food packaging, as they are impermeable to gas, thermally stable, flexible, and recyclable, with antimicrobial activity. MgONPs can be synthesized via laser ablation, hydrothermal, sol–gel, wet chemical reaction, microemulsion, microwave-assisted, and ultrasound-assisted methods

Magnesium oxide is available in two forms, fine powder and granular. Only the powder form is suitable for dusting pasture as the granular form falls to the soil and does not dust the leaf. The grass must be at least 8–10 cm tall as the dust cannot adhere if there is inadequate leaf surface area. Dusting must be even, because given the chance, cows prefer to graze the undusted strips of pasture. Fine calcine magnesite should be dusted at weekly intervals at a rate of 17–20 kg ha^{-1} and is best applied in the early morning when there is a dew on the pasture. Dusting is economical at stocking rates greater than 2.5 cow ha^{-1}, but is expensive at lower stocking rates. In addition, it is not suited to extensive grazing systems or in locations where it rains a lot.

PRACTICAL PART

The present chapter covers all the most important details about the methodology that was used in this study starting with materials selection and specification, preparation of sample and the instruments of inspection



1. PVA (0.7), Peg (0.3), attributed by 30ml of water, add oxide magnesium (Mgo), and be on three ratios: (2%, 4%, 6%) We have 4 pure and second samples by 2% and third By 4% and fourth percent by 6%.
2. This substance was dispersed with distilled water by the ultra-sonic device, and then it was gradually added to the mixture while it was on magnetic sturall.
3. We leave samples for a (3-4)day in the laboratory, which leads to drying and working in a circular manner in the Brush Brush device.

3-1 Differential Scanning Calorimetry Test (DSC)

Differential scanning calorimetry measurements (DSC) measurement were carried out according to ASTM D3418-03 under a nitrogen gas atmosphere. The prepared samples with a weight of (8-10) ± 0.5 mg was put in aluminum crucible and heated from room temperature up to160°C at a rate of 10°C/min.

3-2Tensile test

A mechanical tester was used to perform the tensile test. The ASTM Standard Sheeting (D882-01"Standard Test Protocol for Tensile Properties of Thin Plastic Film," where a film was 80 mm in length and 10 mm wide thickness 0.15 mm. using a strain rate of 5 mm/min.

3-3 Contact angle Test:

Contact angle test was carried out using the device, SL 200C – Optical Dynamic I Static Interfacial Tensiometer & Contact Angle Meter. The purpose of this test is to study the effect of polyester fibres on the wettability of polymer which impose an effect on the growth of living cells and create blood clots. The left and right contact angles of the water drop are measured.

3-4 Fourier Transformation Spectroscopy (FTIR):

The test of FTIR was achieved by using Fourier transform infrared spectrometer, FTIR instrument type IR Affinity-1 (made in Japan) available in laboratory of the Materials Engineering Faculty/ Babylon University. It is equipped with a room temperature DTGS detector, mid-IR source (4000 to 400) cm-1 and a KBr beam splitter. FTIR were performed on a spectrum for blend PVA, PAN/PEG and polymer Nano composites reinforced by ZnO.

CHAPTER 4

4-1 FTIR Test

FTIR spectroscopy is one of the most common techniques, which provides useful information regarding the interactions between their functional groups. It is also considered a powerful method for studying the conformational changes in biopolymer systems [29,30]. It is clear from the spectra of all PVA/PEG blends that extensive H-bonding exists in the range 3000–3500 cm-1 due to stretching vibration of –OH groups which results from strong H-bonds that form during blending. Figure (4-1) and Table (4-1) revealed to FTIR spectrum for blend 70% PVA/30% PEG and nanocomposite (70% PVA/30% PEG +0.4% MgO). Table (4-1) show the transmitted bands which referred to CH stretching band at 2893 ,CH_2 bending at 1481, C=O at 1658 and OH stretching at 3394 which are shifted from band of standard (3450 and 3280) which referred to create hydrogen bonding between PVA and PEG [31,32],. However, there was a slight shift observed for peak position and relative intensity of the stretching vibration of most bands of nanocomposite , moreover, the absorption band of OH groups observed got wider and with higher intensity in the spectra of the nanocomposites indicating occurrence of H-bond interactions between the –OH groups present in the blend and the oxygen groups of magnesium oxide [33-34].

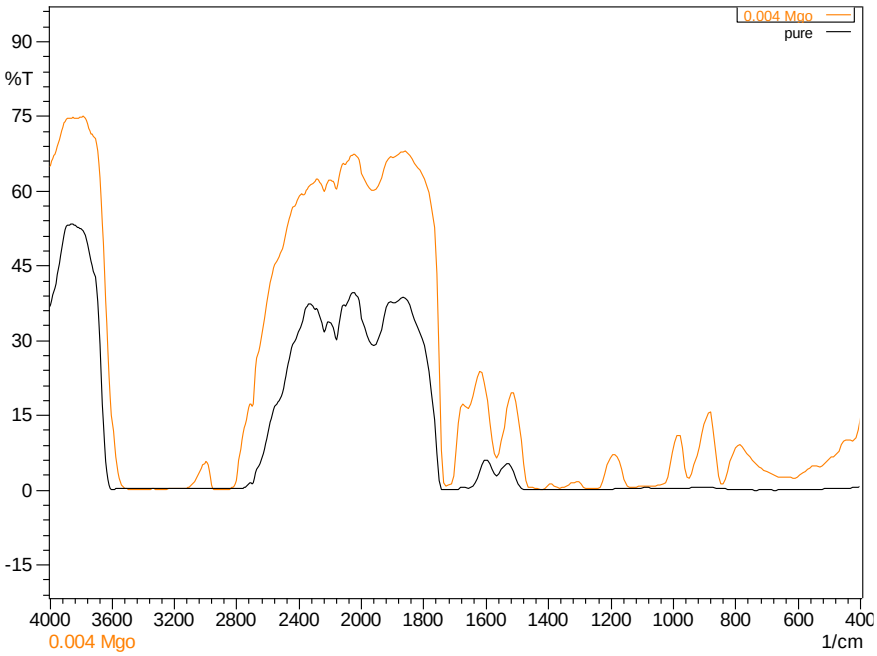


Figure (4-1) FTIR Spectrum of blend (70%PVA+30%PEG) &Nanocomposite Materials (70%PVA+30%PEG+ 0.4% ZnO).

Table (4-1) The Transmission Bands of IR Spectrum Characteristic of blend (70%PVA+30%PEG) &Nanocomposite Materials (70%PVA+30%PEG+ 0.4% MgO).

Types of bond	Standard PVA [8]	Standard PEG [31]	Exp. Blend (70%PVA+30%PEG)	Blend(70% PVA+30%PEG)+0.4% MgO
CH_2 stretching	2917	3863	2893	2854
OH stretching	3280	3450	3394	3433
CH_2 bending	1425	1456	1481	1458
C=O	1690	1658	1658	1658

4-2 Wettability Test

Table (4-2) shows the contact angle of blend of PVA/PEG and nanocomposite as a function of nanoparticles of MgO and the stability the droplets with the time that indicate the wettability of these materials. The contact angle of blend was 56.289° which indicate that the blend had a hydrophilic behavior which enhance the degradability after used it as a wound dressing and prevent the accumulated the waste of polymers.

Moreover, Due to the small particle size of Nanoparticles of MgO, which does not obstruct the flow of water within the constructed film[35],Therefore, the contact angle decreased to (51.159, 38.111and, 26.164) when the blend is reinforced with different weight fraction of magnesium oxide (MgO) (0.2, 0.4, and 0.6) w.t%, respectively that enhanced the wettability and made the film more hydrophilic which increased the biocompatibility of the film and enhance the adhesion of livening cells which accelerate the healing process of the wound .

Moreover, from the Table (4-2), the contact angle of the blend and nanocomposite decreased with the time that referred the stability of the contact angle decreased with the time that enhance the biocompatibility , healing process and biodegradability process

Table (4-2) Contact Angle Neat PEG ,PVA, Blend PVA/PEG and Nanocomposite

Sample	Contact Angle(CA)°		
	(0) sec	(30) sec	(60) sec
Blend (70% PVA +30% PEG)+ 0% MgO	56.289	49.609	42.591
Blend+ 0.2% MgO	51.159	44.170	37.397
Blend+ 0.4% MgO	38.111	33.567	23.524
Blend+ 0.6% MgO	26.164	17.998	0

4-3 DSC Test

Thermal behavior of the blend PVA / PEG, Nanocomposites reinforced with (0.2,0.4 and 0.6) %.w.t MgO are analytic by DSC and exhibit endothermic peaks shown in Figure (4-2) .

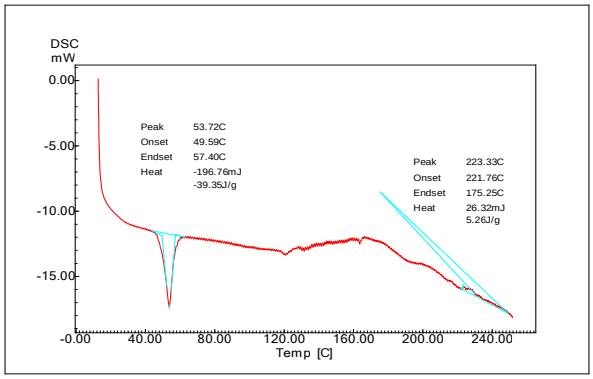
The T_m of blend PVA/PEG was 53.16 °C and the T_m of nanocomposite increased with the addition of different weight fraction of MgO nanoparticles (as shown in Table (4-3)) It has been postulated that adding nanoparticles has improved the thermal stability of the film, possibly as a result of interactions between the three components of the nanocomposite PVA/PEG/n-MgO [37] and also, due to uniform distribution of nanoparticles within the polymeric matrix chains that restricted the motion of molecules chains [38]

The percentage of crystallinity can be determined by divided crystallization enthalpy (ΔH) by integrating the area under endothermal peak and dividing it with ΔH^o, the crystallization enthalpy of the theoretical 100% of PVA. The formula was shown in equation (1).

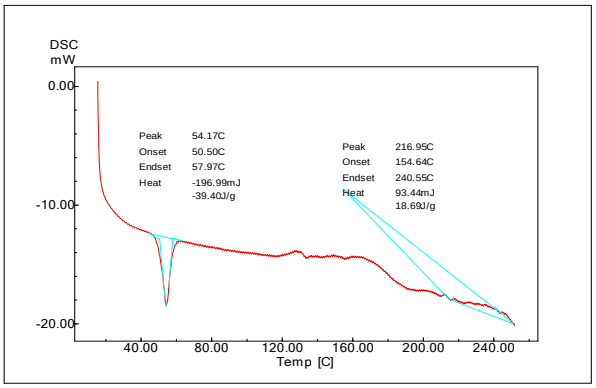
$Xc = \Delta H / (1-Ø) \Delta H°$ ----------(1) [39]

Where ΔH is the apparent enthalpy of fusion per gram of composite, ΔH^o is the heat of fusion of a 100% crystalline PVA which is (138.6) Jg-1 [40] and Ø is the weight fraction of the PEG and filler in the composites.

(A)

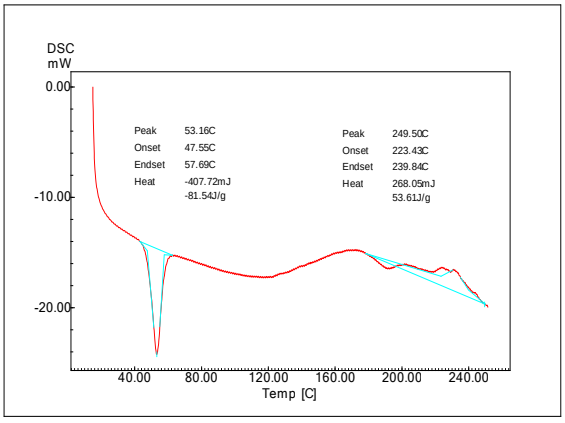


(B)



The degree of crystallization of the PVA component lowered noticeably as PVA was incorporated, suggesting that PEG molecules do inhibit the growth of PVA particles in the blend. The interaction between PVA and PEG molecules lowered PVA 's crystalline abilities, suggesting good interaction among blend substances and great dispersion of nanoparticles within the blend [35]

(C)



(D)

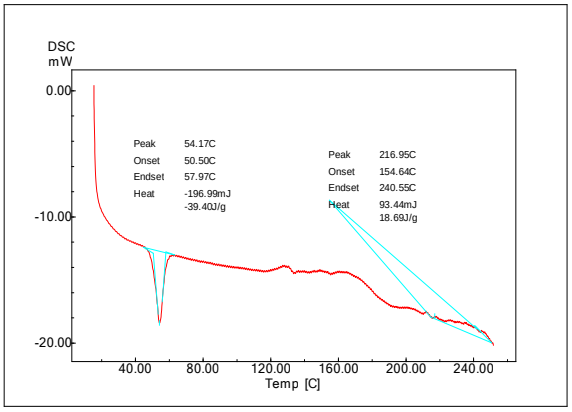


Figure (4-2) DSC for Melting Endotherm and in Nitrogen Atmosphere A- Blend PVA/PEG, B- PVA/PEG/0.2%MgO, C- PVA/PEG/0.4%MgO, and PVA/PEG/0.6%MgO

Table (4-3) DSC for Melting Endotherm at Nitrogen Atmosphere for PVA/PEG, Nanocomposite as a Function to Percent of Nanoparticles of MgO

Samples	T_m	ΔH J/g	Xc (%)
PVA /PEG	53.16	-81.54	84.044
PVA /PEG/0.2MgO	53.91	-60.27	62.299
PVA /PEG/0.4MgO	53.72	-39.35	40.791
PVA /PEG/0.6MgO	54.17	-39.40	40.961

4-4 Tensile Test

From Figures (4-3) and (4-4) show the effect of blending PEG and addition different weight fractions of magnesium oxide on the tensile strength and elastic modulus of PVA.

Moreover, show the tensile strength and elastic modulus increased with increased the weight fraction of MgO nanoparticles due to good adhesion between the blend and reinforcement phase and due to the nature of particles of MgO that is a ceramic material has a high mechanical properties which enhances the tensile strength and elastic modulus of the polymer [41-42].

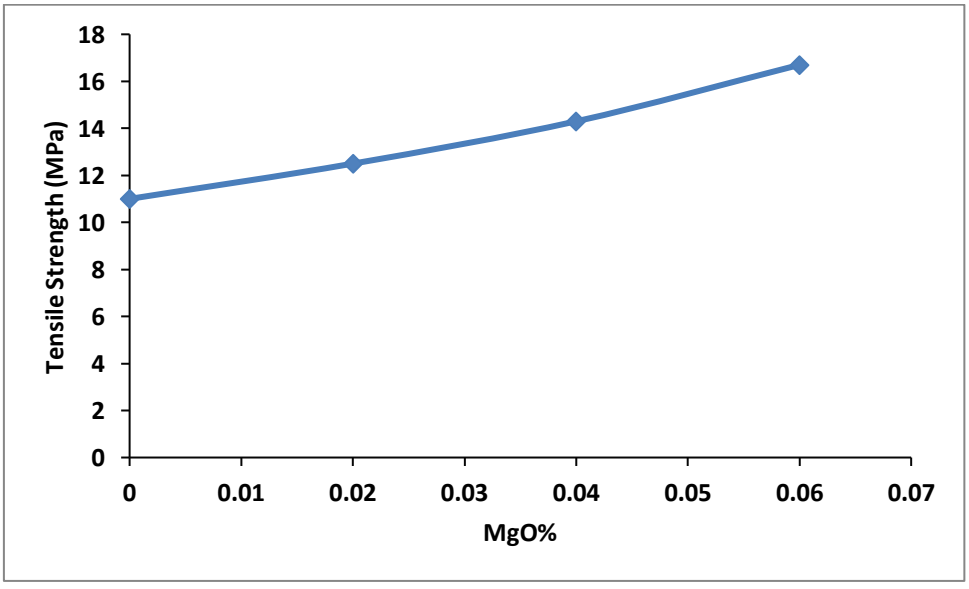


Figure (4-3) Tensile Strength for Blend (PVA/PEG) and Nanocomposite as a Function of Different Percent of MgO Nanoparticles

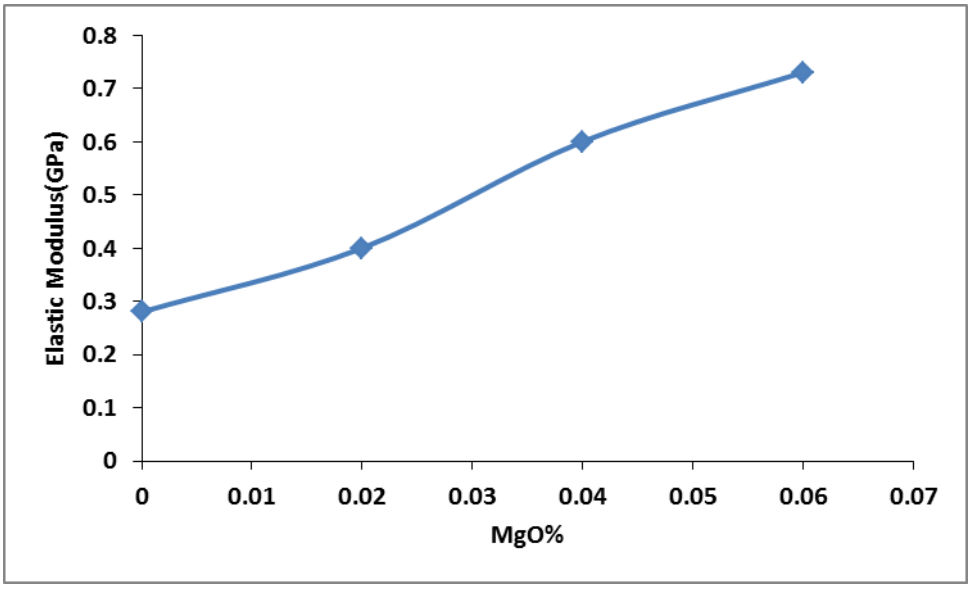


Figure (4-4) Elastic Modulus for Blend (PVA/PEG) and Nanocomposite as a Function of Different Percent of MgO Nanoparticles

Figure (4-5) exhibit the effect of PEG and nanoparticles of MgO on the elongation of PVA. From the figure, the elongation decreased with increased percent of MgO because the nanoparticles restricted the motion of the polymer chains as well as there was some agglomerates of nanoparticles which behaved as a defects restricted the elongations [42].

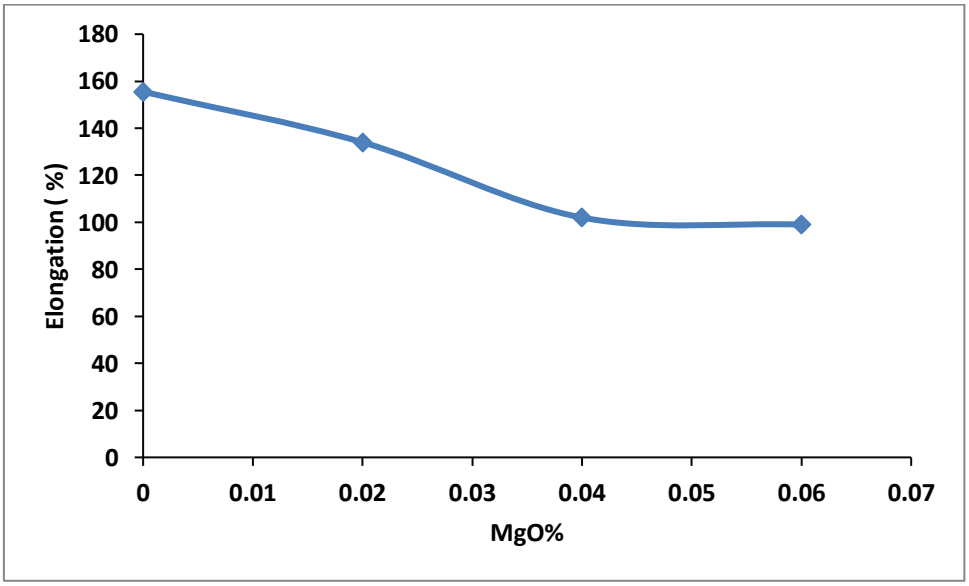


Figure (4-5) Elongation for Blend (PVA/PEG) and Nanocomposite as a Function of Different Percent of MgO Nanoparticles

Conclusions & Recommendations

5-1 Conclusions

From the current study results are mentioned in previous chapters that interested for used nanocomposites for wound dressing applications. It concluded the following:

1. 1. There is a good compatibility between PVA and PEG which get a good
   blend between them. The best ratio is (70%PVA + 30% PEG).

2. From the test of the wettability, it was found that the addition of MgO to PVA decreased the contact angle, and made the film was more hydrophilic which enhance biocompatibility , livening cell adhesion which accelerate the healing process and biodegradability of the dresses after the heling process

3. From the FTIR results, it can have concluded the are no create chemical bond between polymers but also it create hydrogen bonding between PVA
   and PEG and also it creates hydrogen bonding between PVA and MgO. The shifting in bands indicated to good distribution of MgO within the matrix.

4. From DSC test, the T_m of nanocomposite increased with the addition of different weight fraction of MgO nanoparticles It has been postulated that adding nanoparticles has improved the thermal stability of the film, possibly as a result of interactions between the three components of the nanocomposite PVA/PEG/n-MgO

5. From DSC test, the degree of crystallization of the PVA component lowered noticeably as PVA was incorporated, suggesting that PEG molecules do inhibit the growth of PVA particles in the blend. The interaction between PVA and PEG molecules lowered PVA's crystalline

abilities, suggesting good interaction among blend substances and great dispersion of nanoparticles within the blend

The tensile strength and elastic of modulus increased with increased the weight fraction of MgO nanoparticles due to create interaction between the PVA and MgO that enhanced the adhesion between them

5 Recommendation

From the present study, the following recommendation can be helpful for further studies:

1. Addition another nanomaterials and study their effect on wettability behavior and antibacterial properties. Such as Nano Ag and TiO_2.
2. Test the nanocomposite SEM, AFM, and biodegradability.

REFERENCES

1. Robson MC, Steed DL, Franz MG. Wound healing: biological features and approaches to maximize healing trajectories. Curr Prob Surg 2001; 38: 77–89.
2. Lazurus GS, Cooper DM, Knighton DR, Margolis DJ, Pecoraro RE, Rodeheaver G, *et al*. Definitions and guidelines for assessment of wounds and evaluation of healing. Arch Dermatol 1994; 130: 489–3.
3. Baxter E. Complete crime scene investigation handbook: CRC press. 2015; p 31–3
4. Khalili, S.; Khorasani, S. N.; Saadatkish, N.; Khoshakhlagh, K. *Polym. Sci. Series A*. 2016, **58**, 399
5. Morgado, P. I.; Aguiar-Ricardo, A.; Correia, I. J. *J. Membr. Sci*. 2015, **490**, 139.
6. Daunton C, Kothari S, Smith L, Steele D. A history of materials and practices for wound management. *Wound Pract Res*. 2012;20:1748–6. [Google Scholar]
7. Jayesh BS. The history of wound care. *The journal of the American college of certified wound specialists*. 2011;3:65–6. doi: 10.1016/j.jcws.2012.04.002. [PMC free article] [PubMed] [CrossRef] [Google Scholar]
8. Sujatha S. Recent advances in topical wound care. *Indian J Plast Surg*. 2012;45:379–87. doi: 10.4103/0970-0358.101321. [PMC free article] [PubMed] [CrossRef] [Google Scholar]
9. Sonas Home Health Care. (3 July 2019) *Wound Dressing Types*
10. Swezey, L. (4 August 2011) Wound Source. *Wound Dressing Selection: Types and Usage.*
11. H.C. Gwak, S.H. Han, J. Lee, S. Park, K.S. Sung, H.J. Kim, D. Chun, K. Lee, J.H. Ahn, K. Kwak, H.J. Chung, Efficacy of a povidone-iodine foam dressing (Betafoam) on diabetic foot ulcer, Int. Wound J. 17 (2020) 91–99.
12. Politecnico di Torino, Mechanical and Aerospace Engineering Department, Corso Duca degli Abruzzi 24, 10129, Torino, Italy
13. Qian Pang MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, 310027 China
14. Pooria Mostafalu Biomaterials Innovation Research Center, Department of Medicine, Brigham and Women's Hospital, Harvard Medical School, Boston, MA, 02139 USA
15. Li S., Li L., Guo C., Qin H., Yu X. A promising wound dressing material with excellent cytocompatibility and proangiogenesis action for wound healing: Strontium loaded Silk fibroin/Sodium alginate (SF/SA) blend films. *Int. J. Biol. Macromol*. 2017;104:969–978. doi: 10.1016/j.ijbiomac.2017.07.020. [PubMed] [CrossRef] [Google Scholar]
16. Kalaycıoğlu Z., Kahya N., Adımcılar V., Kaygusuz H., Torlak E., Akin-Evingue G., Erim F.B. Antibacterial nano cerium oxide/chitosan/cellulose acetate composite fi lms as potential wound dressing. *Eur. Polym.*

J. 2020;133:109777.
doi: 10.1016/j.eurpolymj.2020.109777. [CrossRef] [Google Scholar]
17. Basu P., Narendrakumar U., Arunachalam R., Devi S., Manjubala I. Characterization and Evaluation of Carboxymethyl Cellulose-Based Films for Healing of Full-Thickness Wounds in Normal and Diabetic Rats. *ACS Omega*. 2018;3:12622–12632. doi: 10.1021/acsomega.8b02015. [PMC free article] [PubMed] [CrossRef] [Google Scholar]
18. Hussain Z., Thu H.E., Shuid A.N., Katas H., Hussain F. Recent Advances in Polymer-based Wound Dressings for the Treatment of Diabetic Foot Ulcer: An Overview of State-of-the-art. *Curr. Drug Targets*. 2017;18:527–550. doi: 10.2174/1389450118666170704132523. [PubMed] [CrossRef] [Google Scholar]
19. Alven S., Aderibigbe B.A. Fabrication of Hybrid Nanofibers from Biopolymers and Poly (Vinyl Alcohol)/Poly (ε-Caprolactone) for Wound Dressing Applications. *Polymers*. 2021;13:2104. doi: 10.3390/polym13132104. [PMC free article] [PubMed] [CrossRef] [Google Scholar]
20. van Zuijlen PP, van Trier AJ, Vloemans JF, Groenevelt F, Kreis RW, Middelkoop E. Graft survival and effectiveness of dermal substitution in burns and reconstructive surgery in a one-stage grafting model. Plast Reconstr Surg. 2000;106(3):615–23.
21. A. Krishnan K and S. Thomas, “Recent advances on herb-derived constituents-incorporated wound-dressing materials: A review,” Polymers for Advanced Technologies, vol. 30, no. 4. pp. 823–838, 2019. doi: 10.1002/pat.4540.
22. V. Vivcharenko and A. Przekora, “Modifications of wound dressings with bioactive agents to achieve improved pro-healing properties,” Appl. Sci., vol. 11, no. 9, 2021, doi: 10.3390/app11094114.
23. Oh, Gun-Woo, et al. "Preparation and properties of physically cross-linked PVA/pectin hydrogels blended at different ratios for wound dressings." *Journal of Applied Polymer Science* 139.9 (2022): 51696.
24. Zhao, Yanan, et al. "Construction of antibacterial photothermal PCL/AgNPs/BP nanofibers for infected wound healing." *Materials & Design* (2023): 111670.
25. Kaczmarek, Beata, et al. "Development of tannic acid-enriched materials modified by poly (ethylene glycol) for potential applications as wound dressing." *Progress in biomaterials* 9 (2020): 115-123.
26. Samatya Yılmaz, Sema, and Ayse Aytac. "The highly absorbent polyurethane/polylactic acid blend electrospun tissue scaffold for dermal wound dressing." *Polymer Bulletin* (2023): 1-27.
27. Chen, Mingtao, et al. "Fast, strong, and reversible adhesives with dynamic covalent bonds for potential use in wound dressing." *Proceedings of the National Academy of Sciences* 119.29 (2022): e2203074119.
28. D’souza, O. J., Hiremani, V. D., Gasti, T., Goudar, N., Masti, S. P., Mudigoudra, B. S., ... & Chougale, R. B. (2022). Fabrication and study of poly (vinyl alcohol) film functionalized with basella alba stem extract. *Journal of Polymers and the Environment*, *30*(7), 2888-2904.

29. B. J. Goodfellow and R. H. Wilson, “A fourier transform IR study of the gelation of amylose and amylopectin,” Biopolymers, vol. 30, no. 13-14, pp. 1183–1189, 1990.
30. Fahad H. Falqi,Osamah A. Bin-Dahman, M. Hussain , and Mamdouh A. Al-Harthi , " Preparation of Miscible PVA/PEG Blends and Effect of Graphene Concentration on Thermal, Crystallization, Morphological, and Mechanical Properties of PVA/PEG (10wt%] Blend ", Volume 2018, Article ID 8527693, 10 pages.
31. N.B. Halima, Poly(vinyl alcohol]: review of its promising applications and insights into biodegradation, RSC Adv. 6 (2016]39823–39832. Ashok M. Sajjan , Manu L. Naik , Akshay S. Kulkarni , Umme FazalE-HabibaRudgi , Ashwini M , Geeta G. Shirnalli , Sharanappa A , and Prakash B. Kalahal," Preparation and characterization of PVA-Ge/PEG-400 biodegradable plastic blend films for Packaging applications ", 2020.
32. J. Jose, M. A. Al-Harthi, M. A.-A. AlMa'adeed, J. B. Dakua, and S. K. De, “Effect of graphene loading on thermomechanical properties of poly(vinyl alcohol]/starch blend,” Journal of Applied Polymer Science, vol. 132, no. 16, 2015
33. X. Yuan, “Enhanced interfacial interaction for effective reinforcement of poly(vinyl alcohol] nanocomposites at low loading of graphene,” Polymer Bulletin, vol. 67, no. 9, pp. 1785– 1797, 2011.
34. Alireza Kharami, Nastaran Faraji, Roslina Mat Hussin, Beilstein Journal of Nanotechnology 6, 2015.
35.] Sura Kamel (2021). Enhancement of Polymeric Nano Composite Performance for Bone Cement Application. Ph. D, Babylon University.
36. Dalal Abbas Kadham (2023) ‘’ Synthesis of wound dressings from Nanofiber Textile by electrospinningTechnique’’.
37. Shakir, M., Jolly, R., Khan, M. S., Iram, N. E., Sharma, T. K., & Al-Resayes, S.I.(2015).Synthesis and characterization of a nano-hydroxyapatite/chitosan/polyethylene glycol nanocomposite for bone tissue engineering. Polymers for Advanced Technologies, 26(1), 41-48.
38. Peng, Z., Kong, L. X., and Li, S. D. (2005). Non-isothermal crystallization kinetics of self-assembled polyvinylalcohol/silica nano-composite. Polymer, 46(6), 1949-1955.
39. Prithwiraj Mandal, Killian Stokes, Guiomar Hernández, Daniel Brandell, and Jonas Mindemark " Influence of Binder Crystallinity on the Performance of Si Electrodes with Poly(vinyl alcohol) Binders ", April 2021

40. Ba Linh, N. T., Min, Y. K., & Lee, B. T. (2013). Hybrid hydroxyapatite nanoparticles-loaded PCL/GE blend fibers for bone tissue engineering. Journal of Biomaterials Science, Polymer Edition, 24(5), 520-538.
41. Masar najim (2020). Characterization of Biomaterials and StructuralAnalysis of aKnee Joint Replacement Applications Ph. D, Babylon university.
42. Asra Ali Hussein "fabrication and characterization of advanced blend polymer nanocomposite for human bone structural application", Ph.D., Babylon university ,2017.