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Effect Of Gamma Irradiation and Tannic Acid On The Chemical And Physical Properties Of Poly(Vinyl Alcohol)/Wheat Gluten (Pva/Wg) Polymer Blends

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Abstract

Films of poly(vinyl alcohol)/wheat gluten (PVA/WG) polymer blends at different compositions were prepared by solution casting and then exposed to a constant dose of gamma irradiation. In addition, the PVA/WG polymer blends were modified by adding a constant ratio (4%) of tannic acid (TA) to the casting solution. The PVA/WG polymer blends before and after gamma irradiation as well as those modified by tannic acid were characterized by Fourier transform infrared (FTIR) spectroscopic analysis, thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and measuring the tensile mechanical properties. The antimicrobial activity of PVA/WG polymer blends was also investigated. FTIR spectroscopic analysis indicated that a hydrogen bond was formed between TA and PVA also irradiation improves the adhesion between PVA and WG this conclusion also supported by scanning electron microscopy (SEM) and measuring the tensile mechanical properties. The antimicrobial properties indicated that irradiated sample was better than unirradiated samples.

Poly(vinyl alcohol); Wheat gluten; Gamma irradiation; Tannic acid; Tensile properties; Thermal properties

1. Introduction

The use of low cost polymers such as proteins from crops can be considered beneficial to worldwide agriculture. Wheat gluten (WG) (plant protein), Corn zien, Egg albumin, Whey protein (animal protein), Soya protein, and Casein have been utilized for their film forming ability [(1).] Protein films are good in gas berries (O2, CO2) so, wheat gluten has a potential as a raw material for many technical applications. [(2, 3)] It has a unique cohesive and elastic properties [(4)], but, the disadvantage in wheat gluten (WG) films was its water sensitivity, therefore, to improve its water resistance and film forming property it was blended with poly vinyl alcohol (PVA) and cross-linked. Cho[(5)] and other[(6)] reported that high energy radiation can be used to generate hydroxyl and superoxide anion radicals in blend solution which can modify the molecular properties of proteins. Poly vinyl alcohol (PVA) a well-known soluble polymer and widely used in many applications such as textile, paper and adhesives but, the conventional biological degradation is not effective in Poly vinyl alcohol (PVA) and its degrading capacity by most organisms is very limited. [(7-11)]. Blending process is one of the common methods that can alter the property profile of a single polymer, however, when two or more polymers are mixed the most frequent results is a system that exhibit a phase separation due to the limited solubility of one polymer in another. The compatibilization of polymer blends by high energy radiation can be achieved without adding ionomers or multifunction monomer and this type of compatiblization (radiation) has been a topic of interest due to its efficiency and economically to produce new materials. [(12)]**.** Tannic acid is a natural polyphenolic material composed of five digallic acid units attached to central glucose core as in scheme1 .

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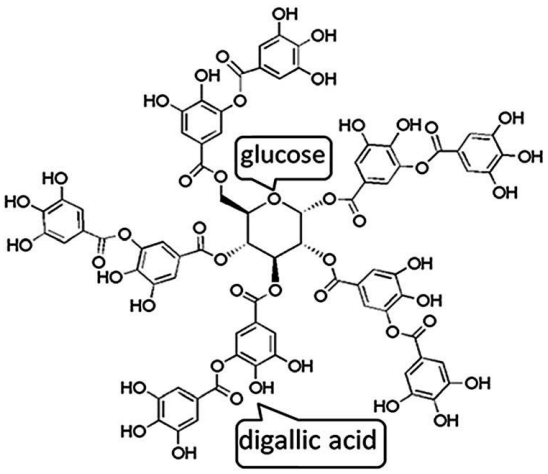

Scheme 1.Chemical structure of Tannic (TA) containing a macromolecular aromatic ester with two or three −OH groups.

Due to numerous numbers of phenolic and carbonyl groups, tannic acid (TA) can form different types of interaction such as hydrogen bonding, ionic bonding and hydrophobic interaction with small molecules and polymers. Some authors[13] prepared hydrogel from Poly vinyl alcohol (PVA) and tannic acid (TA) for wound dressing applications through freeze-thawing processes Also, Chen [14] found that the PVA/TA hydrogel has good mechanical properties and shape memory behavior in which a strong hydrogen bonding occur. The aim of the present work is to use gamma irradiation to improve the compatibility of Poly vinyl alcohol (PVA) as film forming material, wheat gluten (WG) as natural biodegradable material, and study the effect of tannic acid (TA) addition to these blends for wound dressing properties. In this regard the properties of blend composition in terms of Fourier transform infrared (FTIR), mechanical, thermal, SEM and antimicrobial properties were evaluated.

Experimental:

Materials

Poly(vinyl alcohol)(PVA) (Mw = 146,000-186,000) was a laboratory-grade chemical and purchased from Backer Chemical Co., USA in the form of powder, partially hydrolyzed. Laboratory-grade wheat gluten (WG) with viscosity at 20˚C of 1500 cp was purchased from El-Gomhoria Co., Cairo, Egypt. Tannic Acid (TA) was obtained from Riedel-DeHaen Co., Germany, and was used without further purification

Preparation of PVA/ wheat gluten blends

Solutions were prepared from a single solvent system. Initially, the Poly vinyl alcohol (PVA) (3 wt %) solution was prepared by dissolving Poly vinyl alcohol (PVA) powder in distilled water at about 90°C with constant stirring for one hour. After the solution was cooled to room temperature, aqueous solution of gluten (3 wt % gluten/0. 1M of NaOH) was added to Poly vinyl alcohol (PVA) solutions with the ratios 10, 20, 30 and stirred for another one hour to acquire a homogeneous solution. Poly vinyl alcohol (PVA) mixture showed a phase separation by adding higher amounts of gluten. Films were prepared by casting method and drying in air.

Preparation of poly vinyl alcohol/ wheat gluten/ tannic acid blends

Blends prepared by the method mentioned above and with the same ratios and adding 4 % tannic acid deduced from the ratio of Poly vinyl alcohol (PVA) solution. Films were prepared by casting method and drying in air.

Gamma irradiation

Gamma irradiation to the 20 kGy was carried out in a Canadian cell facility at dose rate of 2.86 kGy/h that installed at the National Center for Radiation Research and Technology, Cairo, Egypt.

FTIR spectroscopic analysis

The Fourier-Transform Infrared spectroscopy analysis was carried out using model Mattson-Genssis, made by Unicam, England, over the range 500- 4000 cm-1.

Thermogravimetric analysis (TGA)

The TGA thermograms were performed on a Shimadzu instrument TGA-50 (Kyoto, Japan) at a heating rate of 10ºC/min under flowing nitrogen (20 ml/min) from room temperature to 600ºC.

Scanning electron microscopy (SEM)

The morphology of the fracture surfaces of the different prepared films were examined by SEM. The SEM micrographs were taken with a JSM-5400 electron microscope, JEOL, Japan. A sputter coater was used to pre-coat conductive gold onto the fracture surfaces before observing the micrographs at 30 kV.

Mechanical measurement

The stress-strain properties were determined according to an ASTMD-638 method using the (Mecmesin,-United Kingdom) Multi Test 25-I model, at crosshead speed 10 mm / min.). For all mechanical measurements, the recorded data is the average of three measurements for each sample.

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Results and Discussion

Characterization of PVA/WG blends

FTIR spectroscopy measurements

FTIR is one of an important instrument to determine the chemical changes in compound functional groups. The assignments of the most bands of pure PVA, WG and TA as reported in literatures [15] are shown in Table (1).

Effect of blend composition

The FTIR spectra of unirradiated films of pure PVA and its blends with WG at different ratios are shown in Fig. 1. The characteristic bands can be observed at 2650- 3650 cm-1 which due to O-H stretching from Intra intermolecular hydrogen bonding and overlapped with alkyl stretching at (2800 3000 cm-1). In particular, the intensity and width of the O-H stretching vibration peak was decreased as compared to pure PVA. These lower intensities may be due to weaker polymer-water interactions when the concentration of WG increases, suggesting a relative dehydration of PVA after WG addition, as already reported by other studies [15].

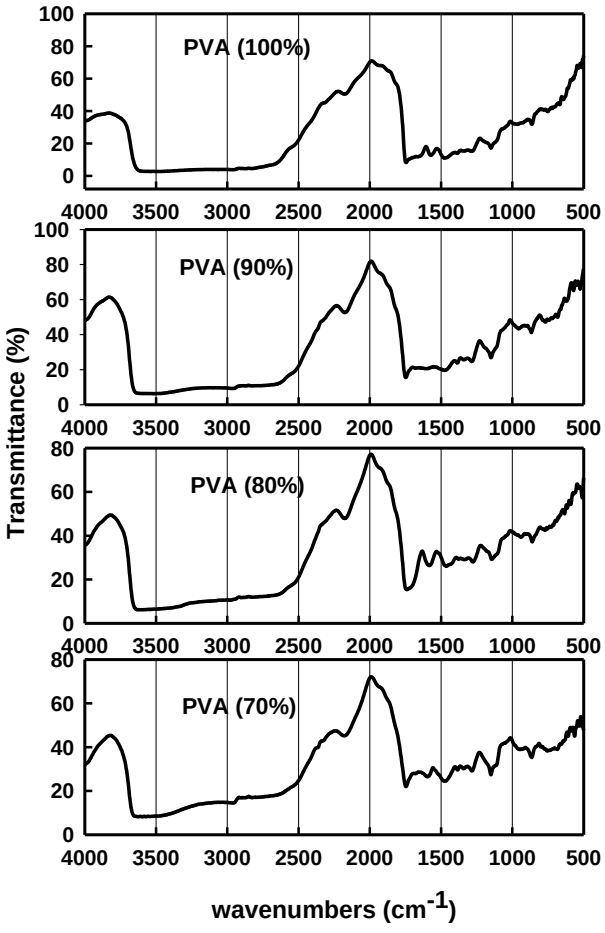


Fig 1.Effect of gamma irradiation on the structure of PVA /WG blends

The FTIR spectra for PVA /WG blends at different composition ratios and irradiation at a dose of 20 kGy are shown in Fig.2. It can be seen the decrease in OH-broadening in PVA (100%), (90%) and (80%) and separation between OH stretching and alkyl stretching (~ 2920 cm-1). This decrease may be raised from the decrease in OH hydrogen bonding (under effect of radiation the formation of bonds between chains well restricted probability of hydrogen bonding). At high ratio of WG the increase in radiation degradation of WG increases OH formation.

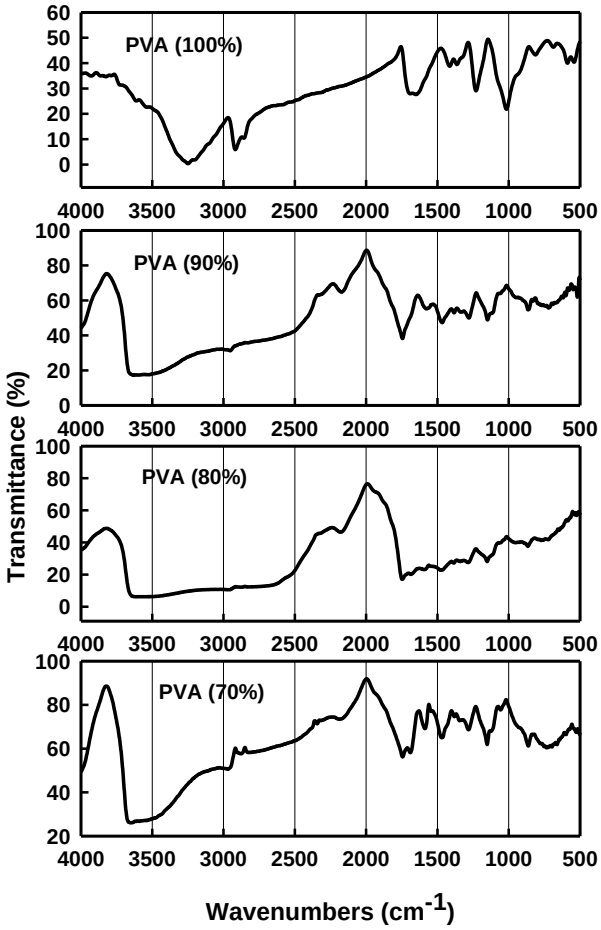


Fig.2. FTIR spectra of gamma irradiated poly(vinyl alcohol)/ wheat gluten (PVA/ WG) polymer blends to a dose of 20 kGy.

Regarding to the PVA/WG/TA films, the peak position of the stretching vibrations of the –OH groups gradually were shifted to higher wavenumbers or frequencies with the WG and TA content. The peak position was increased from 3296 cm-1 for pure PVA films to higher wavenumbers for the PVA/WG/TA composite. This shift indicate a new hydrogen bonding (O–H….O) being formed between the PVA, WG and TA complex. Hydrogen-bonding network formed in the PVA/WG/TA system where the phenolic groups of

TA and the hydroxyl groups of PVA alternatively served as proton donors or proton acceptors, as shown in Scheme 2 and Figs. (3&4). The results confirmed the existence of hydrogen bonding interactions between PVA/WG/ and TA. Irradiation of these blends may be induces free OH groups and crosslinks between different polymeric chains which restricted the hydrogen bonding.

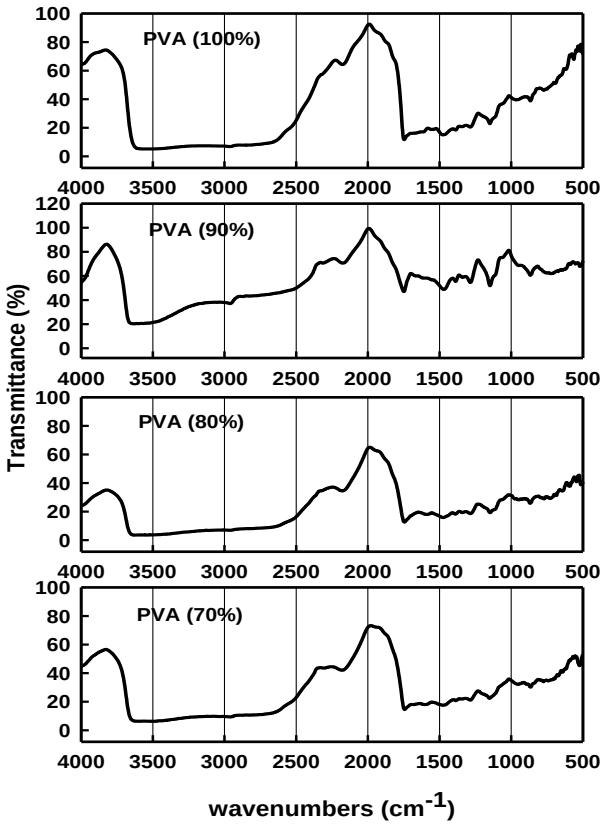
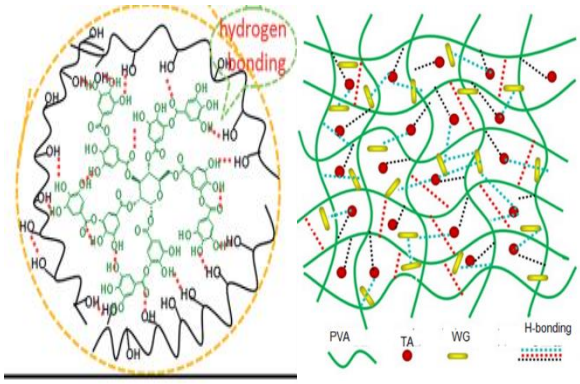


Fig.3. FTIR spectra of unirradiated poly(vinyl alcohol)/ wheat gluten (PVA/WG) polymer blends at different ratios and containing a constant ratio (4%) of tannic acid (TA).



Scheme 2. A complex hydrogen-bonding network formed in the PVA/WG/TA system

Thermogravimetric analysis

TGA analysis of polymers gives an understanding of the polymer composition and thermal stability. A detailed understanding of the degradation of polymers when heated is relevant when choosing materials for specific applications. The thermal stability of any polymer is largely dependent on the strength of the covalent bonds between the atoms forming the polymer molecules.

Figs 5 and 6 show the TGA thermograms and the rates of thermal decomposition reaction of poly(vinyl alcohol)/wheat gluten (PVA/WG) polymer blends before and after gamma irradiation to dose of 20 kGy. The initial weight loss from room temperature to 150oC can be attributed to the evaporation of the physically weakly and chemically strongly bound water, and was observed in all samples. Above 250oC, we clearly observed a difference between PVA and PVA/WG composites. For the pure PVA, the TGA curves showed three distinct peaks corresponding to mass loss associated with three decomposition steps.

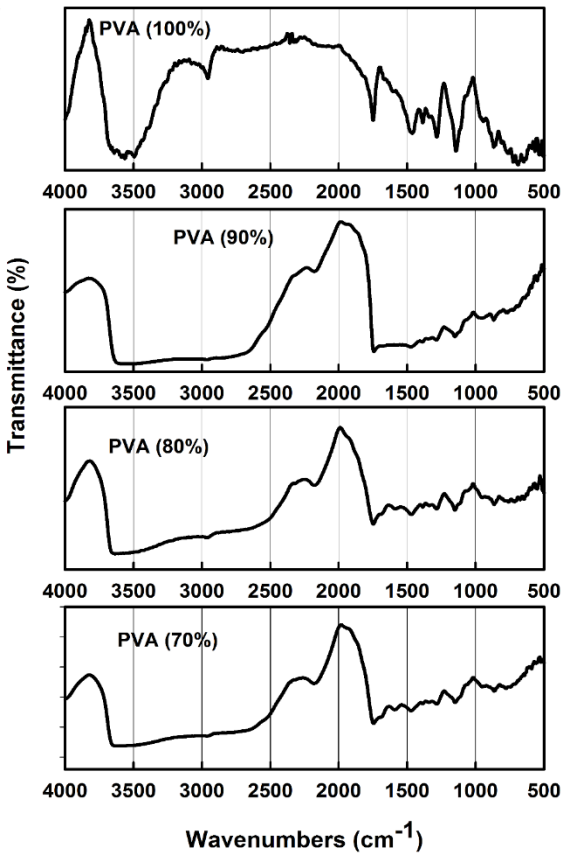


Fig.4. FTIR spectra of gamma irradiated poly(vinyl alcohol)/ wheat gluten (PVA/WG) polymer blends at different ratios to a dose of 20 kGy and containing a constant ratio (4%) of tannic acid (TA).

The first peak (~110oC) and the second peak (~340oC) can be assigned to the decomposition of the side chains of PVA with the formation of volatile products while the third weak peak (~450oC) can be identified as the decomposition of the main chains of PVA. This behavior was observed also in PVA/WG with decrease in temperature of main maximum rate of decomposition reaction with increasing WG percentage.

The effect of WG concentration on the gamma irradiated (20 kGy) PVA blends are shown in Fig 7, where it can be seen that the thermal stability of gamma irradiated (20 kGy) was improved but it decreased as WG % increased as in unirradiated samples. Based on the TGA data, it can be concluded that the addition of TA to PAV and PVA/WG improve its thermal stability at low WG concentration or in PVA alone. However, the addition of WG to PVA decreases its thermal stability and this decrease was improved by addition of TA and irradiation blends Fig 8. The improvement in thermal stability with irradiation may attribute to increasing interfacial adhesion between the PVA and WG through free radicals formed at boundary surfaces. Also, the rate of thermal decomposition reaction curves displayed similar trends going through maximum, indicating a high degree distribution of the WG within the PVA. The Tmax values reveal that the distribution and phase adhesion is better in case of the gamma-irradiated blends than in the other samples (Scheme 2).

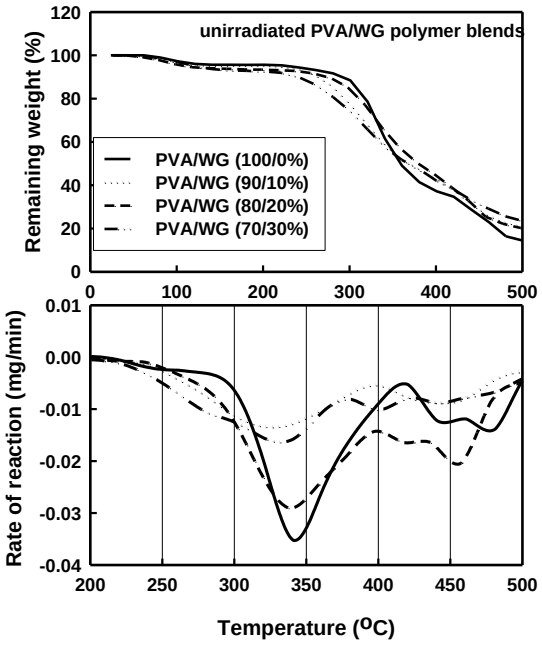


Fig.5. TGA thermograms and the rates of thermal decomposition reaction of, unirradiated poly(vinyl alcohol)/wheat gluten (PVA/WG) polymer blends.

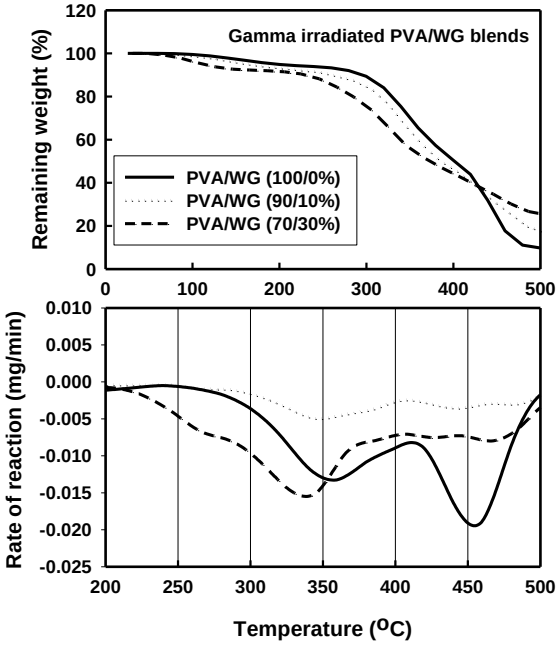


Fig.6.TGA thermograms and the rates of decomposition reaction of gamma irradiated poly(vinyl alcohol)/wheat gluten (PVA/WG) polymer blends to at a dose of 20 kGy.

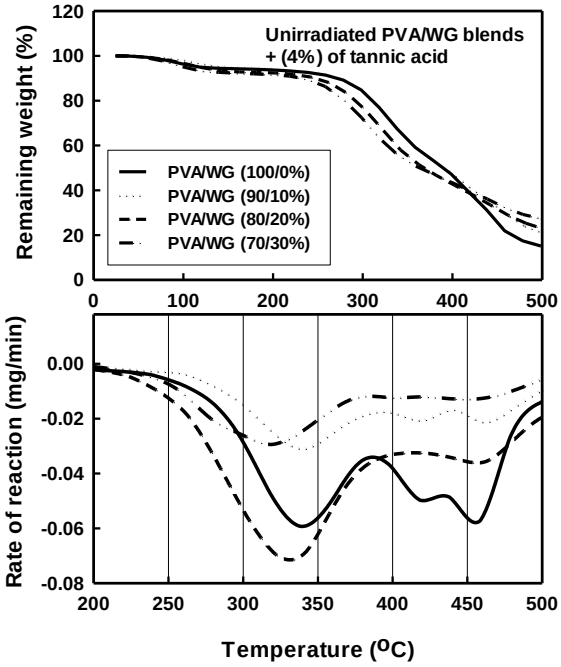


Fig.7. TGA thermograms and rate of decomposition reaction of unirradiated poly(vinyl alcohol)/wheat gluten (PVA/WG) polymer blends and containing a constant ratio (4%) of tannic acid (TA).

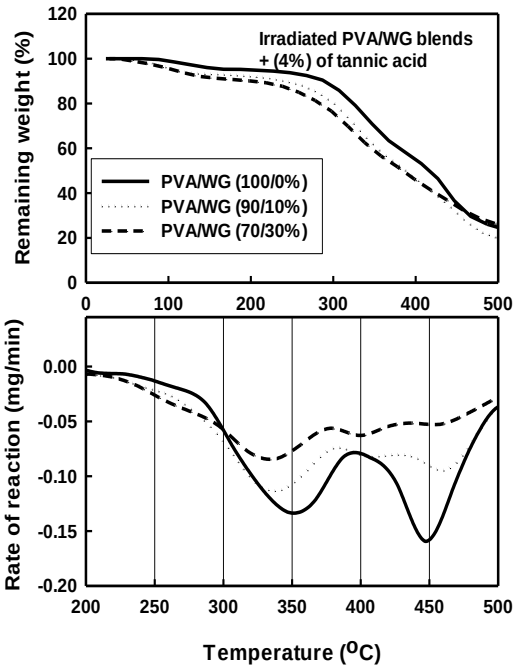


Fig. 8.TGA thermograms and rate of decomposition reaction of gamma irradiated poly(vinyl alcohol)/wheat gluten (PVA/WG) polymer blends to a dose of 20 kGy and containing a constant ratio (4%) of tannic acid (TA).

Tensile Mechanical Properties

Mechanical properties considered as an important property of polymers foremost applications. Polymers had three types according to their stress-strain curves. Brittle polymers (polystyrene), the stress-strain curves are linear up to the fracture point. Tough polymers (polyethylene) exhibit a yield point followed by a cold draw. Elastomers (polyurethane) had anon linear curve up to break point, and the elongation % about several hundred percent.

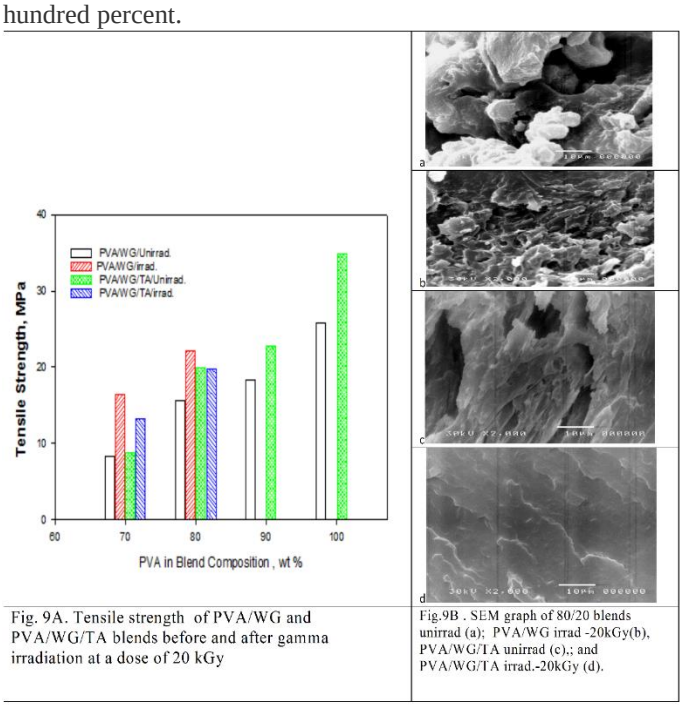


Fig. 9A. Tensile strength of PVA/WG and PVA/WG/TA blends before and after gamma irradiation at a dose of 20 kGy

Fig.9B . SEM graph of 80/20 blends unirrad (a); PVA/WG irrad -20kGy(b), PVA/WG/TA unirrad (c),; and PVA/WG/TA irrad.-20kGy (d).

Fig. 9.Tensile strength and SEM of PVA/WG and PVA/WG/TA blends before and after gamma irradiation.

Fig 9a the line of curves shows the tensile strength variations for different compositions of blends; it can be seen that tensile strength of PVA decreases by increasing the percentage of WG in the blend. This may be due to the poor interaction between PVA and WG resulting from the strong intermolecular disulfide covalent bonds of WG (Fig. 9b-1). On other hands, gamma irradiation (20 kGy) of PVA/WG blends increased its tensile strength; tensile strength increased from 15.5 to 22 MPa for (80//20) and 8 to 15 MPa for (70/30). This increase may be due to the cleavage of disulphide bonds, and/or to the fragmentation of wheat gluten to low molecular weight fragments, so the chance to form hydrogen bonds between WG and PVA was increased (Fig. 9b-3). The tensile strength of PVA increased (25-34 MPa) by adding TA to PVA or PVA blends. Since TA contains various types of oxygen

functional groups, PVA chains can be entangled and/or physically cross-linked with the TA molecule by forming multiple hydrogen bonds, which is desirable for improving the strength. In addition, there is a further increase in tensile strength with irradiation to 20kGy.

Fig. 10 shows the line curves of the elongation percent of blends (with different compositions). It can be seen that elongation % is maintain constant by increasing WG % to PVA from 10% to 20%; while by increasing its percentage up to 30, its percentage of elongation is also increased (6.6 to 34.2).WG may play a plasticizing role in the PVA matrix, that plasticizers might induce the intermolecular interactions and increased the amount of hydrogen bonding. Polar groups (–OH) of the plasticizer was believed to form polymer–plasticizer hydrogen bonding, replacing polymer–polymer interactions and hence leading to higher values of elongation percentage. Gamma irradiation causes the cleavage of disulphide bonds in WG so elongation percentage is increased to large extent from 7.8 to 91 for irradiated 80/20 blend.

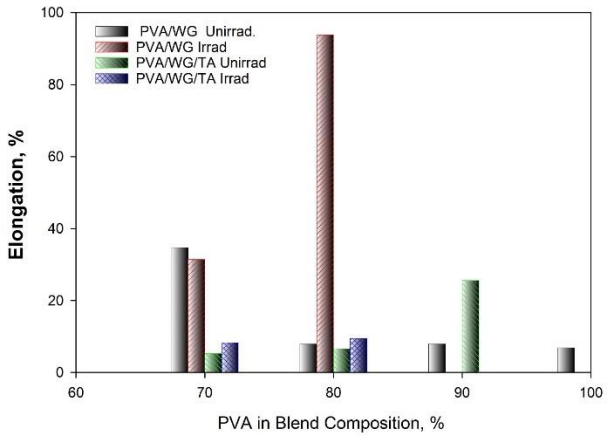


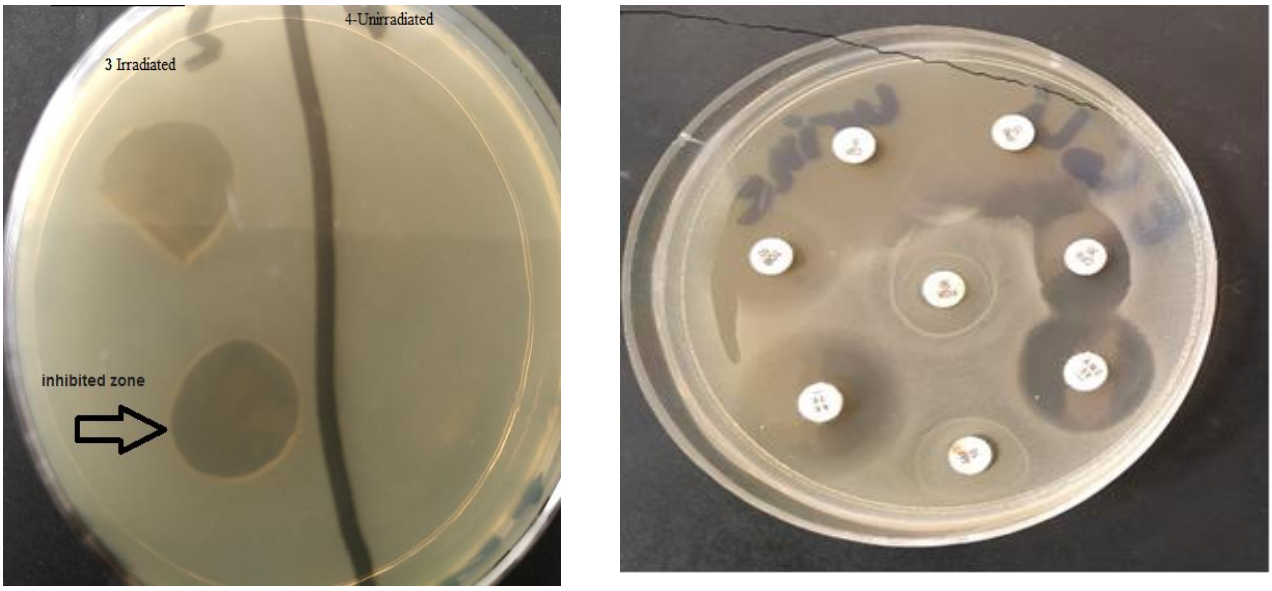
Fig.10. Elongation percentage of PVA/WG and PVA/WG/TA blends before and after gamma irradiation.

Antimicrobial properties

The antimicrobial activity of PVA/WG/TA composites against Pseudomonas that was applied as wound bacterial model and studied by an agar diffusion method. After 24 hr incubation at 37 0C, the contact areas of all PVA/WG/TA with agar surface turned transparent indicating the inhibition of bacteria growth (Fig. 11a). However, clear zones surrounding the standard discs were observed only for CRF, on the other hand FOX, AK, TOB, CiP and AM were less effective (Fig. 11b). a & b on the figure 11 implies that PVA/WG/TA exhibited inhibitory activity against Pseudomonas. The antibacterial activity of PVA/WG/TA may due that hydroxylated phenols have been shown to be toxic to microorganisms [16]. This result indicates that PVA/WG/TA nanocomposites have a biocidal effect and potential in reducing bacterial growth for practical applications.

Table 1: Assignments of some FTIR absorption bands for poly(vinyl alcohol),wheat gluten and tannic acid polymers

Polymer	Wavenumbers (cm^{-1})	Assignments
Poly(vinyl alcohol), PVA	3200-3570	O-H stretching from Intra intermolecular hydrogen bonding
	2850-3000	alkyl stretching
	1725-1740	C=O stretching from acetyl group
	1650	absorbed water
	1430	C-H bending
	1375	O-H bending
	1260	residual acetate
	1140-1100	C-O double hydrogen bonded in crystalline domain, C-O deformation
	916	O-H stretching from intraintermolecular hydrogen bonding
Wheat gluten, WG	3200-3570	O-H stretching
	2850-3000	alkyl stretching
	1640 - 1720	amide I
	1480 - 1580	amide II
	1430 - 1480	amide II
Tannic acid, TA	3500–3700	Stretching, free hydroxyl groups
	3418	stretching vibrations of O-H
	1712	stretching vibrations of C=O



a- PVA/WG/TA unrradiated 4, Irradiated 3

b- Standard antibiotic discs

Fig.11. The antimicrobial activity of PVA/WG/TA composites against

Table 2: Temperature at the maximum rate of the thermal decomposition reaction poly(vinyl alcohol)/wheat gluten (PVA/GW) polymer blends of different ratios before and after gamma irradiation to a dose of 20 kGy and those blends modified by a constant ratio (4%) of tannic acid (TA).

Blends ratios	Temperature at maximum degradation rate (T_{max}) (°C)			
	PVA/WG (unirradiated)	PVA/WG/TA (unirradiated)	PVA/WG 20 kGy	PVA/WG/TA 20 kGy
100/0	330	334	345	351
90/10	323	332		
80/20	325	325	325	344
70/30	321	309	334	330

Conclusions

Different compositions can be prepared by solution casting and irradiated to a constant dose of gamma irradiation. The produced PVA/WG polymer blends were modified by adding a constant ratio (4%) of tannic acid (TA) to the casting solution. The PVA/WG polymer blends were modified by tannic acid and irradiation. FTIR spectroscopic analysis indicated that a hydrogen bond was formed between TA and PVA also irradiation improves the adhesion between PVA and WG this conclusion also supported by scanning electron microscopy (SEM) and measuring the tensile mechanical properties..

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