

## Characterization and Antimicrobial Properties of Gamma Synthesized Plasticized Starch/Poly(vinyl alcohol)/ZnO Composites as Protective Coating for papers

Yasser K. Abdel Moneam<sup>1</sup>, Heba Allah A. Sakr<sup>1</sup>, Hussein E. Ali<sup>2</sup>, Salwa A. Khalil<sup>2</sup>  
and Abdel Wahab M. El-Naggar<sup>2,\*</sup>

<sup>1</sup>Chemistry Department, Faculty of Science, El- Minufiya University

<sup>2</sup>Radiation Chemistry Department, National Center for Radiation Research and Technology, B.O. Box 29 Nasr City, Cairo, Egypt.

\*Corres. author: ab\_nagga@yahoo.com

**Abstract:** Unlike conventional methods of polymerization and crosslinking based on chemical initiators, in this work gamma irradiation has been used for the preparation of protective composite for papers against the attack of microbes. In this regard, blends based on plasticized starch (PLST) as major constituent and poly(vinyl alcohol) (PVA) were prepared in the form of thin films by casting solutions. The gamma irradiated blends were characterized by IR spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), mechanical testing, swelling and scanning electron microscopy (SEM). The results of TGA indicated that PLST/PVA blends are thermally more stable than pure PLST. DSC scans do not show the glass transition temperature ( $T_g$ ) of PVA or PLST, but instead a new single glass transition, indicating the occurrence of compatibility. The mechanical properties of PLST/PVA blends showed that the tensile strength and elongation at break was found to increase by increasing the ratio of PVA. At any ratio of PLST/PVA, the tensile strength and elongation at break was found to increase with increasing irradiation dose. As an application in the field of paper surface modification, solutions of gamma irradiated PLST/PVA blends in the presence of zinc oxide, as an antimicrobial agent, were applied to paper by surface coating. The results showed this technique might provide suitable materials for the protection of papers against microbial attack.

**Keywords:** Poly(vinyl alcohol), ZnO, Gamma radiation, Antimicrobial, properties, Surface Coating.

### 1. Introduction

Paper is the most widely used material in packaging applications due to its characteristics of printability, recyclability and biodegradability[1]. However, since paper is hygroscopic and highly porous, hydrophilic paper is easily subjected to microbial attack, ultraviolet degradation and higher water vapor transmission. In addition, the sizing agents like starch that are applied to the surface of paper make the condition still worse.

Development of environmental friendly materials is a continuing area of challenge for food packaging and coating technology. The excellent chemical resistance, optical and physical properties of poly(vinyl alcohol) (PVA) polymer enables a broad industrial uses. In addition, it was reported that PVA is a biodegradable polymer, in which the mechanism of biodegradation involves first dehydrogenation into the corresponding carbonyl groups to form  $\beta$ -hydroxy ketone which followed by aldolase-type cleavage [2].

Packaging films depend entirely of starch; however, lack the strength and rigidity to withstand the stresses to which many packaging materials are subjected [3]. Starch, on the other hand, is a naturally occurring polymer, renewable, low effective cost, and easy to handle. Both PVA and starch are polar polymers; thus a blend of PVA and starch is likely to produce a material having excellent mechanical properties and barrier behavior. Moreover, the blending of naturally occurring polymers like starch with other polymeric materials could provide biodegradable materials [4,5]. Incorporation of starch into the PVA matrix changes the physico-mechanical properties of the material and thus modifies the polymer structure at both the molecular and the morphological levels [6–9]. Blends of Sago starch, poly(vinyl alcohol) (PVA) and poly vinyl pyrrolidone) (PVP) polymers were studied [10]. They found that blending of Sago starch with PVA showed a significant increase in gel content especially at higher irradiation doses of more than 20 kGy. On the contrary, Sago/PVP blends showed crosslinking properties lower than Sago/PVA. Preparation and mechanical properties of composite films based on agro-industrial wastes (lignocellulose fibers byproducts derived from sugar cane and apple and orange juice extraction) and PVA was reported [11]. The development of biodegradable films based on blends of *Amaranthus cruentus* flour and PVA was investigated [12]. It was found that the blends with higher hydrolysis degree PVA were more resistant, showing greater tensile strength and puncture force, however, the films with lower hydrolysis degree PVA showed more flexibility, greater elongation at break and greater puncture deformation. The thermal stability, water permeability and biodegradation properties of composite films prepared from blends of PVA, cornstarch and lignocellulosic fibers were studied [13]. The thermal, mechanical and surface characterization of starch/PVA blends, crosslinked with borax in situ and post treatment methods was reported [14]. Meanwhile, synthesis of PVA/starch grafted hydrogels by gamma and electron beam irradiation at room temperature was reported [15]. It was found that the gel strength was improved after adding starch into PVA, but the swelling properties decreased slightly due to the poor hydrophilicity of starch.

High-energy irradiation is a well-known technology for modifying polymers [16-18], in which radiation processing has the potential of playing a great role in polymer blends similarly as in the case of individual polymers. Irradiation of polymer blends can be used to crosslink or degrade the desired component polymer, or to fix the blend morphology through free radical formation at the boundary surfaces in the polymer blend phases. The present work is undertaken to study the effect of gamma irradiation on the structure-property behavior of polymer blends based on plasticized starch and poly(vinyl alcohol). As an application in the field of paper surface modification, solutions of gamma irradiated PLST/PVA blends in the presence of zinc oxide, as an antimicrobial agent, were applied to paper by surface coating.

## 2. Experimental

### 2.1. Materials

Maize starch (amylase, 27% and amylopectin, 73 %) used throughout this study was supplied by the Egyptian Company for Starch and Glucose, Cairo, Egypt. Poly (vinyl alcohol) (PVA), used in this study is a laboratory grade in the form of powder, partially hydrolyzed (88%), has an average molecular weight (Mw) of 125,000 and was obtained from Laboratory Rasayan, India. Zinc oxide, used as antimicrobial agent was a laboratory-grade chemical and purchased from El- Gomhoria Company, Cairo, Egypt.

### 2.2. Preparation of plasticized starch

Plasticized starch was prepared by treating maize starch with 20 wt% of glycerol (based on starch weight) and subsequently dissolved in excess water with continuous stirring and heating for one hour at > 100°C to complete gelatinized solution.

### 2.3. Preparation of PLST/PVA blends

Plasticized starch/poly(vinyl alcohol) (PLST/PVA) blends of different ratios were prepared by adding the required amount of PVA, dissolved in hot water to the gelatinized solution with continues stirring. Thin films were obtained by casting the blend solutions on Petri dish and allowed to air-drying. The films were then placed in vacuum oven at 80°C for four hours to remove the residual water.

### 2.4. Preparation of PLST /PVA/zinc oxide composites

Films PLST/PVA blends with a constant ratio of zinc oxide (5%) were prepared at different composites. the required amount of zinc oxide was added to the PLST /PVA blends. Film were obtained by

casting the blends on glass Petri dish, and allowed to air-drying at room temperature.

### 2.5. Gamma irradiation

Irradiations to the required doses were performed at a dose rate of 4.8 kGy /h in air in the Co-60 gamma cell facility of the National Center for Radiation Research and Technology, Cairo, Egypt.

### 2.6. FT-IR spectroscopic analysis

The infrared analysis was carried out using Fourier-Transform Infrared Spectroscopy (FT-IR) model Mattson-Genisis, made by Unicam, England, over the range 400- 4000  $\text{cm}^{-1}$ .

### 2.7. Thermogravimetric analysis (TGA)

The TGA thermograms were performed on a Shimadzu instrument (Kyoto, Japan) at a heating rate of 10°C/min under flowing nitrogen (20 ml/min) from room temperature to 500°C.

### 2.8. Differential scanning calorimetry (DSC)

DSC measurements were performed using a Shimadzu DSC calorimeter (Kyoto, Japan) equipped with data station. A heating rate of 10°C/min was utilized and the scans were carried out under a flowing nitrogen gas at a rate of 20 ml/min.

### 2.9. Tensile mechanical testing

Mechanical testing of PLST/PVA blends including tensile strength and elongation at break points was performed at room temperature using an Instron Machine (model 1195, England) employing a crosshead speed of 5 mm/min. according to ASTM D-638 standards. The recorded value of the tensile strength and elongation at break is average of five measurements.

### 2.10. Scanning electron microscopy (SEM)

The morphology of the fracture surfaces of the different PLST/PVA blend films was 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.

### 2.11. Antimicrobial studies

Antibacterial activity of the PLST/PVA/ZnO blends against *Escherichia coli* was evaluated by comparing zones area. Films were placed on Petri dishes contain medium and *Escherichia coli* culture and then incubated at 37°C for 18 h.

## 3. Results and Discussion

### 3.1. IR spectroscopy

FT-IR spectroscopic analysis can give useful information about chemical changes occurring in polymer systems due to blending process as well as gamma irradiation. However, the detection of such changes may be restricted because often different polymer compounds in the polymer blends are chemically similar, so their absorption peaks are masked. To facilitate the detection of changes, a comparison between the characteristic bands of the compounds is investigated.

IR spectra of PLST and different compositions of PLST/PVA blends, before and after gamma irradiation to different doses are shown in Figs 1-3. As shown in Fig.1, the IR spectrum of PLST showed an absorption band at 2500-3200  $\text{cm}^{-1}$  due to  $\text{CH}_2$  stretching groups as almost all organic compounds. The intensity of this band was found to increase with the increase of PVA ratio. An absorption band can be seen in the IR spectra of PLST/PVA blends at about 3100-3700  $\text{cm}^{-1}$ , which is due to OH stretching arises due to addition of PVA to the blends. As shown, there is no significant shift in the position of the IR peaks compared to those of the IR spectrum of pure PLST, which indicates that there is no intermolecular interaction between PLST and the PVA. The only intermolecular forces expected to develop between PLST and PVA are weak Van der Waals interaction forces [10, 20]. However, the broadness of the stretching band

due to the OH groups in the IR spectra of PLST/PVA blends is indication of the formation of hydrogen bonds between the OH groups of the starch and PVA component in the blend.

IR analysis can be used to illustrate the chemical change that might be occurring in the polymer materials due to irradiation. Irradiation of polymers in air creates oxidative products (C=O and O-H) that can be followed by FT-IR analysis [21]. As shown in Figs.2 and 3, there is an increase in the intensity of transmittance bands due to oxygenated groups formed during electron beam irradiation. This increase is more pronounced in PLST/PVA blends than that of pure PLST. Also, the intensity of these bands was found to increase with increasing the ratio of PVA in the blends. This increase is due to the degradation ability of starch which is more than that of PVA under gamma irradiation.

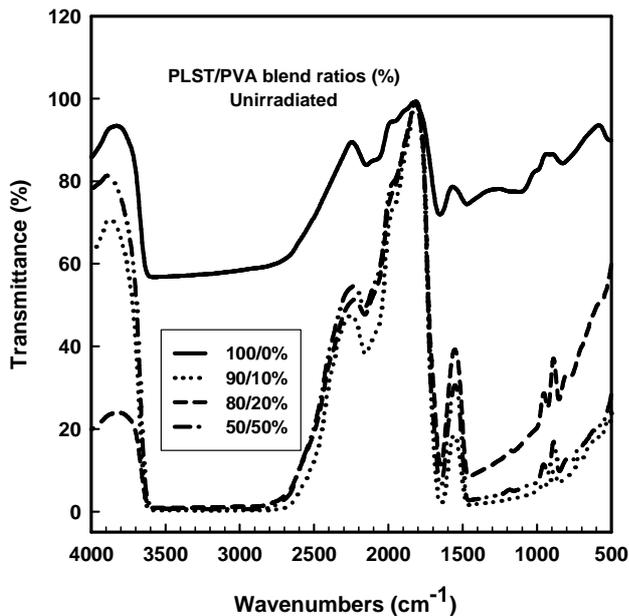


Fig.1. IR spectra of unirradiated PLST/PVA blends, prepared at different ratios.

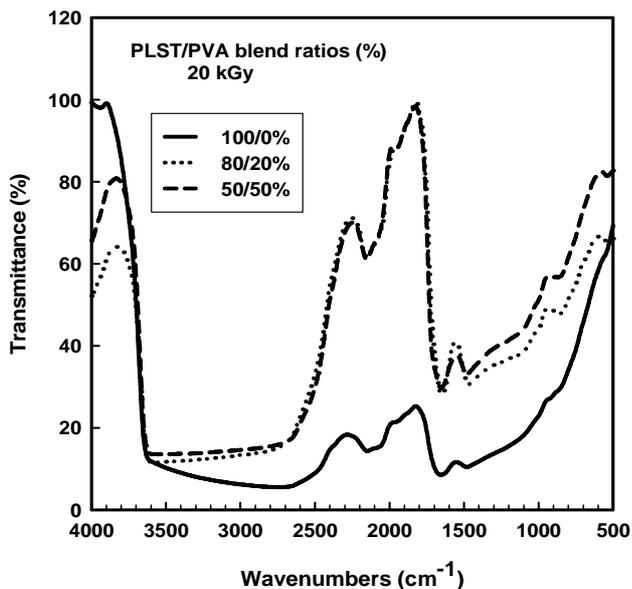
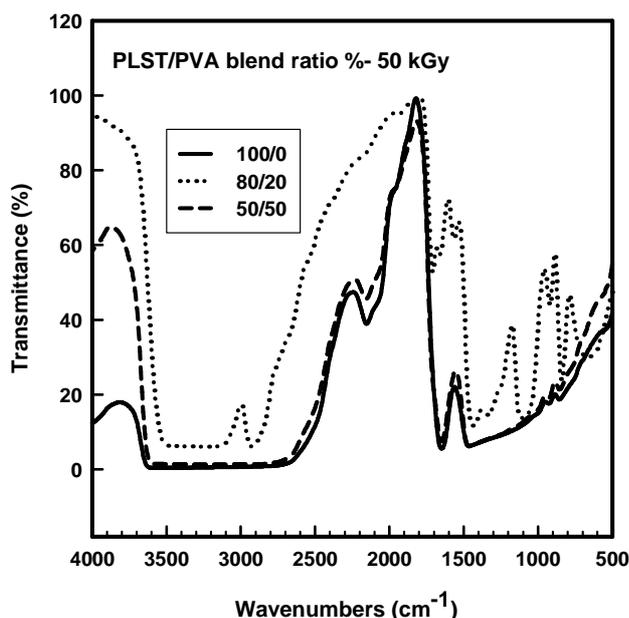


Fig.2. IR spectra of PLST/PVA blends, prepared at different ratios and gamma irradiated at a dose of 20 kGy.



**Fig.3.** IR spectra of PLST/PVA blends, prepared at different ratios and gamma irradiated at a dose of 50 kGy.

### 3.2. Thermogravimetric Analysis (TGA)

The thermal stability of any polymeric material is largely determined by the strength of the covalent bonds between the atoms forming the polymer molecules. The dissociation energy for the different covalent bonds C-H, C-C, C-O and O-H was reported to be 414, 347, 351, 464 and 611 kJ/mol, respectively [22]. On the basis of these values, the average complete dissociation energy of PVA and starch is calculated to be 419 and 385.9 kJ/mol. Thus it may be concluded that PVA possesses higher thermal stability than starch and that the blends of PLST with any ratio of PVA will eventually result in blends with higher thermal stability than pure PLST. However, the limited macromolecular chain mobility as a result of the formation of intermolecular hydrogen bonds, as well as the association between the macromolecules of the blend components is also expected to increase the thermal stability.

Thermogravimetric analysis (TGA) was used to investigate experimentally the thermal stability of PLST/PVA blends. **Figures 4-6** show the initial TGA thermograms and the corresponding rate of reaction curves of different ratios of PLST/PVA blends, before and after gamma irradiation at different doses. In addition, the weight loss (%) at different decomposition temperatures for the same materials taken from the corresponding TGA thermograms is summarized in **Table 1**. Based on the TGA study, few points may be concluded:

- (1) The major loss in weight (20-70%) for unirradiated or irradiated blends occurs within the range of 200-350°C, in which irradiated blends possess higher thermal stability than unirradiated blends.
- (2) As shown, it seems that the effect of irradiation dose on thermal stability depends largely on the ratio of PVA. For the blend contains 20% PVA, at the same temperature, the weight loss (%) decreased with increasing irradiation dose. Thus, thermal stability of blends increases with increasing the ratio of PVA in the blend and irradiation dose. This increase in thermal stability can be explained as due to increased degree of crosslinking of PVA associated with the increase in irradiation dose. This also agrees with a sharp increase in tensile properties for PLST/PVA blends as we see later.
- (3) The rate of thermal decomposition reaction curves displayed similar trends, in which all the blends go through one maximum indicating a good distribution between PLST and PVA in their blends. Visual observation also showed that all the solutions of PLST/PVA mixture were clear at room temperature and the films of the blends appear transparent. The temperatures of maximum value of the rate of reactions ( $T_{max}$ ) indicate clearly that gamma irradiated PLST/PVA blends possess higher thermal stability than unirradiated blends. The  $T_{max}$  was found to increase with increasing irradiation dose and the ratio of PVA in the blends. These results indicate that PLST/PVA blends are thermally more stable than pure PLST.

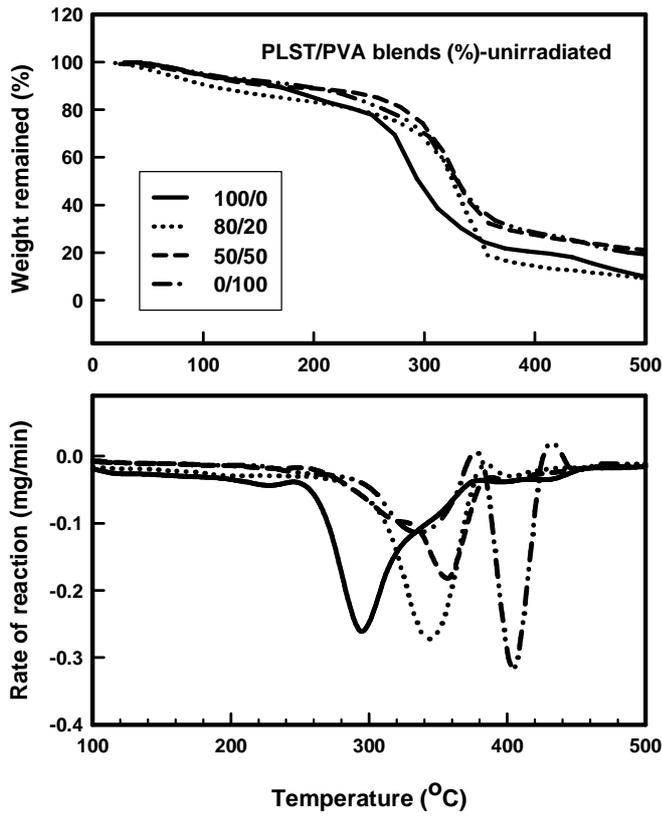


Fig.4.TGA thermograms and the corresponding rate of reaction curves of unirradiated PLST/PVA blends, prepared at different ratios.

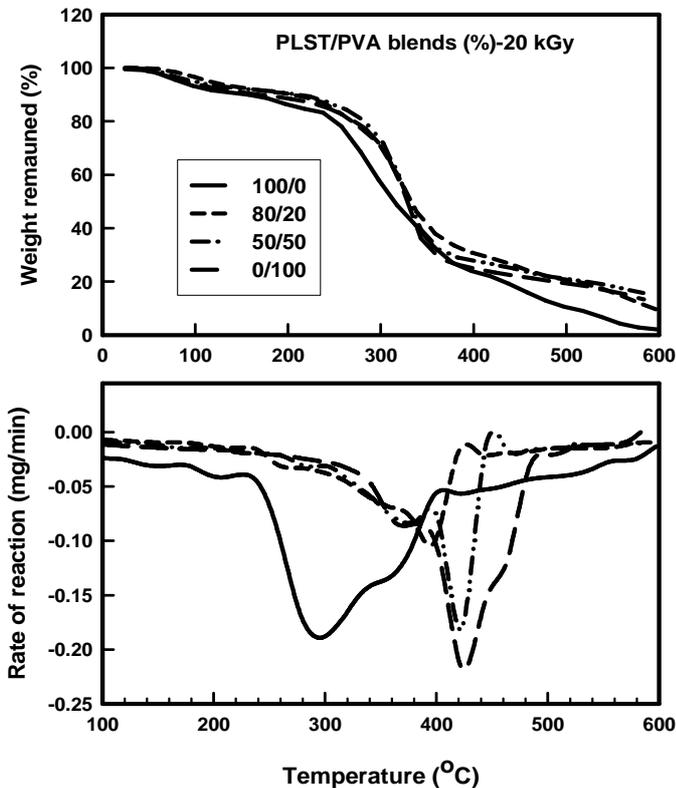
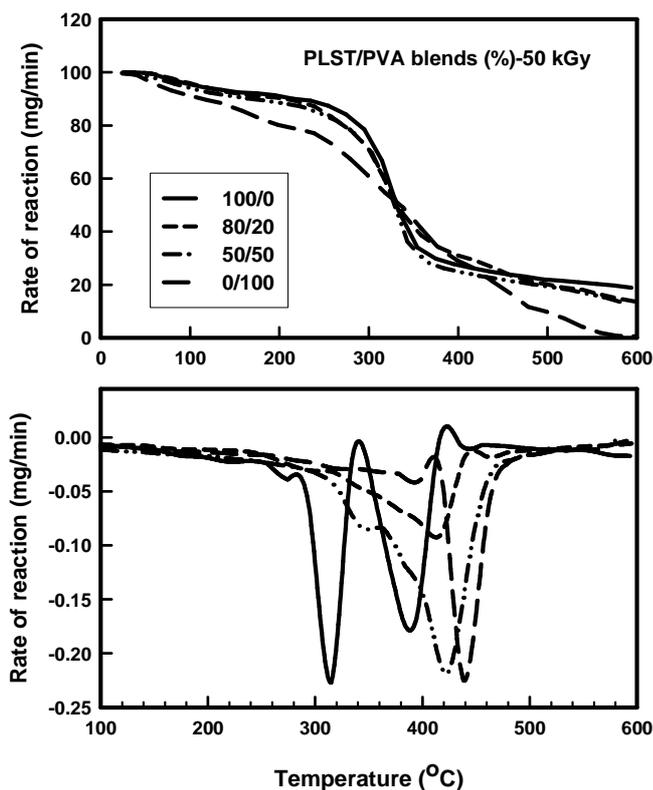


Fig.5. TGA thermograms and the corresponding rate of reaction curves of different ratios of PLST/PVA blends, gamma irradiated to a dose of 20 kGy.



**Fig.6.** TGA thermograms and the corresponding rate of reaction curves of different ratios of PLST/PVA blends, gamma irradiated to a dose of 50 kGy.

Van Krevelen developed a correlation for the temperature of half-decomposition ( $T_{d1/2}$ ), which defined as the temperature at which the loss of weight during pyrolysis reaches 50 % of its final value at a constant rate of temperature rise [23]. In this correlation,  $T_{d1/2}$  is approximated in terms of the ratio of the molar thermal decomposition function ( $Y_{d1/2}$ ) divided by molecular weight ( $M$ ) per repeat units:  $T_{d1/2} = Y_{d1/2} / M$ . It should be noted that  $Y_{d1/2}$  is estimated by group contribution and is expressed in Kelvin Kg/mol; and because  $M$  is in grams/mol, a conversion factor of 1000 must be used. Based on this correlation, the  $T_{d1/2}$  value for PVA was calculated to be 322°C [24]. As shown in **Table 1**, the experimental value of  $T_{d1/2}$  is in accordance with the theoretical calculations.

**Table 1:** Weight loss (%) at different heating temperatures and the temperatures of the half-decomposition,  $T_{d1/2}^*$ , of PLST/PVA blends before and after gamma irradiation to different doses.

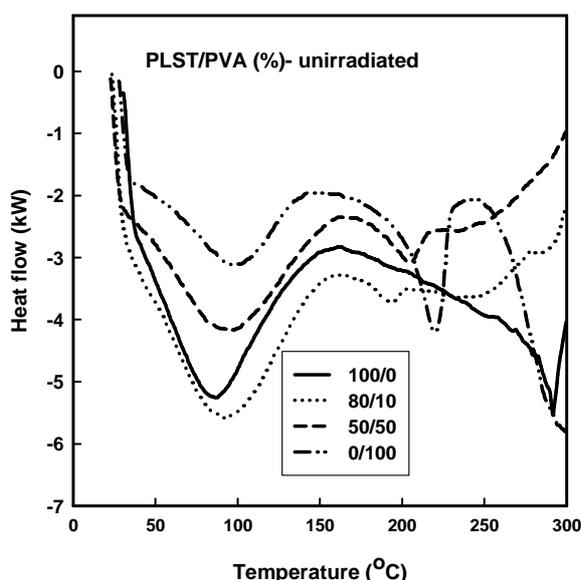
PLST/PVA blend ratios (%)	Dose (kGy)	Weight loss (%)					$T_{Max}$ (°C)	$T_{d1/2}$ (°C)
		500°C	400°C	300°C	200°C	100°C		
100/0	0	90.67	80.41	61.53	16.90	6.58	293.4	293.4
	20	89.42	75.99	41.93	13.55	6.69	297.7	297.7
	50	77.98	72.25	21.54	18.58	5.67	395.1	333.7
80/20	0	90.57	85.33	30.51	17.90	11.06	337.2	317.0
	20	79.30	69.29	28.76	9.66	3.45	398.6	338.5
	50	79.92	68.85	28.36	9.69	4.10	418.7	317.6
50/50	0	80.99	71.91	31.46	11.11	5.29	358.4	318.3
	20	80.82	75.33	30.35	11.64	6.22	423.0	322.8
	50	80.165	70.84	38.80	19.90	8.80	423.5	322.8
0/100	0	78.88	72.44	25.81	11.07	5.55	404.3	322.8
	20	79.21	72.42	28.16	9.72	5.43	423.5	322.8
	50	80.82	75.33	30.35	11.64	6.22	438.3	318.4

\*The values of  $T_{d1/2}$  were taken from the experimental TGA thermograms

The increase in thermal stability associated with the increase of irradiation dose can be attributed to crosslinking of PVA component. It has been reported that the increased thermal stability of polymer networks made of vinyl terminated polyurethane, vinyl benzyl alcohol and poly(methyl methacrylate) results from crosslinking, as concluded from TGA study [25]. Also, it was reported that the increase of thermal stability of polyesters, polypropylene and rayon fibers brought about by increasing the irradiation dose is due to the formation of double bonds and crosslinking [26]. Moreover, it was reported that crosslinking increases the thermal stability of polymers as a result of structural effects on the thermo-oxidative stability.

### 3.3. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) technique is one of the convenient methods for investigating the compatibility of polymer blend. It was used to investigate the effect of blending PVA and PLST on the glass and melting transitions of PLST/PVA blends. **Figures 7-9** show the DSC thermograms for unirradiated PVA and PLST as well as PLST/PVA blends of different ratios before and after they had been exposed to different doses of gamma irradiation. **Table 2** summarizes the different kinetic parameters taken from these thermograms. As shown in **Fig 7**, the DSC thermograms of unirradiated PLST showed a well-defined fusion peak with maximum fusion temperature at 67°C, whereas the DSC thermograms of unirradiated PVA showed an endothermic peak due to the melting temperature ( $T_m$ ) and a baseline inflexion due to the glass transition temperature ( $T_g$ ). It should be noted that the  $T_g$  was taken as the temperature of the onset of the baseline inflexion peak, which is the enthalpy relaxation of the amorphous part, while the  $T_m$  was taken as the onset of the second endothermic peak which is due to the melting of the crystalline part of the blend. The reported glass transition temperatures in the literature for PLST and poly(vinyl alcohol) were 84 and 99°C, respectively [27]. The DSC thermograms of unirradiated PLST/PVA blends showed different features from that of PLST or PVA, in which they displayed one endothermic peak around 240°C. No changes were observed in the endothermic peak with increasing the ratio of PVA from 20 to 50%. It is clear that the increase of irradiation dose from 20 to 50 kGy increased the  $T_m$  of PLST/PVA (80/20%) from 237.3 to 240.7°C. This effect is due to the crosslinking of PVA. However, it is evident that the DSC scans of the glass transition do not show either the  $T_g$  of PVA or PLST, but instead a new single glass transition, which may suggest the occurrence of compatibility. It can be seen that the value of  $T_g$  increased with increasing irradiation dose. Also, there is a drop in the  $T_m$  due to the gamma irradiation of the blends from 20 to 50 kGy, regardless of the blend composition.



**Fig.7.** DSC scans of unirradiated PLST/PVA blends.

Based on the thermodynamic theory of glass transition temperature, the familiar Fox equation (shown below) derived to predict the  $T_g$  of random copolymers of complete miscible polymers was applied to the present PLST/PVA blends [28].

$$1/T_g = M_1/T_{g1} + M_2/T_{g2}$$

Where  $T_g$ ,  $T_{g1}$  and  $T_{g2}$  are the glass transition temperatures of the polymer blend and the individual polymers, respectively.  $M_1$  and  $M_2$  are the mass fractions of the individual polymers. The expected  $T_g$  values for the PLST/PVA blends of ratios 80/20 and 50/50% calculated according to the Fox equation are 72.2 and 77°C, respectively. The deviation of the  $T_g$  values (from DSC) from those calculated on the bases of the Fox equation for the same blends were found to 25.83 and 21.03°C, respectively. This deviation is due to the occurrence of crosslinking, which restrict the mobility of chains.

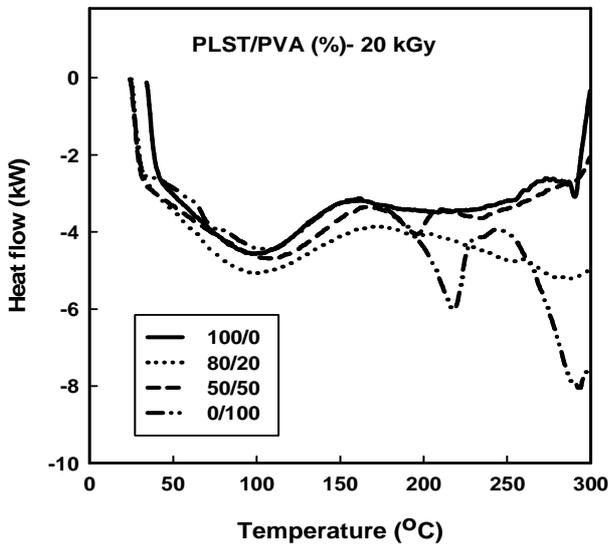


Fig.8. DSC thermograms of PLST/PVA blends, prepared at different ratios and gamma irradiated at 20 kGy.

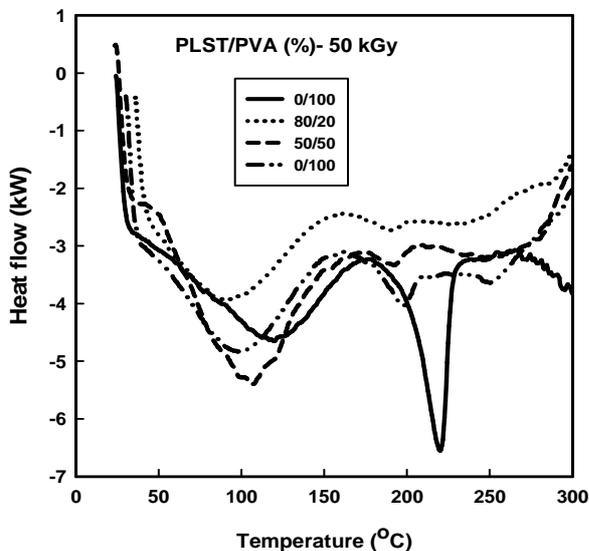


Fig.9. DSC thermograms of PLST/PVA blends, prepared at different ratios and gamma irradiated at 50 kGy.

**Table 2:** DSC parameters of pure PLST and PLST/PVA blend of different compositions, before and after they had been gamma irradiation to various doses.

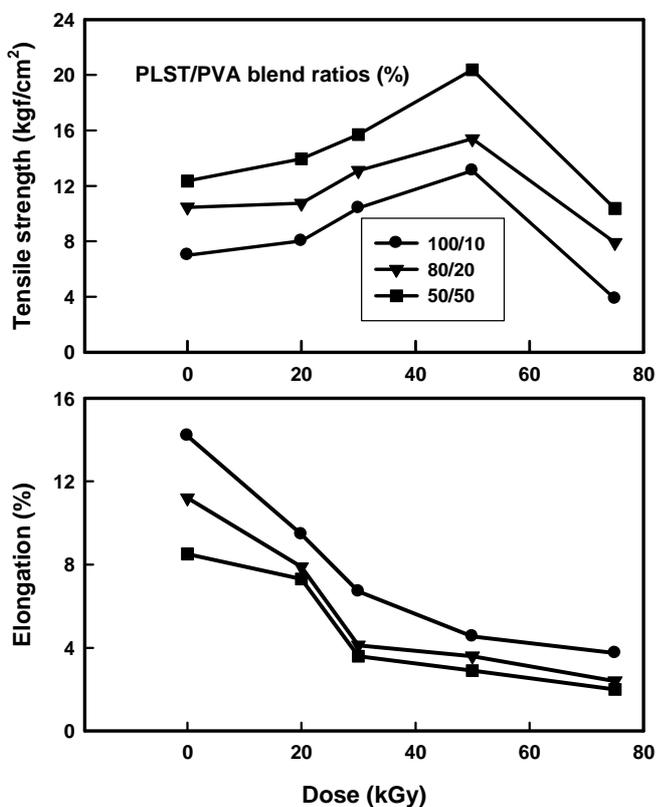
PLST/PVA blend ratio (%)	Dose (kGy)	$T_m$ (°C)	$T_g$ (°C)
PLST (100)	Unirradiated	-	67.5
80/20	Unirradiated	243.1	97.8
	20	237.3	118.0
	50	240.7	125.3
50/50	Unirradiated	243.3	98.0
	20	227.1	91.2
	50	238.3	114.4

### 3.4. Mechanical Properties

Most plastic materials are used because they have desirable mechanical properties at an economic cost. For this reason, the mechanical properties may be considered the most important of all the physical properties of high polymers for most applications. There are many structural factors, which affect the mechanical behavior of such materials. In addition to the chemical composition, molecular weight, crosslinking and branching, crystallinity and crystal morphology, copolymerization, plasticization, molecular orientation and fillers are structural factors, which affect the mechanical properties. Starch is a semi-crystalline polymer having a highly branched amylopectin molecules, the partially crystalline component, and nearly linear amylose molecules apparently the amorphous part [29]. When starch is heated with water it displays the gelatinization phenomena caused by the insoluble amylopectin component. The stress-strain test is the most widely method used of all the mechanical tests.

In this work, the effect of gamma irradiation on the mechanical properties of PLST/PVA blends of different ratios was studied as shown in **Fig 10**. While the tensile strength of PLST/PVA blends was found to increase by increasing the ratio of PVA, the elongation at break was found to decrease by increasing the ratio of PVA. However, the tensile strength was found to increase up to a dose of 50 kGy and tends to decrease at higher doses. The elongation at break was found to decrease with increasing irradiation dose.

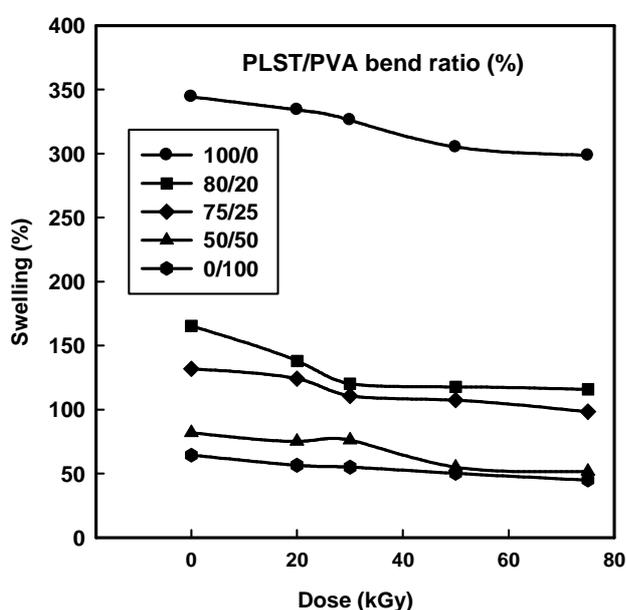
The improvement in the tensile strength of unirradiated PLST/PVA blends with increasing the ratio of PVA may be attributed to the formation of hydrogen bonds or chemical interactions between the –OH group of PVA and the –OH group of starch. On the other hand, the improvement in mechanical properties after gamma irradiation is due to the occurrence of crosslinking to the PVA component in the blend. The introduction of PVA as flexible polymer into plasticized starch would result in formation of hydrogen bonding between PLST and PVA in the blend. However, the presence of PVA prevent the retrogradation process that may occur in the amylopectin component of starch and consequently, the elongation at break will increase. The increase in elongation at break in irradiated samples may be due to the occurrence of oxidative degradation to starch component and crosslinking to PVA component.



**Fig.10.** Tensile strength and elongation at break (%) of PLST/PVA blends, prepared at different ratios and gamma irradiated at different doses.

### 3.5. Swelling Characters

Water absorption is an important factor in the evaluation of coatings formulations. This is because water absorption is very essential for thrive of the microorganisms, which depends on the presence of moisture, water and nutrients. Thus, the higher the ability of the material to absorb water, the higher is the capability to undergo biodegradation. **Figure 11** shows the swelling in water at room temperature and pH 7 of PLST/PVA blends, prepared at different ratios and gamma irradiated at different doses. It is clear that the addition of PVA to PLST decreased the water swelling. In this regard, the swelling (%) for the unirradiated PLST is ~ two times that for PLST/PVA (80/20%) blend. This is due to the hydrophilic character of PLST, which contains about 27% of its weight as water soluble (amylase component). On the other hand, the swelling (%) decreased with increasing irradiation doses up to 75 kGy. The crosslinking properties were increased and consequently, the water absorption was decreased. At higher doses, the water absorption was affected with PVA crosslinking, starch degradation and formation of oxygenated groups in PLST. Thus, the decrease of swelling (%) of these blends is expected to prevent the attack by microorganisms.



**Fig.11.** Swelling in water at room temperature and pH 7 of PLST/PVA blends, prepared at different ratios and gamma irradiated at different doses.

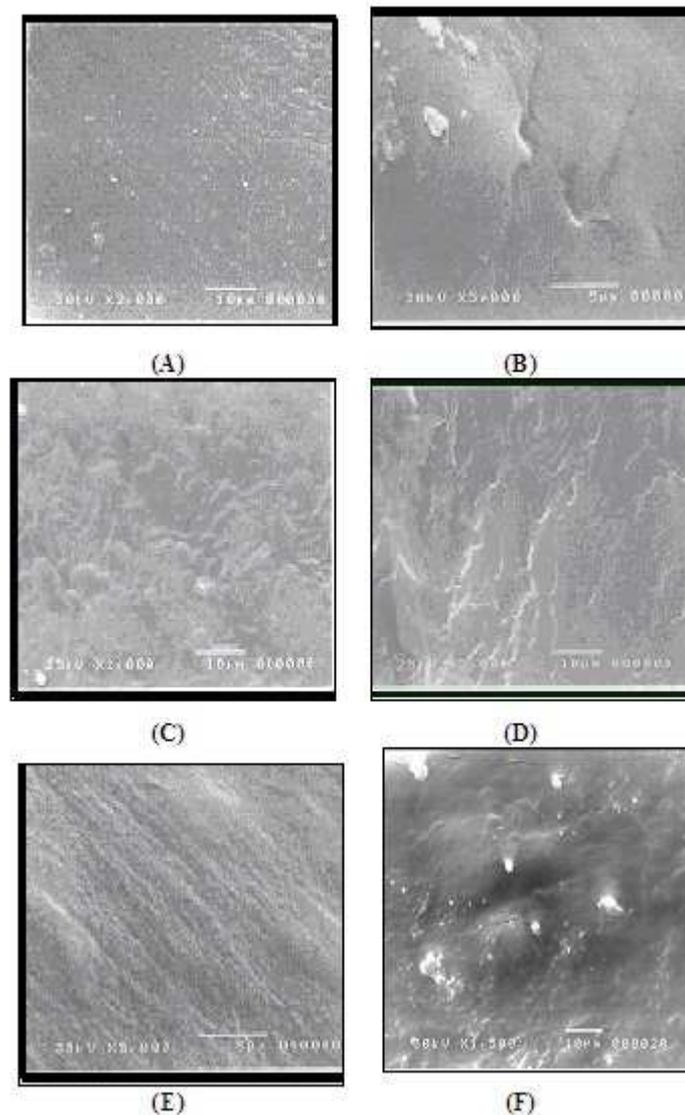
### 3.5. Scanning Electron Microscopy (SEM)

In compatible blends such as PLST/PVA, the mechanical properties depend on the phase dispersion as well as on phase size. Thus, in the PLST/PVA blends, PVA is expected to be the dispersed phase. **Figure 12** shows the SEM micrographs of the fracture surfaces of unirradiated pure PLST and PLST/PVA blends of different ratios before and after gamma irradiation to different doses. As can be seen, the fracture surface of pure PLST is smooth and characterized with the presence of white particles due the gelatinization. However, the SEM micrographs of unirradiated PLST/PVA blends showed a different surface morphology, in which the surface is not smooth and with different texture and this texture changes with increasing the PVA ratio in the blend. The effect of gamma irradiation is very clear, in which it is difficult to distinguish the PLST phase, which seems to become a part of the whole matrix. In addition, there is an evidence for the formation of crosslinking and degradation of the PLST phase. The crosslinking through the matrix appears as continuous phases and compact structures corresponding to each blend composition.

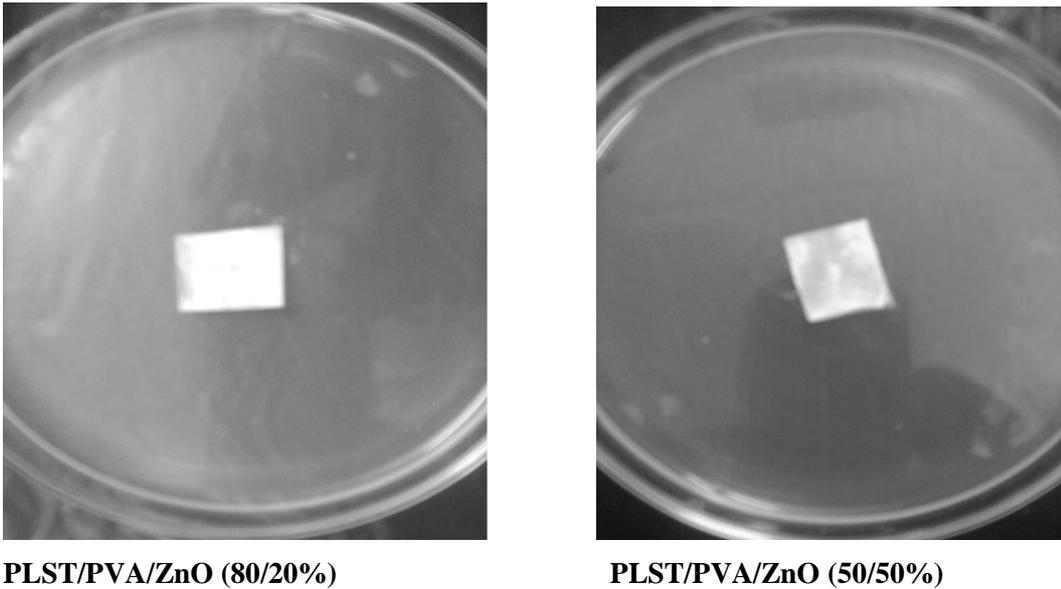
### 3.6. Application of PLST/PVA/ZnO as Protective Composites for papers

Paper is reported to be the most widely used material in packaging applications due to its characteristics of printability, recyclability and biodegradability[30-32]. However, since paper is hygroscopic and porous, its barrier properties against water-vapor, gases and aromas are poor. To improve its barrier properties, paper is often impregnated with coatings from synthetic polymers such as polyethylene, poly(vinyl alcohol), rubber latex and fluorocarbon. Theses polymers fill the paper pores and form a dense layer at the paper surface. Unfortunately, the use of such synthetic polymers leads to the loss of the paper's biodegradability. In an effort

to produce more environmentally friendly and renewable materials, biodegradable polymers have been investigated as surface-coating materials on paper or paperboard. Biopolymer-based coating materials originated from naturally renewable resources such as polysaccharides, proteins, and lipids or combinations of those components have the potential to replace current synthetic paper coatings, since they offer favorable environmental advantages of recyclability and reutilization. Moreover, biodegradable polymers developed for coating materials have suitable application properties and can be disposed of after use in an economically and ecologically acceptable way.



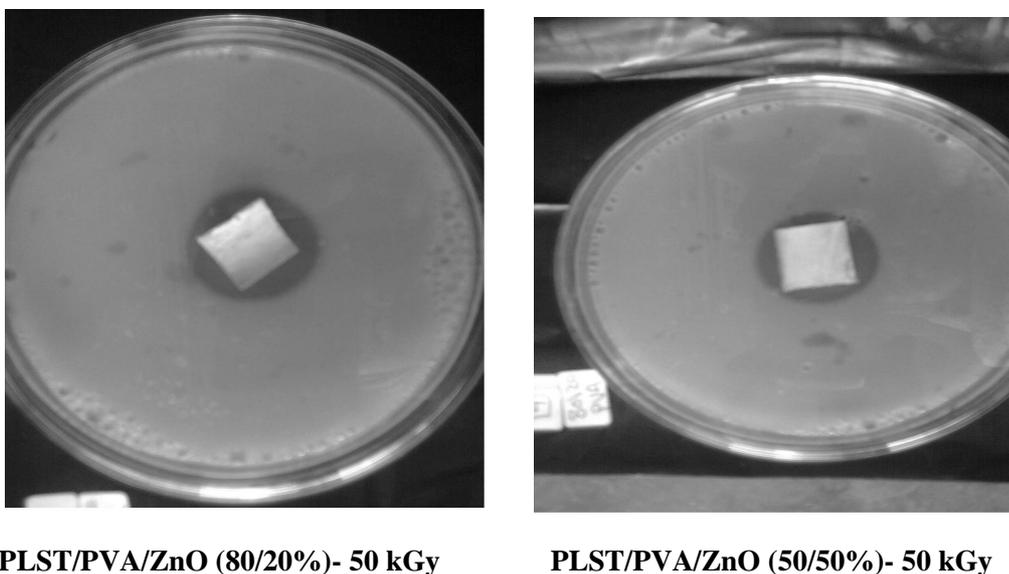
**Fig.12.** SEM micrographs of the fracture surfaces of: (A) unirradiated PLST (100%), (B) unirradiated PLST/PVA (80/20%), (C) unirradiated PLST/PVA (50/50%), (D) PLST (100%)-50 kGy, (E) PLST/PVA (80/20)-50 kGy, (F) PLST/PVA (50/50%)-50 kGy.



**Fig.13.** Photographs of the antimicrobial inhibition zone of unirradiated PLST/PVA/ZnO blends of different compositions used for paper surface coating after testing against microbial resistance.

Gamma irradiated PLST/PVA/ZnO of different compositions was applied as coating materials for paperboard. **Figure 13** shows photographs of the antimicrobial inhibition zone of unirradiated PLST/PVA/ZnO composites of different ratios used for paper surface coating after testing against microbial resistance, respectively. It is clear that the unirradiated composites are completely covered with the microbes. This means that the paper coated with unirradiated blend could not resist the microbes.

**Figure 14** shows photographs of the antimicrobial zone inhibition of PLST/PVA/ZnO blends of different compositions, prepared by gamma irradiation at a dose of 50 kGy, used for paper surface coating after testing against microbial resistance. It is clear the gamma-irradiated films of PLST/PVA/ZnO blends with improved mechanical and thermal properties will eventually withstand and protect the paper against microbes. On the basis of the inhibition zones, it may conclude that the composition PLST/PVA/ZnO (70/30%) is more resistant against microbes than the composition containing 20% of PVA component. These findings may be explained based on the following points: (1) the antimicrobial effect of zinc oxide, which prevents the attack of microorganisms. (2) The homogenous coating would prevent the transfer of humidity and oxygen to paper.



**Fig.14.** Photographs of the antimicrobial zone inhibition of PLST/PVA/ZnO blends of different compositions, gamma irradiated to the dose of 50 kGy, used for paper surface coating after testing against microbial resistance.

## Conclusions

Development of friendly materials based on blends contain major constituent of natural polymers is a continuing area of challenge for food packaging and coating technology. The main objective of this work is to investigate the physical and chemical properties of plasticized starch/poly(vinyl alcohol)/zinc oxide blends before and after gamma irradiation as well as their application as antimicrobial materials. The data showed that gamma irradiation improved all the physical properties, the mechanical properties of PLST/PVA blends are increased by increasing the ratio of PVA. At any ratio of PLST/PVA, the tensile strength and elongation at break was found to increase with increasing irradiation dose. In addition, the thermal parameters in terms of weight loss and rate of reaction indicate that the thermal stability was increased with increasing PVA ratio and radiation dosage. On the basis of the inhibition zones, it may conclude that the gamma irradiated PLST/PVA/ZnO blend protects the package against microbes.

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