Carbohydrate Polymers 98 (2013) 1166–1172

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Morphological and antibacterial properties of modified paper by PS nanocomposites for packaging applications

Ahmed M. Youssef[a,*], S. Kamel[b], M.A. El-Samahy[a]

[a] Packing & Packaging Materials Department, National Research Center, Dokki, Cairo, Egypt
[b] Cellulose & Paper Department, National Research Center, Dokki, Cairo, Egypt

ARTICLE INFO

Article history:
Received 6 June 2013
Accepted 26 June 2013
Available online 4 July 2013

Keywords:
Paper
Polystyrene nanocomposites
Mechanical properties
Permeability
Antibacterial

ABSTRACT

With the increasing sustainability trend with packaging materials, paper and polymer nanocomposites represent a novel class of packaging materials. This study evaluates the potential achievement of alternative sustainable materials as antibacterial packaging application. Paper sheet from rice straw coated with 5 or 10% polystyrene (PS) nanocomposites using titanium dioxide nanoparticles (TiO_2-NPs) doped or undoped with sliver nanoparticles (Ag-NPs) were prepared. The morphology of the uncoated and coated paper sheets was studied by SEM. The treated paper sheets were analyzed for their elemental composition using EDAX. The Barrier, air permeability, cob test, as well as mechanical properties and tensile strength were also evaluated. The inhibitory effect of modified paper sheets against *Pseudomonas*, *Staphylococcus aureus*, *Candida*, and *Staphylococcus* were investigated.

1. Introduction

Concerns on environmental waste problems caused by non-biodegradable packaging materials as well as the consumer's demand for high quality food products, has caused an increasing attention in developing biodegradable packaging materials using natural recourses such as rice straw and polymer. Intrinsic shortcomings of polymer-based packaging materials such as low mechanical properties and low water resistance can be recovered by applying a nanocomposite technology to prepare modified paper using polymer nanocomposites. Also, with the growing public health awareness of disease transmissions and cross-infection caused by microorganisms, uses of antimicrobial materials has increased in many application areas like protective clothing for medical and chemical works, and other health related products (Duran, Marcato, De Souza, Alves, & Esposito, 2007; Margaret, Sau, Vincent, Ivan, & Andrew, 2006; Youssef, 2013). Additionally, antibacterial packaging materials can improve product quality and keep it free from microbial adhesion (Park & Zhao, 2004). Nanotechnology has allowed paper technologists to produce multifunctional paper products. Silver, zinc, copper, gallium, etc. have been produced with particle size in the nanometer range, i.e. 1–100 nm; these are known as nanometals. When nanometals like silver are incorporated into the paper matrix, the paper becomes antibacterial (Nassar & Youssef, 2012).

One of thesis methods is by introducing silver, gold or copper nanoparticles into polymer film which coated paper sheet. In particular, silver has been recognized for its broad-spectrum antimicrobial activities (Galeano, Korff, & Nicholson, 2003; Youssef & Abdel-Aziz, 2013). In a recent work by Rasika et al. acrylamide was grafted onto filter paper, followed by incorporation of silver nanoparticles results in development of a novel biomaterial which demonstrates fair biocidal action against *Escherichia coli*, and it can be used as an antibacterial packaging material to prevent food stuff from bacterial infection (Rasika & Bajpai, 2009). Also, nano-ZnO impregnated onto cotton textiles showed excellent antibacterial activity against two bacteria: *Staphylococcus aureus* and *Klebsiella pneumoniae*, and gave protection against UV radiation (Samal, Jeyaraman, & Vishwakarma, 2010). TiO_2, SiO_2 and ZnO are common additives (Adams, Lyon, McIntosh, & Alvarez, 2006; Hebeish, Abdelhady, & Youssef, 2013) with improved applications at the nanoscale. The antibacterial activity of TiO_2, which has important ecosystem health implications, is understood. However, less attention has been paid to the antibacterial activity of SiO_2 and ZnO, although they also produce reactive oxygen species.

Polystyrene (PS) is a thermoplastic resin with good processing properties, where it is used in many applications (Youssef, Malhat, & Abdelhakim, 2013) including food packaging, domestic appliances, electronic goods, toys, household goods and furniture Although polystyrene films are frequently used as packaging material but their non-degradability has been a matter of great concern for environmentalists, and therefore attempts have been made to develop such materials which can undergo degradation and become ecofriendly. So, in this work we have developed

* Corresponding author. Tel.: +202 33322418; fax: +202 33370931.
E-mail address: amyoussef27@yahoo.com (A.M. Youssef).

0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.06.059

unbleached rice straw paper as antibacterial packaging material by coating it with PS nanocomposites containing (TiO_2-NPs, Ag-NPs and TiO_2-NPs doped/or undoped with Ag-NPs). The degradable nature of rice straw paper makes it an attractive alternative for using as packaging material.

2. Experimental

2.1. Materials

Rice straw raw pulp is kindly provided by Rakta Company, Alexandria, Egypt. Commercial polystyrene (PS) was obtained from CHIMEI Corporation, Taiwan. Titanium dioxide (P-25, Degussa) (Min assay 99.7%), Toluene was obtained from El Nasr Pharmaceutical chemicals. High purity silver nitrate ($AgNO_3$) was purchased from the No. 1 Chemical Reagent Company in Shanghai. Unless otherwise noted, all other chemicals were reagent grade and used as received.

2.2. Methods

2.2.1. Synthesis of Ag@TiO_2 nanocomposite

TiO_2 nanoparticles was taken and mixed with 20 ml of $AgNO_3$ solution (Vasant & Ghulam, 2009). It was placed on stirring for 6 h under UV lamp. After that, the mixed TiO_2 and $AgNO_3$ solution slurry was centrifugation at 5000 rpm. The clear supernatant was second centrifuged at 13,000 rpm for Ag@TiO_2 nanocomposite precipitation, and dried in an oven at 100 °C to form dried impregnated Ag@TiO_2 nanocomposite. The dried powder retained its grayish color of the combined material.

2.2.2. Preparation of paper sheets

The paper sheets were prepared according to the S.C.A standard, using the model S.C.A sheet former (AB Worentzen and Wettre). In the apparatus a sheet of 165 mm. diameter and 214 cm^2 surface area was formed. The weight of oven dry pulp used for every sheet was about 1.43 g. After sheet formation, the sheet was pressed for 4 min using a hydraulic press. Drying of the test sheets was made with the help of a rotating cylinder or drum at 60 °C + 5 for 2 h.

2.2.3. Coating process

20 or 10 g of commercial PS dissolved into 200 ml toluene and 4 g of Nitrile Rubber (NBR) and Styrene Butadiene (SBR) add to PS solution as plastizer then different ratios of TiO_2 nanoparticles doped by Ag nanoparticles (2.5, 5, and 7.5%) were added. The prepared sheet was coated by PS solution containing different ratios of titanium dioxide and/or Ag nanoparticles by immersing the sheet into the solution for 5 min and waiting to dry the sheet at normal conditions.

2.2.4. Characterization

2.2.4.1. Mechanical. The treated and untreated paper samples were conditioned for 24 h in a standard atmosphere (at 23 °C and 50% relative humidity), prior to testing for tensile strength. Tensile testing was carried out on 15 mm wide strips between jaws set 100 mm apart, using a Zwick universal testing machine.

2.2.4.2. Air permeability. The samples measure using ASANO air permeability Instrument according to ASTMD737 under pressure of 12.7 mm.

2.2.4.3. Cobb test. The water absorption of paper sheets was carried out as follows: the weighed sheet was put in Cobb apparatus, 100 ml of water was added over the sheet, left for 1 min, and then poured the water. Paper sheet dried well between two filter papers and weighed the sheet.

2.2.4.4. SEM/EDAX analysis. Samples for SEM/EDAX were taken using FEI INSPECTS Company, Philips, Holland environmental scanning without coating. Elemental micro-probe and elemental distribution mapping techniques were used for analyzing the elemental constitution of solid samples.

2.2.4.5. The antimicrobial study of the prepared sheet. The disk diffusion method was used to determine the antimicrobial activity of the prepared coating recycled carton by polymer nanocomposites. A volume of 0.1 ml of the tested microorganisms grown in Brian Heart Infusion Broth (at 42 °C for 24 h, 108–109 cells/ml), was inoculated on Brian Heart Infusion media, and then spread on the entire surface of the dish using a sterile spatula. Subsequently, sterile discs were placed onto agar at certain intervals by passing gently. After the plates were incubated at 42 °C for 24 h, the inhibition zones around the discs where no growth occurred, were measured in millimeters, the experiments were repeated in duplicated for all of the test strains.

3. Results and discussion

Recently, nanomaterials have drawn much consideration in the scientific community due to their unique properties, which include quantum imprisonment and increased reactivity related to the changes in their molecular electronic structure and increases in surface-to-volume ratio. Ag, TiO_2 nanoparticles and Ag@TiO_2 nanocomposites are used as nanomaterials to prepare PS nanocomposites and use it for coatings paper.

3.1. Barrier properties

Regarding the barrier properties of packaging materials, the critical compounds that can penetrate the packaging materials and degrade food quality are water vapor and oxygen of the surrounding atmosphere. To avoid the moisture transfer that can affect food quality, Water penetration control is important to assure stability and safety during distribution and storage (Khaoula, Elmira, & Stephane, 2010). A water barrier can be formed by changing the wetability of the paper surface with sizing agents or through coating with hydrophobic materials.

According to Table 1, the untreated paper sheet had the highest absorption rate of water during the 1 min time interval and increasing PS% or nanoparticles% decreasing water absorption. This can be attributed to the coating by PS on the surfaces of paper sheet, from observations this coating seems to resist water for a longer period of time compared to the untreated paper sheet. By comparing the effect of Plasticizers it was found that using of SBR give less water absorption than NBR. Also, using of TiO_2 nanoparticle without Ag giving the lost water absorption.

Data for air permeability of untreated and treated paper sheets is presented in Table 2. The application of coating to the paper based on 5 or 10% PS nanocomposite should therefore yield a paper with air permeability lower than that of the uncoated paper. Paper coated with PS in presence of nanoparticle especially TiO_2 nanoparticle without Ag has very low air permeability, also increasing the TiO_2 nanoparticles decreasing air permeability.

3.2. Mechanical properties

In many packaging applications, barrier properties as well as mechanical resistance are required. In general, mechanical properties of coated films in a composite structure tend to rely strongly on the substrate or base film rather than the coating (Hong, Han, & Krochta, 2004a; Hong, Han, & Krochta, 2004b; Youssef, El-Samahy,

Table 1
Cobb test results (g/m^2 min) of uncoated and coated paper sheets.

Samples	Types of plasticizer		Types of nanomaterials (%)			Cobb g/m^2 min
	NBR (%)	SBR (%)	Ag-NPs	TiO_2-NPs	TiO_2 doped by Ag-NPs	
Uncoated paper sheet	–	–	–	–	–	500
T_1	2	–	––	–	2.5	368
T_1	2	–	–	–	5	323
T_1	2	–	–	–	7.5	225
T_1	–	2	–	–	2.5	210
T_1	–	2	–	–	5	120
T_1	–	2	–	–	7	098
T_2	2	–	–	–	2.5	124
T_2	2	–	–	–	5	050
T_2	2	–	–	–	7	031
T_2	–	2	–	–	2.5	050
T_2	–	2	–	–	5	046
T_2	–	2	–	–	7	028
T_1	2	–	5	–	–	045
T_1	–	2	5	–	–	040
T_1	2	–	5	–	–	038
T_1	–	2	5	–	–	032
T_2	2	–	–	5	–	025
T_2	2	–	–	5	–	020
T_2	–	2	–	5	–	022
T_2	–	2	–	5	–	018

T_1, paper sheet coated with 5% PS nanocomposites; T_2, paper sheet coated with 10% PS nanocomposites.

& Abdel Rehim, 2012). The mechanical property frequently measured to characterize paper-based packaging materials is tensile strength. Tensile strength is a measure of the ability to resist breaking under tension, which is dependent on the strength of fibers, their surface area, and length, and also the bonding strength between them.

The tensile test is used to determine the tensile strength with varying percentages of PS and TiO_2 nanoparticle doped and undoped Ag nanoparticles. As expected, the results according to the Table 3 show that the treated paper sheets exhibited the highest tensile strength characteristics while untreated sheet exhibits tensile strengths far below any of the treated sheet. Also increasing the TiO_2% decreasing the tensile strength but still higher than the untreated paper sheet. In comparing the effect of TiO_2 with Ag nanoparticles; the result shows TiO_2 nanoparticles improve the tensile strength more than Ag nanoparticle.

3.3. SEM

The surface morphological properties of the paper coated by PS nanocomposites were examined by SEM and illustrated in Fig. 1 since the percolation threshold in nanocomposites is associated to the homogeneity of the mixing nanoparticles and polymer matrix in the prepared nanocomposites which containing TiO_2, Ag nanoparticles and different ratios of TiO_2 doped by Ag nanoparticles. Fig. 1 illustrates the SEM photographs of the paper coated by PS containing different plasticizer (NBR and SBR) this additive increasing the elasticity of the prepared paper. Also, Fig. 1 displays the homogeneity of the composites and uniformity of sheet surface which produced with high content of PS in the sheet and this homogeneity increased as the concentration of nanoparticles and plasticizer increased. A comparison of the original sheet matrix with that of the paper coated by PS nanocomposites

Table 2
Air permeability (cm^3/cm^2 s) of uncoated and coated paper sheets.

Samples	Types of plasticizer		Types of nanomaterials (%)			Air permeability (cm^3/cm^2 s)
	NBR (%)	SBR (%)	Ag-NPs	TiO_2-NPs	TiO_2 doped by Ag-NPs	
Uncoated paper sheet	–	–	–	–	–	3.494
T_1	2	–	–	–	2.5	1.882
T_1	2	–	–	–	5	1.122
T_1	2	–	–	–	7.5	0.910
T_1	–	2	–	–	2.5	1.360
T_1	–	2	–	–	5	0.918
T_1	–	2	–	–	7	0.843
T_2	2	–	–	–	2.5	0.725
T_2	2	–	–	–	5	0.408
T_2	2	–	–	–	7	0.338
T_2	–	2	–	–	2.5	0.639
T_2	–	2	–	–	5	0.136
T_2	–	2	–	–	7	0.023
T_1	2	–	5	–	–	1.545
T_1	–	2	5	–	–	1.231
T_1	2	–	5	–	–	0.985
T_1	–	2	5	–	–	0.932
T_2	2	–	–	5	–	0.458
T_2	2	–	–	5	–	0.396
T_2	–	2	–	5	–	0.347
T_2	–	2	–	5	–	0.285

T_1 = Paper sheet coated with 5% PS nanocomposites, T_2 = Paper sheet coated with 10% PS nanocomposites.

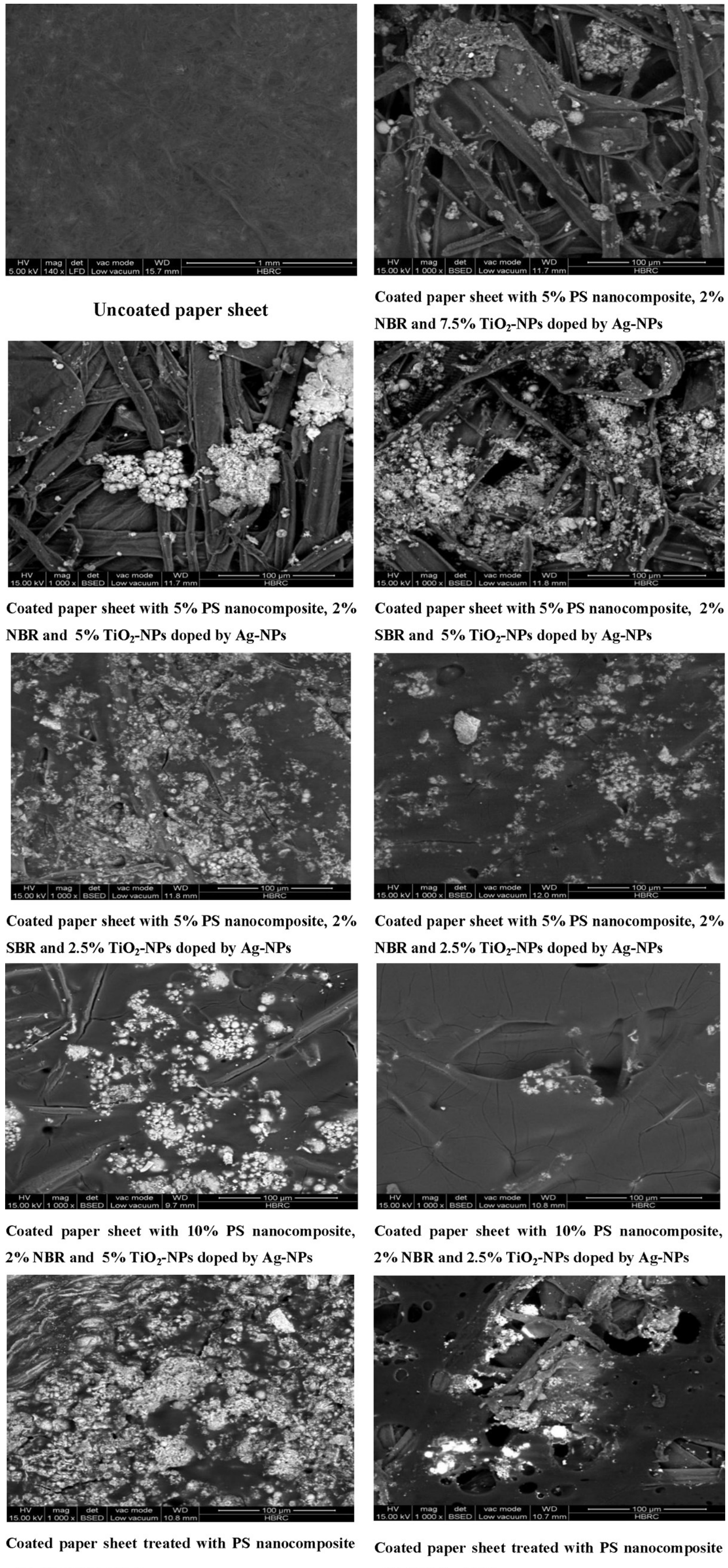

Fig. 1. SEM micrographs of uncoated and coated paper sheets.

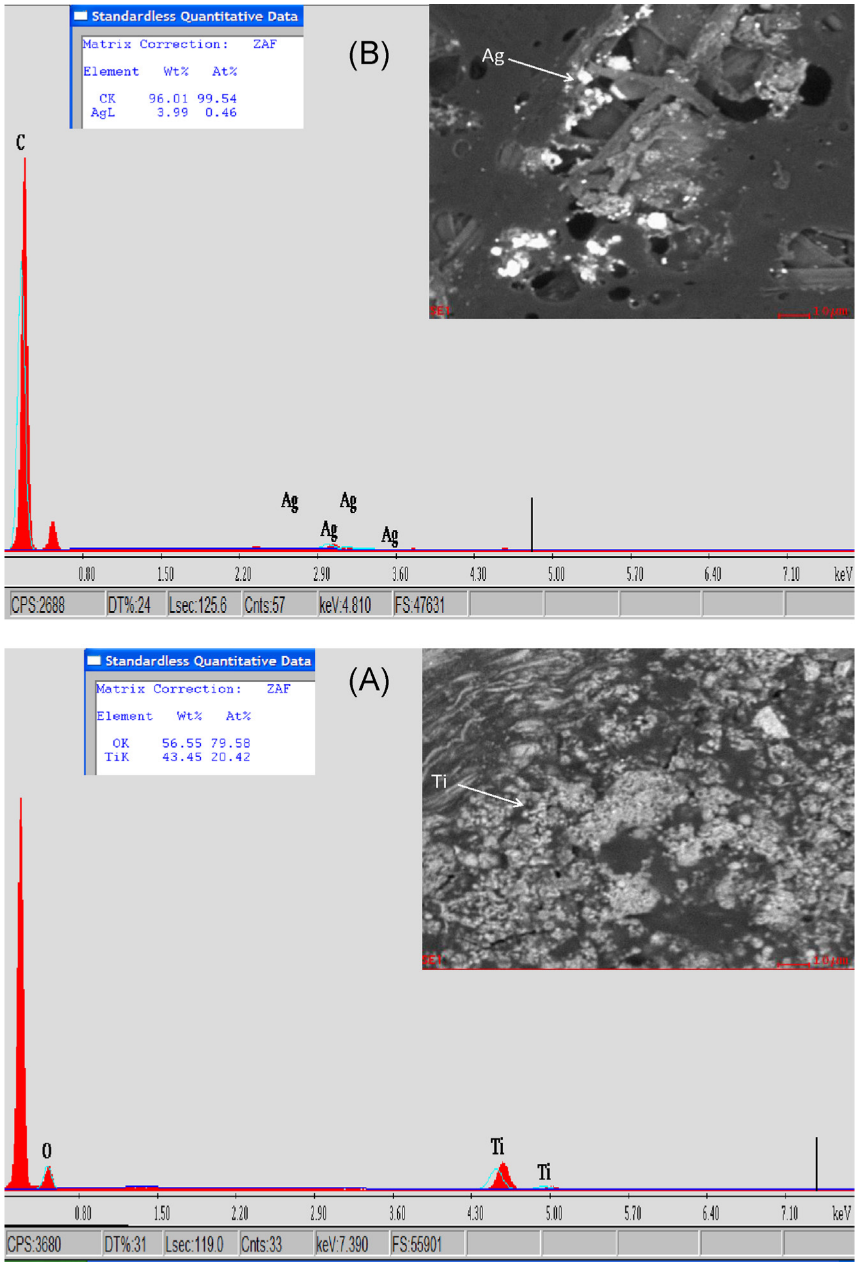

Fig. 2. EDX analysis of coated paper sheets (A) PS nanocomposite with (5% TiO_2–NPs) and (B) PS nanocomposites with (5% Ag-NPs) using NBR as plasticizer.

reveals that although the polymer appear to form largely on the paper fibers, the open structure of the cellulosic matrix has been maintained. This offered a large obtainable surface area of the polymer for chemical and physical interactions and antimicrobial activity.

3.4. EDAX analysis

EDAX analysis provides elemental information. Fig. 2 shows the EDAX plot of SEM image of treated paper sheets with 5% TiO_2 nanoparticle without Ag and 5% Ag nanoparticle without Ti with 10% PS using NBR as plasticizer. The EDAX reading provides presence of Ti and Ag nanoparticles. The graph also shows the presence of Ti and Ag nanoparticles are present in the EDAX picture of coated paper sheets.

3.5. Antibacterial activity

Inorganic antibacterial material is usually in the form of a composite is considered as highly safe (non-volatile) and heat resistant compared to organic materials. Metallic ions having antibacterial and antifungal capabilities, such as Ag, and TiO_2, are impregnated in a mineral or blended with a carrier to form the composite or applied as a coating. Appropriate release of antibacterial metallic ions from the composite can effectively inhibit the birth and growth of harmful microbes. As Ag ions are taken into microbes, they react and bond to the cellular enzyme microbes. This inhibits enzyme activity and multiplication of microbes, thus killing the microbes (Guoyu et al., 2006).

The developed coated papers, 5% TiO_2 nanoparticle without Ag and 5% Ag nanoparticle without TiO_2 using SBR as plastizer were tested for their antimicrobial activity toward Pseudomonas,

Table 3
Tensile test results (m) of uncoated and coated paper sheets.

Samples	Types of plasticizer		Types of nanomaterials (%)			Tensile test (m)
	NBR (%)	SBR (%)	Ag-NPs	TiO_2-NPs	TiO_2 doped by Ag-NPs	
Uncoated paper sheet	–	–	–	–	–	0856
T_1	2	–	–	–	2.5	1602
T_1	2	–	–	–	5	1271
T_1	2	–	–	–	7.5	1245
T_1	–	2	–	–	2.5	1321
T_1	–	2	–	–	5	1058
T_1	–	2	–	–	7	0986
T_2	2	–	–	–	2.5	1380
T_2	2	–	–	–	5	1229
T_2	2	–	–	–	7	1032
T_2	–	2	–	–	2.5	1396
T_2	–	2	–	–	5	1238
T_2	–	2	–	–	7	1091
T_1	2	–	5	–	–	1625
T_1	–	2	5	–	–	1620
T_1	2	–	5	–	–	1605
T_1	–	2	5	–	–	1595
T_2	2	–	–	5	–	1010
T_2	2	–	–	5	–	1025
T_2	–	2	–	5	–	1030
T_2	–	2	–	5	–	1034

T_1, paper sheet coated with 5% PS nanocomposites, T_2, paper sheet coated with 10% PS nanocomposites.

S. aureus, *Candida*, and *Staphylococcus*. Zone of inhibition can be seen on the surface of the nanoparticles loaded coated paper sheets (Fig. 3). Ag has a broad spectrum of antibacterial activity higher than TiO_2 (Table 4). This may simply be explained on the basis of the fact that as paper contains nanoparticles, the colonization of bacteria is greatly inhibited on the nano loaded paper (Suominen, Suihko, & Salonen, 1997). Therefore it may be concluded that TiO_2 and Ag nanoparticles loaded paper possesses strong antibacterial property. Here it is also worth mentioning that this antibacterial PS

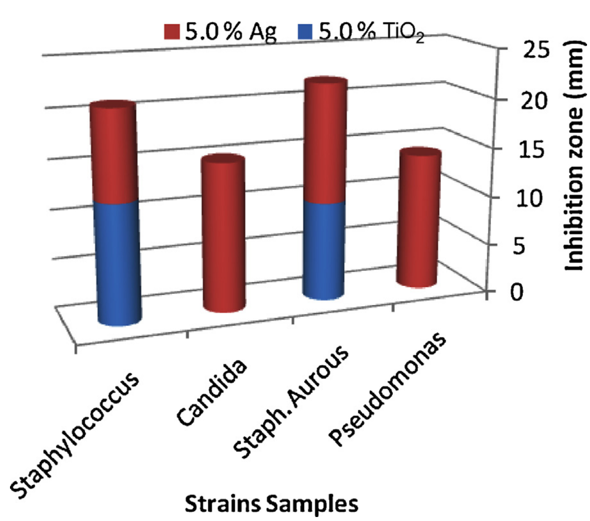

Fig. 3. Antibacterial activity of TiO_2 and Ag nanoparticles loaded paper.

Table 4
Inhibitory zones of paper sheet containing (a) PS nanocomposites (5% TiO_2-NPs) and (b) PS nanocomposites (5% Ag-NPs) against *Pseudomonas*, *S. aureus*, *Candida*, and *Staphylococcus*.

Strains samples	Inhibition zone (mm)			
	Pseudomonas	*S. aureus*	*Candida*	*Staphylococcus*
5.0% TiO_2	00	10	00	12
5.0% Ag	14	12	15	9

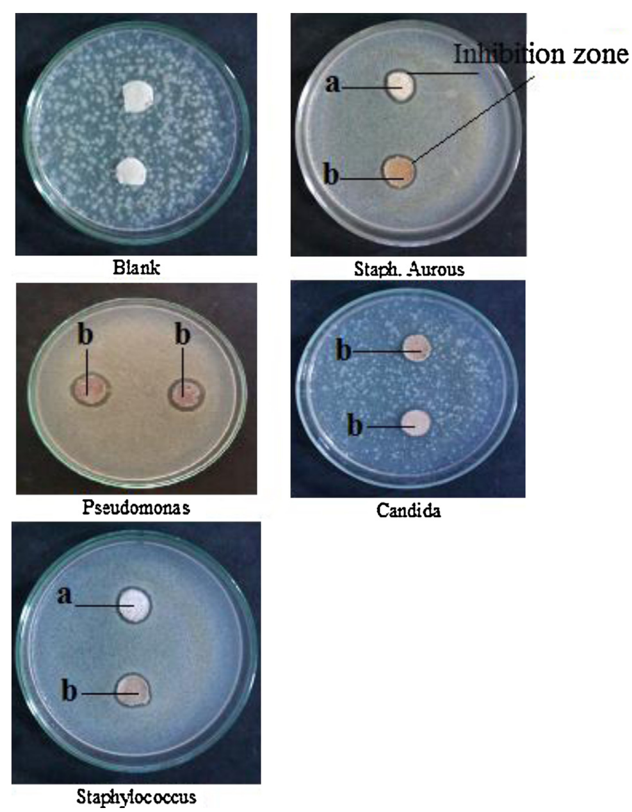

Fig. 4. Inhibitory zones of (a) 5% TiO_2 nanoparticle and (b) 5% Ag nanoparticle without TiO_2 using 10% polystyrene nanocomposites and styrene-butadiene rubber as plastizer against *Pseudomonas*, *S. aurous*, *Candida*, and *Staphylococcus*.

nanocomposites coated paper is proposed to be used as packaging materials to prevent valuable stuff from bacterial infection (Fig. 4).

4. Conclusion

Paper sheets coated with PS nanocomposites in presence of TiO_2 and/or Ag nanoparticles improved tensile strength, water absorption and air permeability especially which treated with 5%

TiO_2 without Ag nanoparticles. Ag nanoparticles showed better antibacterial effect than TiO_2 over all tested of bacteria except with *Staphylococcus*. In addition, TiO_2 nanoparticle showed non inhibition against *Pseudomonas* and *Candida*. Furthermore, the water vapor permeability was improved by the coating process. Thus this modified paper sheets can be used as interesting packaging materials.

Acknowledgements

The authors would like to thank Mohamed Abdel-Aziz, Assistant Prof., at Department of Microbial Chemistry, National Research Center, Dokki, Cairo, Egypt, for his support in carrying out the antimicrobial experiments in his Lab.

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