JOURNAL OF Applied Polymer SCIENCE

Preparation and Characterization of Polyethylene/Silver Nanocomposite Films with Antibacterial Activity

Arefeh Sadat Dehnavi,[1] Abdolreza Aroujalian,[1,2] Ahmadreza Raisi,[1,2] Shahrzad Fazel[1,2]

[1]Department of Chemical Engineering, Amirkabir University of Technology (Tehran Polytechnic), Tehran, Iran

[2]Food Process Engineering and Biotechnology Research Center, Amirkabir University of Technology (Tehran Polytechnic), Tehran, Iran

Correspondence to: A. Raisi (E-mail: raisia@aut.ac.ir)

ABSTRACT: In this work, a novel method was proposed for the fabrication of antibacterial nanocomposite polymeric films, for use in food packaging. In the first step, a stable colloidal solution of silver nanoparticles was prepared by chemical reduction of silver salt using fructose as an environmental friendly reducing agent. In the second step, corona air plasma was used as a pretreatment of low density polyethylene (LDPE) films to increase the adhesion of silver nanoparticles on the film surface. In the third step, silver nanoparticles were coated on the LDPE surface by immersion of the treated films in the colloidal silver solutions. Surface morphology of the silver/LDPE nanocomposite was characterized by FE-SEM and AFM analysis. The amounts of coated silver and silver ion release from the nanocomposite surface were determined. In addition, the antibacterial activity of the fabricated films was evaluated by agar well diffusion and dynamic shake flask methods. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: polyethylene/silver nanocomposite; corona treatment; silver nanoparticles; coating; antibacterial activity

Received 26 September 2011; accepted 27 February 2012; published online
DOI: 10.1002/app.37594

INTRODUCTION

Antibacterial packaging is one of the innovative packaging methods that has been introduced for the improvement of product quality and safety. Indeed, antibacterial packaging is the packaging system, which is able to kill or inhibit the growth rate of microorganisms that contaminate foods.[1] Antibacterial materials can be made by direct incorporation and immobilization of antibacterial substances in packaging material,[2–4] surface modification and surface coating,[5–7] physical vapor deposition,[8] plasma deposition,[9,10] ion implantation,[11,12] or wet chemical processes.[13] Thermal processing such as melt blending, extrusion, and injection molding has been applied for incorporating the antibacterial into polymers.[14,15]

Several compounds have been used as antibacterial agents in the synthesis of antibacterial packaging films. For example, organic acids,[16–18] bacteriocins,[3,5] spice extracts,[19] enzymes,[2,20] isothiocyanates,[21] antibiotics,[22] fungicides,[23] and metals[13,24,25] have been considered to have possible antimicrobial activity when used in food packaging materials. Among these antibacterial agents, silver nanoparticles because of their optical,[26] catalytic, and antibacterial[27] properties as well as high thermal stability and long-term activity deserve special attention. In comparison to other antibacterial substances, silver ions are active against a broad spectrum of bacteria, viruses, and fungi. In an aqueous system the antibacterial effect was observed even for silver ion concentrations as low as 0.1 μg/L.[28] Moreover, the toxicity of silver against human tissue is fairly low, silver ion concentrations higher than 10 mg/L may be toxic to certain human cells.[29]

Low-density polyethylene (LDPE) is the most widely used among thermoplastics, especially for packaging and construction applications because of the acceptable flexibility, transparency, easy processability, thermal stability, environmental recyclability, and inexpensive properties.[30] Generally, plastics have chemically inert and nonporous surfaces with low surface tensions causing them to be nonreceptive to bonding with substrates, printing inks, coatings, and adhesives. Polyethylene is the lowest in surface energy of the various plastics.[31] Recent studies indicated that for coating any substance on the surface of polymers, it must be subjected to surface treatment to improve their bonding characteristics.[32,33] The most practical surface modification techniques are corona discharge,[31] etching with acid,[34] flame treatment,[35] and priming,[36] but corona discharges are often applied for the surface treatment of polymers.[37–40] The advantages of using corona treatments for fabrication of antimicrobial

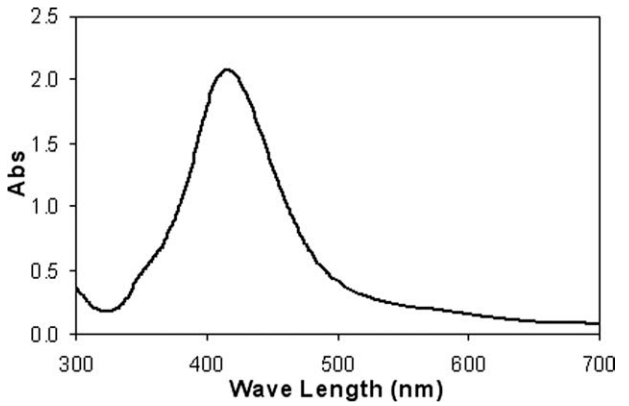

Figure 1. Absorption spectrum of the silver nanoparticles colloidal solution.

polymeric films are operating at atmospheric pressure, their unique properties and growing demands on the environmental friendliness of the finished processes for surface modification and coating of polymers.[40]

The main objective of this study is to fabricate silver/polyethylene nanocomposite films for use as antimicrobial packaging. For this purpose, a colloidal silver nanoparticle solution was prepared by reduction of silver salt using fructose. The possibility of using the corona air plasma for surface treatment of LDPE was investigated and finally, silver nanoparticles were coated on the surface of treaded LDPE films. The fabricated silver nanocomposite films were tested by FE-SEM and AFM analysis and the quantity of coated silver on the films as well as silver ion release from the fabricated films was measured. Besides, the antibacterial properties of nanocomposite films against *Staphylococcus aureus* (*S. aureus*) as the model gram positive bacteria were determined.

MATERIALS AND METHODS

Materials

Silver nitrate ($AgNO_3$), fructose and diammonium hydrogen citrate ($(NH_4)_2HC_6H_5O_7$) of analytical grade purity which were purchased from Merck Ltd. (Darmstadt, Germany) were utilized as starting materials without further purification. Aqueous ammonia and nitric acid with high purity were used for pH adjustment. *S. aureus* (ATCC 29737) was obtained from the Iranian Research Organization for Science and Technology (IROST, Tehran, Iran). Also, Muller Hinton agar (MHA) and Muller Hinton broth (MHB) used in the microbial tests were purchased from Merck Ltd. (Darmstadt, Germany). Blown films of LDPE having a thickness of 100 μm and a density of 0.92 g/cm^3 supplied from the Bandar Imam branch of the Petrochemical Company of Iran, were used in this study.

Preparation of Silver Nanoparticles

In a typical experiment, 1 g of fructose and 0.1 g of diammonium hydrogen citrate were dissolved in 1000 mL of distilled water and the pH of the solution was adjusted to 9.5 by a 1*M* ammonia solution. The solution was stirred continually and heated until the temperature reached 85°C and remained constant at this temperature. Then, 9.35 mL of 0.1*M* $AgNO_3$ solution was added to the heated solution. After a period of time, the solution turned yellow indicating the formation of silver nanoparticles. The mechanism of the reaction can be expressed as follows:

$$2Ag^+ + C_6H_{12}O_6 + H_2O \rightarrow 2Ag + C_6H_{12}O_7 + 2H^+$$

Corona Treatment

Corona treatment of LDPE films was carried out in the air at atmospheric pressure using a commercial device (Naaj Corona, Naaj Plastic, Tehran, Iran). Samples were placed on the backing roller covered with silicon coating, rotating at a given speed. The distance between electrodes was adjusted to a specific value. Corona plasma was generated within the air gap between the electrode and backing roller. The electrode voltage applied across the air gap was equal to 20 kV and discharge frequency was 30 kHz. Before the corona treatment, the LDPE samples was cleaned with acetone, rinsed with water three times, and dried at room temperature to remove the surface impurities.

Coating of LDPE with Silver Nanoparticles

The colloidal solution of silver nanoparticles, which was prepared by the proposed method was stirred continually and heated until the temperature reached 80°C and remained constant at this temperature. The corona treated LDPE samples were vertically immersed into the silver colloidal solution for a given time. Then the samples were rinsed twice with deionized water and dried at 70°C for 5 min.

UV–Vis Spectrophotometery

The absorption spectra of Ag nanoparticle solutions were measured by a Jasco V550 (JASCO, Tokyo, Japan) in the range of 200–900 nm. Also, the reduction of metal ions was monitored by measuring the UV–Vis spectroscopy of the solution according to the method of Mie.[41]

FTIR-ATR Surface Analysis

The spectra of the corona treated and untreated LDPE samples were recorded by a Fourier transform infrared-attenuated total reflection (FTIR-ATR) spectrometry at room temperature. The FTIR-ATR instrument used consisted of a Nicolet Nexus 670

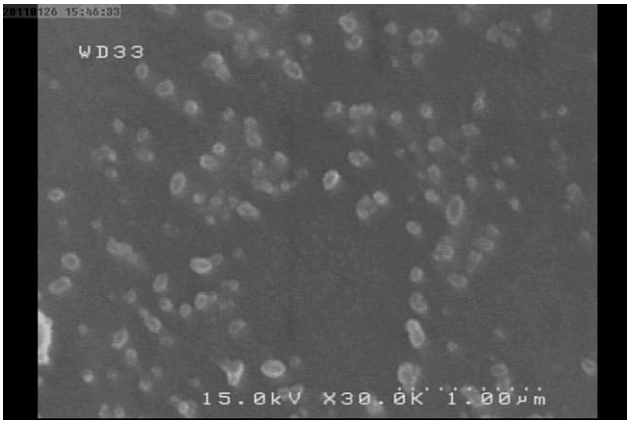

Figure 2. FE-SEM image of the silver nanoparticles colloidal solution.

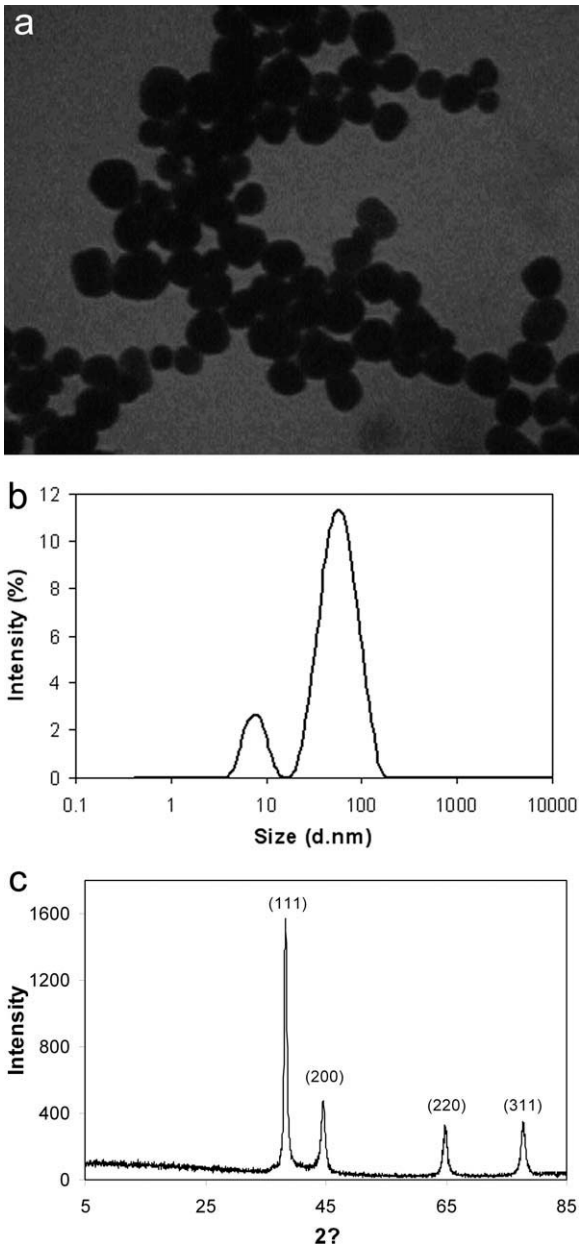

Figure 3. The TEM image (a) XRD pattern, (b) and size distribution, and (c) of the silver nanoparticles.

spectrometer (Nicolet Instrument, Madison, WI) with 4 cm^{-1} resolution over a wave number range of 4000–500 cm^{-1}.

Contact Angle Analysis

The water contact angle (CA) of the corona treated and untreated LDPE samples were measured using an optical CA measurement system (OCA-20, Dataphysics GmbH, Filderstadt, Germany) at room temperature. Measurements were made immediately after 5 μL of deionized water was dropped on the surface by a micro-syringe and the needle tip was removed from the surface. At least six readings were made on different parts of the films and the results were averaged.

FE-SEM and TEM Analysis

The morphology and size of the colloidal silver nanoparticles and the morphology of silver nanoparticles coated on the surface of treated LDPE were determined by the Field emission scanning electron microscope (FE-SEM) using Hitachi FE-SEM model S-4160 (Hitachi, NJ) operating at 100 kV. Before testing, all the samples were dried and attached to a conducting sample holder with double-sided copper tape. The prepared samples were coated under vacuum with a $\sim$ 10–20 nm thin layer of gold by the sputtering system.

Transmission electron micrograph (TEM) image of the silver nanoparticles was obtained by a ZEISS EM-900 electron microscope (Carl Zeiss SMT, Peabody, NY) operating at 80 kV. The samples prepared by placing a drop of the colloidal silver nanoparticles solution onto a small carbon film coated copper grid (200 mesh), followed by solvent evaporation under vacuum.

XRD and DLS Analysis

The X-ray powder diffraction (XRD) patterns were recorded at 25°C on a Philips instrument (X'pert diffractometer using

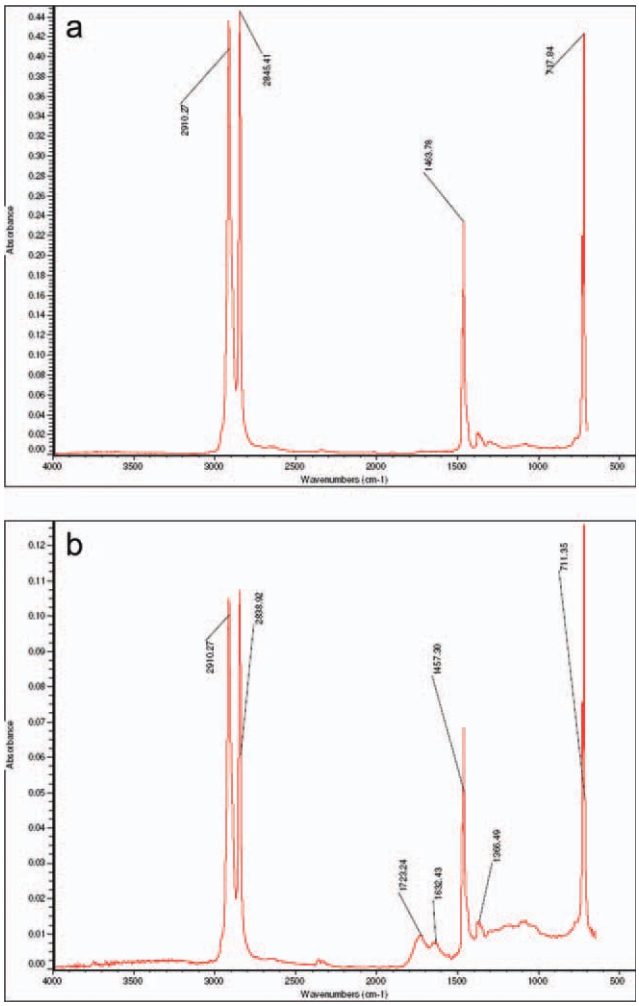

Figure 4. FTIR-ATR spectra of the LDPE film: (a) untreated and (b) corona treated. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Applied Polymer SCIENCE

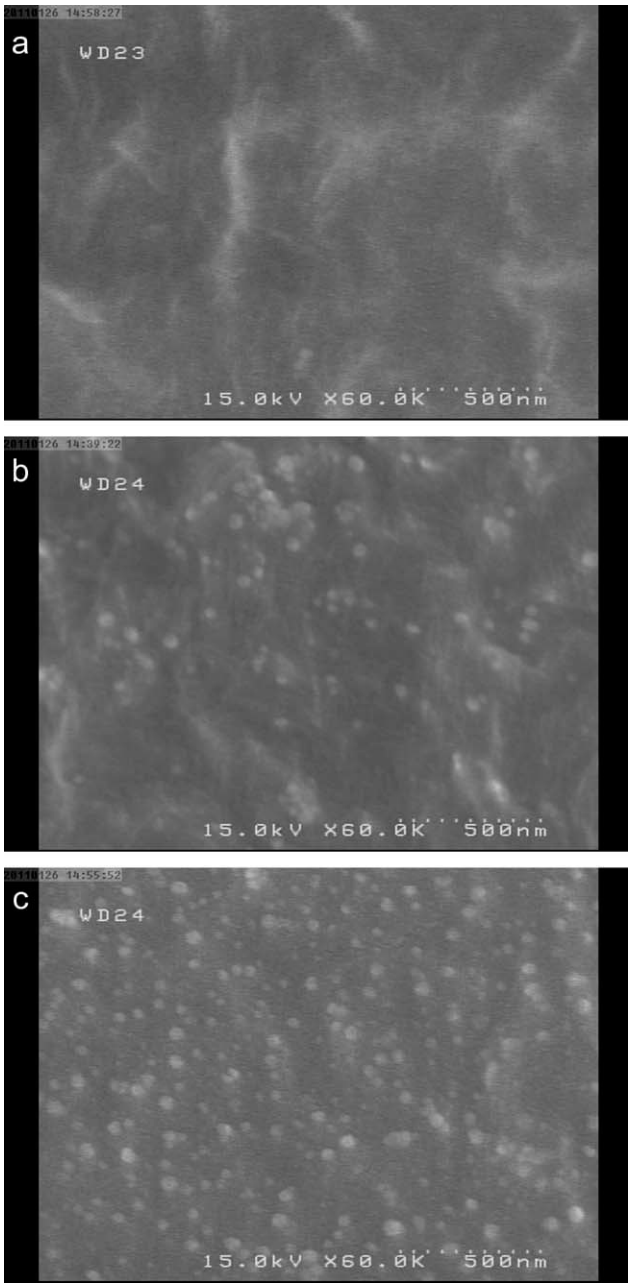

Figure 5. FE-SEM images of the silver nanoparticles coated LDPE films at different time of coating: (a) uncoated, (b) 1 min coated, and (c) 5 min coated.

CuKα radiation) with a scanning speed of 0.03° (2Θ) min^{-1}. The average crystal dimension was calculated using Scherrer's equation.

Besides, the hydrodynamic diameter and size distribution of the silver nanoparticles were determined by dynamic light scattering (DLS) using a Malvern Zetasizer Nano (Malvern Instruments, Worcestershire, UK).

AFM Analysis

Atomic force microscopy (AFM) was used to characterize the surface topography and roughness of silver nanoparticles coated on the surface of treated LDPE samples. Also, the root-mean-square (RMS) average of the surface roughness value was calculated as the standard deviation of all the height values within the given area. The AFM analyses were performed on an AFM microscope (NanoEducator, NT-MDT, Zelenograd, Russia). The instrument was calibrated by standard samples (TGG1 and TGX1, NT-MDT, Zelenograd, Russia). Dried samples were fixed on a holder double-side tape and 10 × 10 μm^2 areas were scanned by semicontact mode in the air. Three different locations were tested and an average value of RMS was reported.

Silver Coated Quantification

To measure the amount of silver coated on the LDPE films, a sample of 4 × 4 cm^2 was submerged in 5 mL of nitric acid [65% (v/v)] for 24 h. After digestion, the solution was diluted

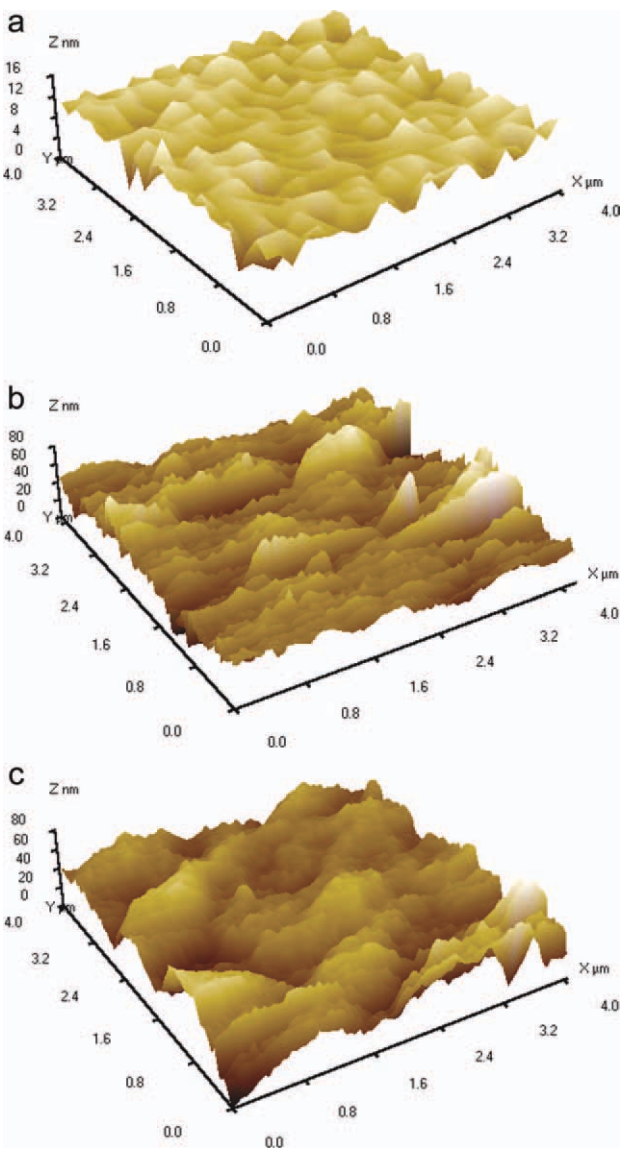

Figure 6. AFM images of the silver nanoparticles coated LDPE films at different time of coating: (a) uncoated, (b) 1 min coated, and (c) 5 min coated. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

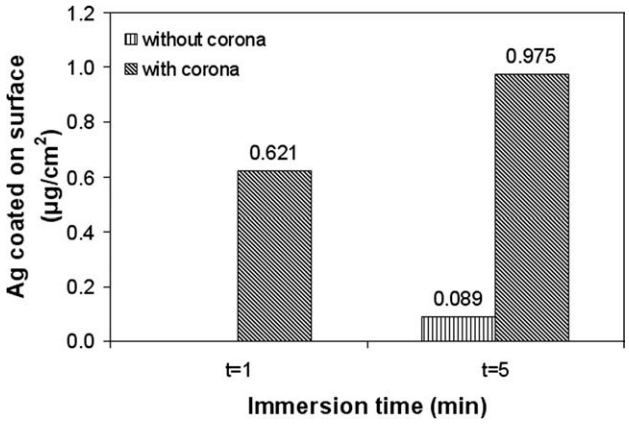

Figure 7. The amount of coated silver on the untreated and corona treated LDPE films at different time of coating.

and analyzed by an atomic absorption spectrometer (AAS) (Varian SpectrAA-300, Varian, CA).

Silver Ion Release

To quantify the silver ion release from the coated LDPE films, a sample of 6 × 10 cm^2 was immersed in 125 mL of deionized water at room temperature. At a defined period of time, 2 mL of the solution was taken and the silver content was analyzed by atomic absorption spectroscopy.

Antibacterial Activities

Antimicrobial efficiency of the silver nanoparticles coated LDPE films against *S. aureus* was carried out by two methods; agar diffusion and dynamic shake flask methods as described by Appendini and Hotchkiss.[2] The agar diffusion method was performed using Muller Hinton medium solid agar. The test was initiated by pouring the MHA onto sterilized Petri dishes and was allowed to solidify. Hundred microliters of incubated testing bacterial solution (10^8 CFU/mL) was spread uniformly over the plate. Each film sample of 1.5 × 1.5 cm^2 in size was placed on the MHA surface. The Petri dishes were incubated for 1 day at 37°C. The clear zone formed around the samples was recorded as an indication of inhibition of the microbial species.

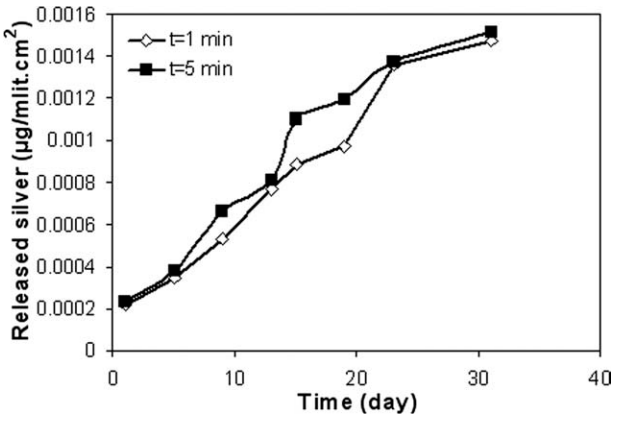

Figure 8. Released silver from the silver nanoparticles coated LDPE at different time of coating.

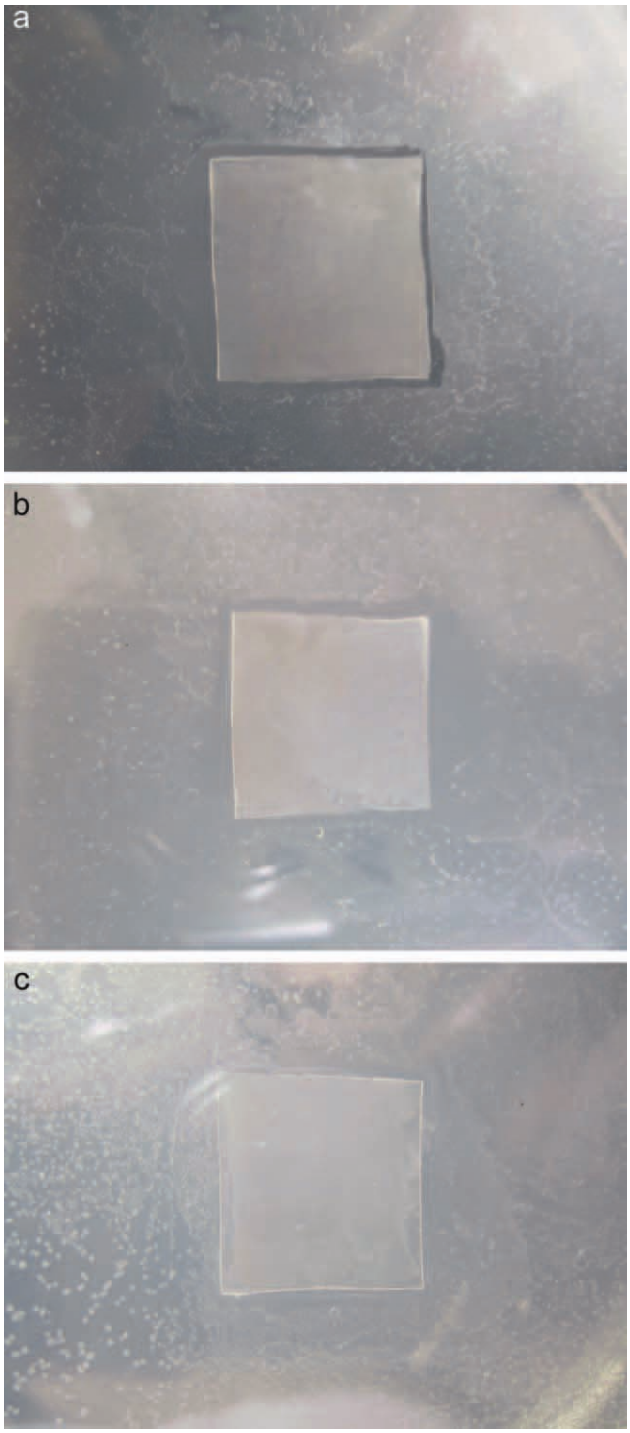

Figure 9. Appearances of inhibitory zones of silver coated film against *S. aureus* (a) 1 min coated, (b) 5 min coated, and (c) control sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Control experiments were performed with uncoated polyethylene films.

For the dynamic shake flask test, inoculations were given from fresh colonies on agar plates into 100 mL of MHB. Growth was allowed over night. Subsequently 2 × 10^5 CFU/mL from above

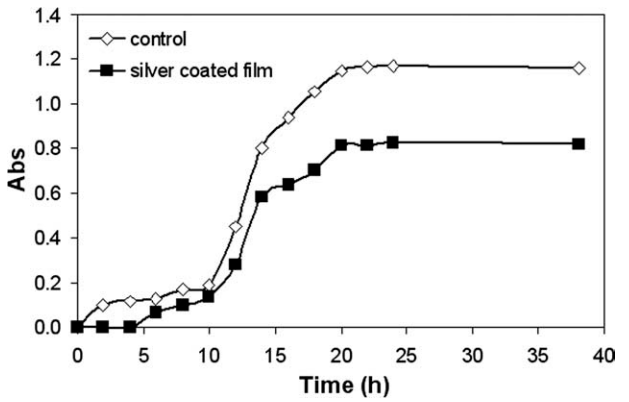

Figure 10. Effect of the antibacterial silver/LDPE nanocomposite films on the growth curve of *S. aureus* (O.D.: optical density).

were added to 100 mL MHB supplemented with six specimens (3×5 cm^2) of the coated films, and then samples were incubated in a shaking incubator with 150 rpm agitation at 37°C for 24 h. Control samples were prepared with the uncoated LDPE films. Evidence of microbial growth was acquired by reading the absorbance changes at 600 nm[42] using a UV–Vis spectrophotometer at regular intervals (2 h). All experimental conditions were repeated three times and the average values were reported.

RESULTS AND DISCUSSION

Characterization of Silver Nanoparticles

UV–Vis absorption spectra have been proven to be quite sensitive to the formation of silver colloids since silver particles exhibit an intense absorption peak due to the surface plasmon excitation. The location and shape of the absorption peak are strongly dependent on the particle size, dielectric medium, and the refraction index of the surrounding matrix material, while the peak width depends on the particle size distribution and its height corresponds to the concentration of the silver metal particles. For silver nanoparticles, the surface plasmon resonance peak is located between 400 and 450 nm for particles that are smaller than 100 nm.[43]

The absorption spectrum of silver nanoparticles colloidal solution was prepared using fructose as a reducing agent is shown in Figure 1. The UV–Vis spectrum reveals the formation of silver nanoparticles by showing a maximum absorption at wavelengths of 416 nm. The position of the symmetric absorption spectrum indicated a narrow size distribution without undesired aggregation.

The morphology of silver nanoparticles in the colloidal solution was analyzed by a high resolution FE-SEM. As shown in Figure 2, uniformly distributed silver nanoparticles in colloid solution with a nearly round shape are achieved.

Besides, the results of TEM, XRD, and DLS analysis of the silver nanoparticles are presented in Figure 3. As one can see clearly from Figure 3(a), the silver nanoparticles with very narrow size distribution were well-formed and well-dispersed. Generally, the sizes of the observed particles in TEM are in good agreement with the values obtained by DLS analysis. Figure 3(a,b) showed that the spherical particles with average size of 36 nm were formed using fructose as a reducing agent. Also, the XRD pattern shown in Figure 3(c) indicated that the silver nanoparticles is well crystallized showing sharp peaks at $2\theta = 38.2°$ (111), 44.4° (200), 64.7° (220), and 77.6° (311) and no peaks of other impurity crystalline phases were detected. The average crystallite size of silver nanoparticles was estimated using Scherrer's equation from the peak width of (111) reflection plane and was found to be 32.2 nm. Therefore, the results of XRD analysis are in good agreement with the results of TEM and DLS analysis.

Surface Modification of Polyethylene

The chemical structure of modified LDPE was characterized by FTIR-ATR spectroscopy. The FTIR-ATR spectra of the corona treated samples clearly show the evolution of the polar groups on the LDPE surface. The presence of these polar groups strongly contributes to the increased hydrophilic nature of the LDPE surface. Figure 4 indicates the FTIR-ATR spectra of the untreated and corona treated samples.

By comparing the FTIR-ATR spectra of the untreated and corona treated LDPE, a peak around wave number of 1650–1560 cm^{-1} indicates the presence of ketone group and a peak in the range of 1000–1300 cm^{-1} shows alcoholic end groups (CO^-). It can be seen that by modifying the surface of LDPE using corona discharge, the polar groups would appear and consequently, the hydrophilic nature of LDPE surface increased. So, a significant increase in polymer wettability and tendency to bonding with other materials is suggested because of the oxidation of the LDPE surface and the formation of new polar functional groups during the corona treatment.

Furthermore, the influence of corona treatment on the surface properties of the treated LDPE films was evaluated by the CA test. The CAs of distilled water in contact with the LDPE surfaces are reduced from 76° to 44° after the modification. Corona treatment on a LDPE film increases surface wettability by the formation of polar groups on the surface, so the CA decreases.

Morphology of Silver Coated Films

FE-SEM Analysis. The changes in LDPE surface morphologies after the loading of silver nanoparticles from the silver colloid solution were analyzed using the FE-SEM technique. FE-SEM images of the untreated and silver loaded LDPE films are shown in Figure 5. These images prove that silver particles were successfully precipitated on the surface of polyethylene films. Most of the silver particles coated on the surface were round shaped and with a diameter of about 70 nm, while a few larger silver particles can be observed. Also, it can be seen that by increasing the immersion time of the corona treated LDPE film in the silver colloidal solution from 1 to 5 min, more silver nanoparticles are loaded on the LDPE films.

AFM Analysis. The AFM analysis was used to evaluate changes in surface morphology and roughness of LDPE films after the coating process. The AFM surface topography of the untreated and silver loaded LDPE films are shown in Figure 6. This figure shows that the surface roughness slightly increases with precipitation of silver nanoparticles on the polyethylene surface. The root mean square (RMS) roughness of the untreated LDPE film

Table I. Performance and Characterization of Different Antibacterial Polymeric Films

Polymer	Antibacterial agent	Fabrication method	Tested microbe	Antibacterial efficiency	Amount of released antibacterial agent	Safety for human cells	Ref.
Cellulose triacetate	Lysozyme	Surface coating	*M. lysodeikticus*	Good	NS[a]	NS	2
Polyethylene	Nisin and lacticin	Blending	*M. flavus* and *L. monocytogenes*	Good	NS	NS	5
Polyethylene	Silver nanoparticles	Surface coating	*P. oleovorans* and *A. niger*	Good	7×10^{-5} g/L[b]	Safe	7
Polyethylene	Silver-containing polyethylenoxide	Plasma deposition	*A. acidoterrestris*	Good	02–1.9 ppm[c]	NS	9
Polyethylene	Triclosan and bronopol	Plasma immersion ion implantation (PIII) + Surface coating	*E. coli* and *S. aureus*	Good	NS	NS	11
Polyethylene	Silver and copper	PIII	*E. coli*	Good[d]	NS	Doubtful	12
Polyethylene	Silver nanoparticles	Melt blending	*E. coli* and *S. aureus*	Good	NS	NS	14
Polyethylene, polystyrene, polyethylene terephthalate and polyvinyl chloride	Silver nanoparticles	Spray coating and melt blending	*E. coli*	Good[f]	341 ppb[g]	NS	15
Polypropylene	Elementary silver powder	Melt blending	*E. coli* and *S. aureus*	Good	1.2×10^{-4} g/L[h]	NS	25
Polyamide	Silver nanoparticles	Melt blending	*E. coli*	Good	17×10^{-6} g/L[i]	NS	45
Polyethylene	Grapefruit seed extract	Coextrusion and solution coating	*M. flavus*, *S. aureus*, *E. coli* and *B. subtilis*	Good	NS	NS	46
Polyurethane	Silver	Magnetron deposition	*S. epidermidis*	A 2–3 log reduction	NS	Safe[j]	47
Polyethylene	Imazalil and EDTA	Melt blending	*B. subtilis*, *A. niger* and *E. coli*	Relative activity[k]	NS	NS	48
Chitosan film	Montmorillonite, silver nanoparticles and silver-zeolite	Solvent casting	*S. aureus*, *L. monocytogenes*, *S. typhimurium*, and *E. coli*	Good[l]	NS	NS	49
Polyethylene	Poly(2-*tert*-butyl aminoethyl) methacrylate	Melt blending	*E. coli* and *S. aureus*	A 4 log reduction	NS	NS	50

Table I *Continued*

Polymer	Antibacterial agent	Fabrication method	Tested microbe	Antibacterial efficiency	Amount of released antibacterial agent	Safety for human cells	Ref.
Polyurethane	Silver nanoparticles	Blending	*B. subtilis* and *E. coli*	Good	NS	NS	51
Polyethylene and polyvinyl chloride	Silver-doped organic-inorganic hybrid	Sol-gel process	*E. coli* and *S. aureus*	Good	6.9×10^{-7}g/L[m]	NS	52
Polystyrene	Silver nanoparticles	*In situ* emulsion polymerization	-	NS	NS	NS	53
Polyethylene	Nisin and bacteriocins	Surface coating	*L. monocytogenes*	Good	NS	NS	54
Polyethylene glycol-polyurethane-titania nanocomposite	Silver	Solution casting	*E. coli* and *B. subtilis*	Good	NS	NS	55
Polyethylene terephthalate	Silver nanoparticles	Plasma treatment + surface coating	*E. coli* and *S. aureus*	Good	NS	NS	56
Chitosan film	Silver nanoparticles	Blending	*E. coli*	Good	NS	NS	57
Polycaprolactone	Silver nanoparticles	Roll-milling method	*E. coli* and *S. aureus*	Good	NS	Safe	58
Polyethylene	Silver nanoparticles	Corona treatment + surface coating	*S. aureus*	Good	1.5×10^{-7} g/L[n]	Safe	This study

[a]Not specified, [b]Concentration of Ag^+ (g/l) for 1 g of nanocomposite in 14 days, [c]Concentration of Ag^+ (ppm) per cm^2 specimen, [d]Silver has better antibacterial properties than the copper in spite of implantation using similar parameters, [e] The PE surfaces after Cu and Ag PIII show little biocompatibility for the Chinese hamster ovary cells but both samples exhibit excellent biocompatibility for bone cells, [f]Dependent on type of polymer, [g]Concentration of Ag^+ in 210 min, [h]Concentration of Ag^+ (g/L) for 1 g of nanocomposite in 5 days, [i]Concentration of Ag (g/L) per day and per cm^2 specimen over 100 days, [j]Coating thickness >28 nm were found to be cytotoxic, [k]Strong activity against *A. niger* and No activity against *E. coli*, [l]Varying degrees of antimicrobial activity depending on the nanoparticles used, [m]Concentration of Ag^+ (g/L) for 1 cm^2 of coating in 48 h, [n]Concentration of Ag^+ (g/L) for 1 cm^2 of coating in 30 days.

Applied Polymer SCIENCE

was 2.01 nm, while the RMS value increased to 11.47 and 12.02 nm for the silver coated films. According to the surface roughness of the untreated LDPE film, it is obvious that by modifying the film and immersion of the treated samples in the silver colloidal solution, the binding between polar groups and silver nanoparticles occurred and thus the roughness of LDPE surface increased. The AFM images indicate that the surface roughness slightly increases with the immersion time. For longer immersion in the silver nanoparticles solution, more nanoparticles participated on the surface of corona treated LDPE film, and thus more surface roughness occurred.

Analysis of Silver Content in Nanocomposite Films

The corona treated LDPE films were immersed in the colloid solution of silver nanoparticles for 1 and 5 min. The amount of coated silver on the corona treated LDPE is shown in Figure 7. It can be seen that by increasing the immersion time, the amount of coated silver increased. Also, it is obvious that no silver was coated on the untreated LDPE at 1 min immersion in the colloid solution of silver nanoparticles, and the amount of coated silver on the untreated samples at 5 min immersion was very low. More coated silver nanoparticles on the surface of corona treated LDPE films are probably the direct consequence of the chemical changes on the surface and increased hydrophilic nature of the films induced by corona treatment, which influence the binding efficiency of silver nanoparticles from colloidal solution.

Release of Silver

In an aqueous environment, silver nanoparticles release silver ions. Elemental silver particles (Ag(s)) need to be oxidized by dissolved oxygen (O_2 (aq.)) according to the equation below in order to release silver ions[44]:

$$4Ag_{(s)} + 4H_3O^+ + O_{2(aq.)} \rightarrow 4Ag^+_{(aq.)} + 6H_2O$$

The amount of released silver from the coated LDPE films is presented in Figure 8. As shown in this figure, release of silver ion from the coated films in aqueous solution is continued with moderate slop over 33 days. Indeed, when the silver loaded films are in contact with water, release of silver ion occurs over a longer period of time because of the involved process of oxidation of the elementary silver nanoparticles to silver ions and a subsequent diffusion of the silver ions to the sample surface.

Besides, Figure 8 indicates that by increasing the immersion time of the LDPE films in the silver colloid solution, the amount of coated silver increased and subsequently the amount of released silver from the coated films would increase. The amounts of released silver ions from the coated films are in a range in which an antimicrobial activity has been found according to Damm et al.[45]

Antimicrobial Activity of Silver/LDPE Nanocomposite

Qualitative and quantitative evaluations of the antibacterial efficiency of the silver coated LDPE films against *S. aureus* were evaluated by agar diffusion and shake flask tests and the results are presented in Figures 9 and 10. Coating of silver nanoparticles on the LDPE films exhibited an interesting antimicrobial activity in the agar disc diffusion test (Figure 9). Colonies of gram-positive microbe (*S. aureus*) could not be viewed in the clear zone directly around the silver coated films. This clear zone around the silver coated films indicates the antimicrobial efficiency of these films, while there was no clear zone for the control sample as shown in Figure 9(c). The microbial inhibition indicates the release of silver ion from the coated film and diffusion into the agar layer, preventing the growth of microbial colonies in the agar medium.

The dynamic shake flask tests provide more detailed information on antimicrobial kinetics. The growth profile of *S. aureus* was shown by plotting absorbance of incubated solutions as a function of time in contact with the uncoated LDPE film (control sample) and the silver coated films. As shown in Figure 10, kinetics growth of *S. aureus* was influenced by the silver coated LDPE film. It was observed that both lag and log phases were affected by silver nanoparticles. The lag phase is a period of slow growth when the cells are adapting to the culture environment and preparing for fast growth and the log phase (i.e., logarithmic phase) is a period where the cells proliferate exponentially and consume the nutrients in the growth medium. The lag time parameter extended about 4 h for *S. aureus*, as contacted with the coated film. By comparing the growth rate of *S. aureus* in the presence of uncoated and silver coated films, it could be found that the antibacterial LDPE films reduces the maximum growth rate up to 30%. The results show that the released silver from the coated film is enough to create antimicrobial activity in the incubated solution, and *S. aureus* is susceptible to silver ion released from the coated film.

Performance of Different Antibacterial Polymeric Films

Several factor such as the chemical nature of polymeric films, fabrication technique, process conditions, residual antimicrobial activity, characteristics of antimicrobial substances, and chemical interaction of additives with the film matrix have significant effects on the performance of resulting antibacterial film. Therefore, direct comparison between various antibacterial polymeric films is difficult. Besides, there is no detailed information about these antimicrobial films in the literature. For examples, the amount of released antibacterial agent and the safety of antibacterial films for human cells have not specified.

For comparison purpose, the performance of some antibacterial films reported by other research groups is listed in Table I. It can be seen that the antibacterial polymeric film fabricated in this study and the work of Sanchez-Valdes et al.[7] and Damm et al.[45] have a steady and prolonged release of silver ions and antibacterial activity. To have an effective and permanent antibacterial activity, a steady and long-term release of silver ions at a suitable concentration level (>0.1 ppb)[59] is required. A too slow or a too fast release of silver ion would be unsuitable for most applications.

CONCLUSIONS

Silver/polyethylene nanocomposite was prepared by the coating of silver nanoparticles on the corona plasma treated LDPE films. Stable and uniform silver nanoparticle solutions, which were successfully synthesized via the chemical reduction of silver nitrate with fructose, were used as an antimicrobial agent. Also,

the possibility of using the corona air plasma for surface treatment of LDPE was investigated.

Analysis of the colloidal silver nanoparticle solution showed the formation of silver particles in the nano form with the maximum absorption at a wavelength of 416 nm. The FTIR-ATR analysis of the untreated and corona treated LDPE films indicated that C—O and C=O groups were formed on the surface of polyethylene by corona air plasma treatment. These polar groups increased the hydrophilicity and reactivity of polymeric films; therefore more silver particles were coated on the surface. Changes in the surface morphology of the silver coated LDPE films were observed and confirmed the formation of Ag particles in the nanosize. Also, the quantity of silver ion release in aqueous solution was determined and the results showed the silver ion concentration of 0.00150 μg/mL cm^2 in the aqueous solution after 30 days. Additionally, the antibacterial activity of the fabricated LDPE films was investigated. The nanocomposite of silver/LDPE showed high antimicrobial and bactericidal activity against gram positive bacteria such as *S. aureus*, which is a highly methicillin resistant strain. Finally, it can be concluded that antibacterial polymeric films can be fabricated by the proposed method for use in food packaging.

REFERENCES

1. Han, J. H. J. *Food Technol.* **2000,** *54*, 56.
2. Appendini, P.; Hotchkiss, J. H. *J. Packag. Technol. Sci.* **1997,** *10*, 271.
3. Scannell, A. G. M.; Hill, C.; Ross, R. P.; Marx, S.; Hartmeier, W.; Arendt, E. K. *Int. J. Food Microbiol.* **2000,** *60*, 241.
4. Tankhiwale, R.; Bajpai, S. K. *J. Appl. Polym. Sci.* **2010,** *115*, 1894.
5. An, D. S.; Kim, Y. M.; Lee, S. B.; Paik, H. D.; Lee, D. S. *J. Food Sci. Biotechnol.* **2000,** *9*, 14.
6. Natrajan, N.; Sheldon, B. W. *J. Food Prot.* **2000,** *63*, 1189.
7. Sanchez-Valdes, S.; Ortega-Ortiz, H.; Ramos-de Valle, L. F.; Medellin-Rodriguez, F. J.; Guedea-Miranda, R. *J. Appl. Polym. Sci.* **2009,** *111*, 953.
8. Akamatsu, K.; Deki, S. *Nanostruct. Mater* **1997,** *8*, 1121.
9. Del Nobile, M. A.; Cannarsi, M.; Altieri, C.; Sinigaglia, M.; Favia, P.; Iacoviello, G.; D'Agostino, R. J. *Food Sci.* **2004,** *69*, 379.
10. Jiang, H.; Manolache, S.; Wong, A. C. L.; Denes, F. S. *J. Appl. Polym. Sci.* **2004,** *93*, 1411.
11. Zhang, W.; Chu, P. K.; Ji, J.; Zhang, Y.; Fu, R. K. Y.; Yan, Q. *Polymer* **2006,** *47*, 931.
12. Zhang, W.; Chu, P. K. *Surf. Coat. Technol.* **2008,** *203*, 909.
13. Shiraishi, Y.; Toshima, N. *J. Mol. Catal. A: Chem.* **1999,** *141*, 187.
14. Jokar, M.; Rahman, R. A.; Ibrahim, N. A.; Abdullah, L. C.; Tan, C. P. *J. Food Bioprocess. Technol.* **2010,** Doi: 10.1007/s11947-010-0329-1.
15. Pongnop, W.; Sombatsompop, K. E; Kositchaiyong, A.; Sombatsompop, N. *J. Appl. Polym. Sci.* **2011,** *122*, 3456.
16. Siragusa, G. R.; Cutter, C. N.; Willett, J. L. J. *Food Microbiol.* **1999,** *16*, 229.
17. Weng, Y. M.; Chen, M. J.; Chen, W. *Lebensm. Wiss. Technol.* **1999,** *32*, 191.
18. Ouattara, B.; Simard, R. E.; Piette, G.; Begin, A.; Holley, R. A. J. *Food Sci.* **2000,** *65*, 768.
19. Scora, K. M.; Scora, R. W. J. *Basic Microbiol.* **1998,** *38*, 405.
20. Ibrahim, N. A.; Gouda, M.; El-shafei, A. M.; Abdel-Fatah, O. M. *J. Appl. Polym. Sci.* **2007,** *104*, 1754.
21. Lim, L. T.; Tung, M. A. *J. Food Sci.* **1997,** *62*, 1061.
22. Simovic, L. M.; Skundric, P. D.; Kostic, M. M.; Tasic, G. M.; Kojic, Z. Z.; Milakovic, B. D.; Medovic, A. H. *J. Appl. Polym. Sci.* **2011,** *120*, 1459.
23. Halek, G. W.; Garg, A. J. *Food Saf.* **1989,** *9*, 215.
24. Ishitani, T. In: Foods and Packaging Materials-Chemical Interactions; Ackerman, P.; Jagerstad, M.; Oglsson, M., Eds.; Royal Society of Chemistry: Cambridge, UK, **1995.**
25. Radheshkumar, C.; Munstedt, H. *React. Funct. Polym.* **2006,** *66*, 780.
26. Feng, M.; Zhang, M.; Song, J.-M.; Li, X.-G.; Yu, S.-H. *ACS Nano* **2011,** *5*, 6726.
27. Baker, C.; Pradhan, A.; Pakstis, L.; Pochan, D. J.; Shah, S. I. J. *Nanosci. Nanotechnol.* **2005,** *5*, 244.
28. Wuhrmann, K; Zobrist, F.; Schweiz, Z. Schweiz. Z. *Hydrol.* **1958,** *20*, 218.
29. Schierholz, J. M.; Beuth, J.; Rump, A. F. E.; Konig, D. P.; Pulverer, G. *Mat-wissu Werkstofftech* **1999,** *30*, 869.
30. Marsh, K.; Bugusu, B. J. *Food Sci.* **2007,** *72*, 39.
31. Markgraf, D. A. Corona treatment: An Overview, Coextrusion Seminar Notes; TAPPI Press: Atlanta, **1986.**
32. Spell, H. L. Surface Analysis of Corona Treated Polyethylene: Bonding Printability Problems; TAPPI Press: Atlanta, **1978.**
33. Markgraf, M. P. *Rad Tech Report* **1993,** *7*.
34. McLaughlin, T. F. The Surface Treatment of Polyolefins for Bonding to Inks and Adhesives, E.I. DuPont de Nemours, **1962.**
35. Thompson, K. In: Polymers, Laminations and Coatings Conference Proceedings, Tappi Press: Atlanta, **1987;** p 213.
36. Isbister, R. In: Polymers, Laminations and Coatings Conference Proceedings, Tappi Press: Atlanta, **1987;** p 225.
37. Desai, S. M.; Singh, R. P. *Long-Term Prop. Polyolefins* **2004,** *169*, 231.
38. Novak, I.; Pollak, V.; Chodak, I. *Plasma Process. Polym.* **2006,** *3*, 355.
39. Zhu, L. P.; Zhu, B. K.; Xu, L.; Feng, Y. X.; Liu, F.; Xu, Y. Y. *Appl. Surf. Sci.* **2007,** *253*, 6052.
40. Kostic, M.; Radic, N.; Obradovic, B. M.; Dimitrijevic, S.; Kuraica, M. M.; Skundric, P. *Plasma Process. Polym.* **2009,** *6*, 58.
41. Mie, G. *Ann. Phys.* **1908,** *25*, 377.
42. Han, J.; Castell-Perez, M. E.; Moreira, R. G. *LWT Food Sci. Technol.* **2007,** *40*, 1545.

43. Henglein, A. *Chem. Mater.* **1998,** *10*, 444.
44. Hoskins, J. S.; Karanfil, T.; Serkiz, S. M. *Environ. Sci. Technol.* **2002,** *36*, 784.
45. Damm, C.; Munstedt, H.; Rosch, A. *J. Mater. Sci.* **2007,** *42*, 6067.
46. Ha, J.-U.; Kim, Y.-M.; Lee, D.-S. *Technol. Sci.* **2001,** *15*, 55.
47. Dowling, D. P.; Donnelly, K.; McConnell, M. L.; Eloy, R.; Arnaud, M. N. *Thin Solid Films* **2001,** *398/399*, 602.
48. Vartiainen, J.; Skytta, E.; Enqvist, J.; Ahvenainen-Rantala, R. J. *Plast. Film Sheet* **2003,** *19*, 249.
49. Rhim, J.-W.; Hong, S.-I.; Park, H.-M.; Ng, P. K. W. *J. Agric. Food Chem.* **2006,** *54*, 5814.
50. Seyfriedsberger, G.; Rametsteiner, K.; Kern, W. *Eur. Polym. J.* **2006,** *42*, 3383.
51. Hung, H.-S.; Hsu, S.-H. *Nanotechnology* **2007,** *18*, 1.
52. Marini, M.; De Niederhausern, S.; Iseppi, R.; Bondi, M.; Sabia, C.; Toselli, M.; Pilati F. *Biomacromolecules* **2007,** *8*, 1246.
53. Wang, D.; An, J.; Luo, Q.; Li, X.; Li, M. *J. Appl. Polym. Sci.* **2008,** *110*, 3038.
54. Storia, A. L.; Ercolini, D.; Marinello, F.; Mauriello, G. J. *Food Sci.* **2008,** *73*, 48.
55. Shah, M. S. A. S.; Nag, M.; Kalagara, T.; Singh, S.; Manorama, S. V. *Chem. Mater.* **2008,** *20*, 2455.
56. Onsuratoom, S.; Rujiravanit, R.; Sreethawong, T.; Tokura, S.; Chavadej, S. *Plasma Chem. Plasma Process.* **2010,** *30*, 191.
57. Tankhiwale, R.; Bajpai S. K. *J. Appl. Polym. Sci.* **2010,** *115*, 1894.
58. Olguna, U.; Tunc, K.; Ozaslan, V. *Polym. Adv. Technol.* **2011,** *22*, 232.
59. Wohrmann, R. M.; Munstedt, H. *Infection* **1998,** *26*, 49.