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Development of a nanocomposite of polypropylene with biocide action from silver nanoparticles

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ABSTRACT: This article presents the production of films based on blends of polypropylene (PP) and modified PP with the insertion of silver nanoparticles (AgNPs) produced to generate a bactericidal effect. The 50/50 blend of PP and PP modified by irradiation in acetylene at a dose of 12.5 kGy was processed in a twin-screw extruder. The addition of AgNPs in poly(*N*-vinyl-2-pyrrolidone) (PVP) solution was performed during processing in the extruder. The material was characterized by ultraviolet–visible spectroscopy, scanning electron microscopy, energy-dispersive spectroscopy, transmission electron microscopy, cytotoxicity assay, and a reduction in colony-forming units. The PP–PVP1% AgNP film showed silver particles in the nanoscale, presented no cytotoxicity for mammalian cells, and presented antimicrobial effects against Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus* bacteria. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42218.

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INTRODUCTION

The linearity of the isotactic polypropylene (iPP) chains of confers a low melt strength (usually measured by tensile strength), which means a low resistance to stretching during elongation. This characteristic limits the use of iPP in processes that require high stretching, for example, the production of blown films and foams and the extrusion coating production of parts free of residual stresses. Branches are introduced into linear polypropylene (PP) to produce high-melt-strength PP having enhanced processability.[1–3]

Nanocomposite polymers are a class of materials with significant commercial appeal. Many types of nanocomposites have been developed, and one feasible alternative, to them, is the inorganic/polymer hybrid nanocomposite. Hybrid polymer nanocomposites have attracted great interest because of their remarkable improvement in material properties and their use of a low percentage of inorganic materials.[4]

Several studies have reported silver nanoparticle (AgNP) activity against a wide range of microorganisms, such as Gram-positive and Gram-negative bacteria.[5] Among metal ions, silver ions have the highest antimicrobial activity. The metallic silver ion is not easily released compared with copper ion, but it is considered safe and relatively inert.[6,7] Silver is particularly attractive because it combines a high toxicity for bacteria with a low toxicity for humans.[8,9]

For technical purposes, antimicrobial substances can be incorporated directly into packing materials by their coating onto the polymer surface or their immobilization in polymers. Thermal processing, such as melt blending, extrusion, and injection molding, have been applied to incorporate antimicrobials into polymers. The heat stability of the active components and their chemical compatibility with the polymer matrix must be considered to evenly distribute antimicrobial substances.[10]

Classic organic biocides have limited applications because of their low heat resistance, high decomposition rate, short life, and high toxicity. One feasible alternative is the incorporation of inorganic biocides into polymer composites.[11–15]

The antibacterial ability of AgNPs in suspension is explained by two mechanisms. The first one considers the adhesion of the nanoparticles to the bacterial surface; this results in cell wall damage and, in some cases, the penetration of nanoparticles

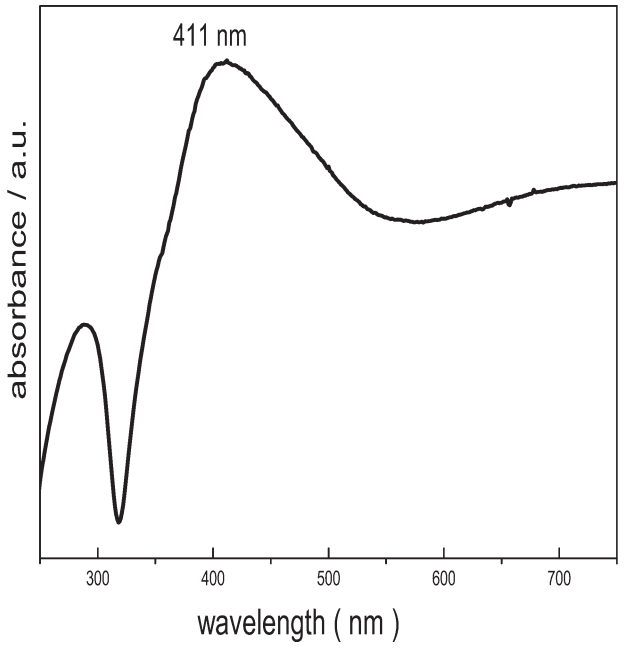


Figure 1. UV–vis absorption spectrum of a solution of PVP with AgNPs.

smaller than 10 nm through the cell wall.[16] Other studies have shown that AgNPs lead to the production of silver ions and, subsequently, reactive oxygen species (ROS), which are the main source of toxicity.[17]

The antibacterial mechanisms of silver nanomaterials are not fully elucidated, but the prevailing paradigm suggests various combinations: (1) the release of silver ions and generation of ROS; (2) the interaction with membrane proteins that affect their correct function; (3) their accumulation in the cell membrane, which affects the membrane permeability; and (4) their entrance into the cell, where they can generate ROS, release silver ions, and affect the DNA. Generated ROS may also affect the DNA, cell membrane, and membrane proteins, and silver ion release will likely affect the DNA and membrane proteins.[18]

Important research was reported by Fages *et al.*[19] on the use of AgNPs with different surfactants, including poly(*N*-vinyl-2-pyrrolidone) (PVP) and oleic acid, to facilitate dispersion. PP–AgNP compounds were prepared by melt mixing, and the effects of the processing conditions on the nanoparticle dispersion were investigated. The antibacterial efficiency of the PP–AgNP compounds against *Staphylococcus aureus* and *Escherichia coli* was evaluated. Their results show that the use of surfactants for AgNPs had important effects on the antibacterial properties of PP filled with coated AgNPs.

Progress in PP nanocomposites with antimicrobial activity has not widely reported. This is probably due to a lack of affinity of AgNPs to nonpolar PP. In the literature, it is common to find studies of the surface treatments of the films and subsequent conditions for the anchoring of nanoparticles of silver,[20,21] silver oxide,[22] zinc oxide,[23] titanium dioxide,[24,25] cooper and titanium dioxide,[26] copper and silver.[27]

In this study, we aimed to examine the morphology and biocidal action of PP–AgNP films obtained by twin-screw extrusion.

EXPERIMENTAL

Materials and Methods

iPP, with a melt flow index (MFI) of 1.5 dg/min and a weight-average molecular weight of 338,000 g/mol Braskem (Brazil) was provided in the form of pellets. The iPP pellets were placed in a nylon container with acetylene (99.8%, White Martins).[28] The irradiation process of the bags was performed in a ^{60}Co source at a dose rate of 5 kGy/h. The dose used was 12.5 kGy and was monitored by a Harwell Red Perspex 4034 dosimeter. After irradiation, the pellets were submitted to heat treatment at 90°C for 1 h to promote the recombination and termination reactions of the radicals.[2,29] The AgNPs were purchased from Sigma Aldrich, and PVP (average molecular weight = 1,300,000 g/mol), which acted as a surfactant for the AgNPs, was Plasdone.

Preparation of the PP–AgNP Nanocomposite Film

The blend of iPP and polypropylene, modified by irradiation in acetylene at a dose of 12.5 kGy (PP 12.5 kGy; 50/50), was mixed with Irganox B 215 ED in a rotary mixer and maintained under these conditions for 24 h.

In a typical procedure, an appropriate amount of PVP was dissolved in 100 mL of water with gradual heating to 70°C. Next, AgNPs were added to the previous solution and ultrasonically dispersed at 2000 rpm for 20 min.

After this period, the PP mixture was processed with the addition of PVP–1 wt % AgNPs in a Haake corotating twin-screw extruder (Rheomex PTW 16/25). The temperatures of the zones were 180 to 195°C, and the screw speed was 100 rpm. Immediately after extrusion, the material was pelletized. The PP–AgNP films were obtained by compression molding at 190°C for 10 min without pressure and 5 min at a pressure of 80 bar; after that, they were dipped in a water bath at 23°C.

The samples used in this study are identified as follows: (1) a blend of iPP and PP 12.5 kGy (50:50), (2) a blend with PP–AgNPs, and (3) a blend of PP–AgNPs with PVP.

MFI and Gel Fraction

The Ceast Italy Melt Flow Modular Line was operated at a temperature of 230°C for 10 min for the MFI test. For preparation of the gel fraction analysis, we used a system of balloons attached to reflux distillers. The samples were involved in a stainless steel of 500 mesh and immersed in boiling xylene at 138°C for 12 h.[30,31]

Ultraviolet–Visible (UV–vis) Spectroscopy

The UV–vis spectrum was obtained with a Shimadzu model UV-2401 spectrometer in the range 200–800 nm.

Scanning Electron Microscopy (SEM) and Energy-Dispersive Spectroscopy (EDS)

Specimens were examined with a Hitachi TM3000, coupled with a Bruker Quantax 70 for the collection of EDS data. SEM coupled with backscattered electron detector (BSE) and energy dispersive X-ray spectroscopy (EDS). Sample sections for the EDS analysis were taken at 15 keV, and the acquisition period was 120 s.

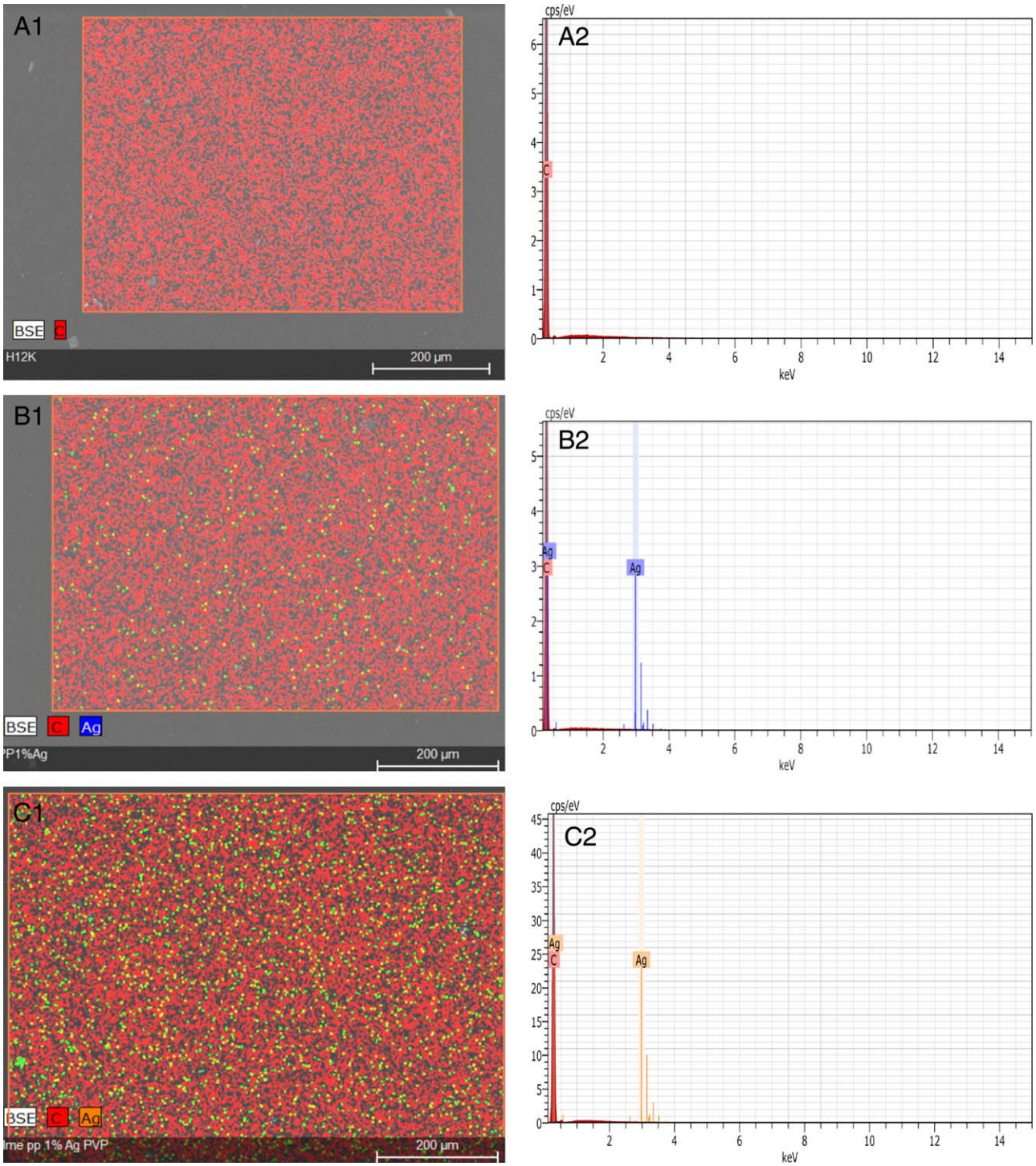


Figure 2. Elemental maps (scale = 200 μm) from SEM–EDS: (A-1) the virgin surface of the PP film shows the distribution of carbon, (B-1) the surface of the PP–1% AgNP nanocomposite film shows the distribution of carbon and silver, and (C-1) the surface of the PP–1% AgNP/PVP nanocomposite film shows the distribution of carbon and silver. (A-2, B-2, C-2) EDS spectra of the PP surface films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Transmission Electron Microscopy (TEM)

The morphology of the samples was examined with a JEOL JEM-2100 transmission electron microscope operating at voltage of 80 kV. Ultrathin sections (80 nm) were prepared with a Leica EM FC6 ultramicrotome with a diamond knife.

Cytotoxicity Test

The test was conducted on the basis of ISO 10993[32] and reports in the literature[33] by the neutral red uptake methodology. The cell line used was NCTC Clone 929 from American Type Culture Collection (ATCC). Cells were cultured in Eagle's minimum medium

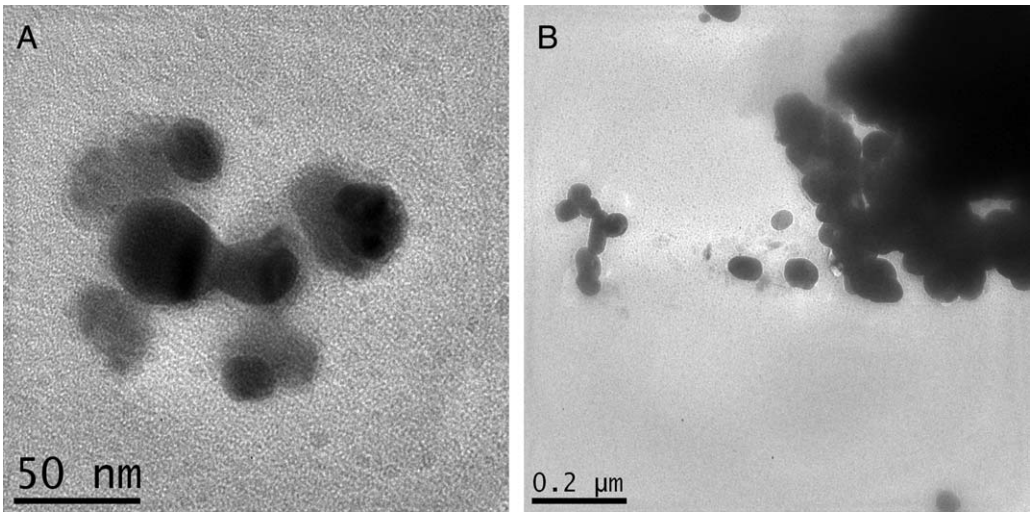


Figure 3. TEM microphotograph of the PP–Ag films: (A) PP–1% AgNPs + PVP and (B) PP–1% AgNPs.

supplemented with 10% fetal bovine serum (FBS), 0.1 m*M* sodium pyruvate, and nonessential amino acids (altogether referred to as MEM-use). High-density polyethylene was used as the negative control, and a natural rubber latex film was used as a positive control. Ninety-six wells were prepared as follows: there was a spread of 200 μL of cell suspension containing 5×10^5 cells/mL in each well, and these were incubated at 37°C in a wet atmosphere with 5% CO_2 for 24 h. The samples and control extracts were prepared by immersion in MEM-use and incubated for 24 h at 37°C (1 cm^2/mL). A serial dilution was made to obtain the following dilutions: 100, 50, 25, 12.5, and 6.25%. The culture medium of the microplate was replaced by diluted extracts of controls and samples in triplicate. The extracts were replaced by a neutral red solution, and the plate was incubated for 3 h. After that, the microplate was washed twice with phosphate-saline-buffer solution, and each well received 200 μL of extracting solution. The absorbance were read in an enzyme-linked immunosorbent assay (Sunrise-Tecan at 540 nm with a 620-nm reference filter), and the cell viability percentages were calculated in relation to the cell control.[34]

Percentage Reduction of Colony-Forming Units (CFU)

The adapted standard JIS Z 2801 (2010)[35] was used for the tests. The cell suspension for the inoculum was 900×10^6 cfu/mL for each tested step. The following procedure was performed separately for each microorganism: samples of the films of PP–AgNPs were placed in a sterile Petri dish and inoculated on the surface of 50 μL of suspension of each organism in an area of 40×40 mm^2. All of them were incubated for 24 h at 37°C.

RESULTS AND DISCUSSION

MFI and Gel Fraction

An increase in the gel percentage was observed with dose. The developed radiation process allowed the production of branched PP on the basis of the grafting of long-chain branches on the PP backbone with acetylene as a crosslinking promoter under a γ-radiation process.[36]

The PP, when modified with 12.5 kGy, showed a reduction of MFI, from 1.5 ± 0.1 to 0.9 ± 0.1 dg/min. This was indicative of the crosslinked and/or branched material,[28] and this corroborated the increase in gel content from 1.14 ± 0.10 to 2.27 ± 0.10%.

UV–vis Spectroscopy

The UV–vis absorption spectra of the solution of PVP with AgNPs is illustrated in Figure 1.

The absorbance peak around 411 nm was attributed to the localized surface plasmon resonance of the AgNPs,[37] and this was characteristic of AgNPs with a spherical shape.[38]

SEM and EDS

The degree of dispersion of nanoparticles plays an important role in the properties of the nanocomposites. EDS combined with SEM was used to analyze the elemental composition comprising carbon and silver on the PP virgin surface and with a PP–Ag matrix (Figure 2).

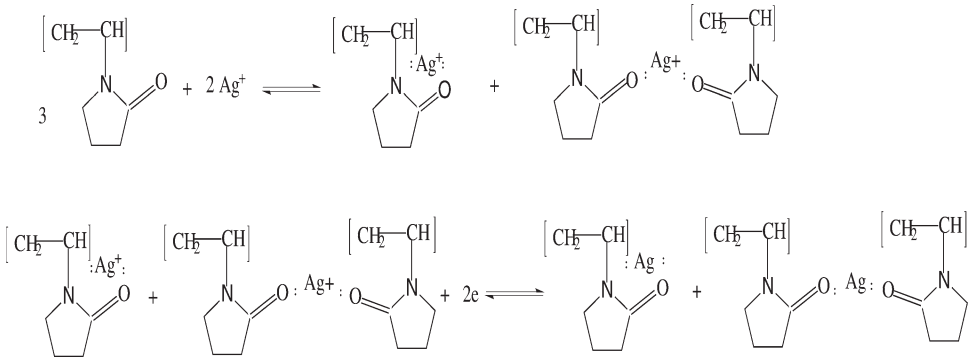
The images in Figure 2(B-1,C-1) are related to the PP film with AgNPs. Both showed bright spots attributed to the presence of AgNPs. The EDS elemental analysis confirmed the presence of silver [Figure 2(B-2,C-2)] by presence of the peak around 3.40 keV, which represented energy bands of AgL state.[39–43]

SEM images indicate the presence of AgNPs on the surface of the PP films that favored the action (by physical contact) of nanosilver in the bactericidal assay, mainly in the sample shown in Figure 2(C-1).

The elemental analysis result suggests that nanosilver was better dispersed throughout the bulk PP–1% AgNPs/PVP nanocomposite films. This supported the observation that the blending process in the presence of PVP was effective.

TEM

The size and morphology of the nanofillers with a spherical format, synthesized with surfactant, were investigated with TEM.



Scheme 1. Reduction and protection mechanism of silver by PVP.[46,47]

The images of the nanostructures are shown in Figure 3 for PP–1% AgNPs/PVP and PP–1% AgNPs.

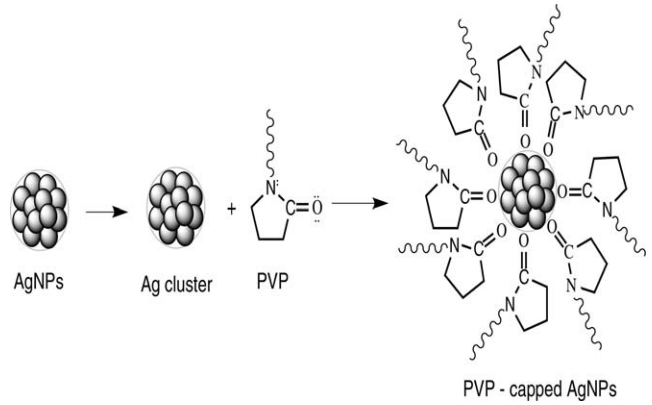
Figure 3(A) shows the spherical shape of the AgNPs and the formation of agglomerates in the PP film. The size of the AgNPs ranged from 21.3 to 41.3 nm in diameter. The image of the AgNPs, moreover, demonstrated a core–shell nanostructure consisting of an Ag core covered by a thin shell of a PVP amorphous whitish layer in PVP-capped AgNPs; this was similar to results reported in the literature.[44]

A layer formed with the introduction of PVP, coordinated with silver ions by N or O, inhibited the growth and agglomeration of the particles, according to the mechanisms[45,46] shown in Scheme 1.

The experimental results demonstrate that PVP, as a protective surfactant agent, played decisive role in controlling the metallic silver size, size distribution, and particle agglomeration. A structure based on ref. 47 of the PVP-capped AgNPs is shown in Scheme 2.

The solid particle clusters were subjected to shearing forces while flowing through process streams; they broke down into smaller components and were distributed in the surrounding medium.[48]

The dispersion of particle agglomerates is a key processing step in many industrial applications. In this study, the mixing process of AgNPs with a PVP solution with an ultrasonic disperser was allowed the AgNP clusters to obtain a structure similar to that shown in Scheme 2.



Scheme 2. Formation and subsequent encapsulation of Ag clusters via the O atom of the C═O group of the PVP molecules.

Cytotoxicity Test and Percentage Reduction of CFU

Cell viability curves were obtained in a graphic traced with cell viability percentages against the extract concentration. The cytotoxicity index ($IC_{50\%}$) was obtained, as shown in the graphic, and it indicates the extract concentration that injures 50% of the cell population in the assay. A sample with a cell viability curve above the $IC_{50\%}$ line is considered noncytotoxic, and one under $IC_{50\%}$ line is considered toxic. $IC_{50\%}$ was obtained by the projection of a line from the 50% cellular viability axis to extract the concentration.

In the cytotoxicity test, the PP film with AgNPs showed similar behavior to the negative control; that is, the film did not show toxicity (Figure 4). Therefore, the PP–AgNP film was characterized as noncytotoxic for human contact.

The test of percentage reduction for CFU in the PP–AgNP film showed an excellent effect for *S. aureus* [Figure 5(C)], with biocide effectiveness after 24 h of incubation. A 68% reduction of *E. coli* of the PP–AgNP films versus the PP film control without AgNPs assured a satisfactory antibacterial efficacy.

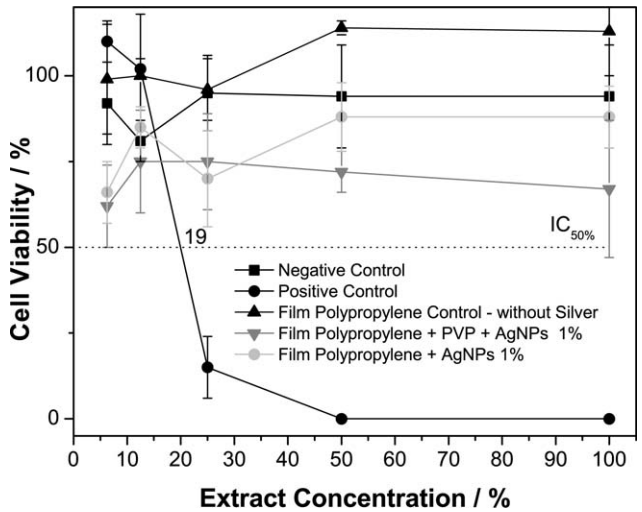


Figure 4. Cell viability curves of a PP film with AgNPs in the cytotoxicity test by the neutral red uptake method.

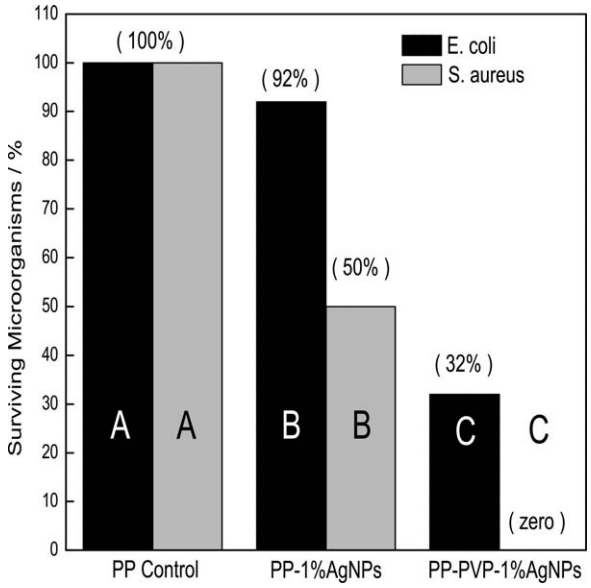


Figure 5. Surviving microorganism percentages after 24 h of incubation for *S. aureus* and *E. coli* in the (A) PP 12.5 kGy (50/50) control, (B) PP 12.5 kGy (50/50) + 1% AgNP, and (C) PP 12.5 kGy (50/50) + PVP + 1% AgNP films.

Similar results were obtained by Fages *et al.*[19] with PP–AgNP compounds prepared by melt mixing. The effects of the processing conditions on nanoparticles were investigated. The results show that good dispersion and antimicrobial properties were obtained with PVP as a surfactant against *S. aureus* and *E. coli*. The addition of coated AgNPs to the PP matrix represented an interesting solution for increasing protection against *S. aureus* and *E. coli*. Fages *et al.* concluded that the AgNPs in the presence of surfactants had a high antibacterial efficiency. The presence of AgNPs also improved the thermal stability of the PP–AgNPs in favor of the processability, a fact attributed to the interaction between the PP chains and surfactant-coated AgNPs.

Gawish *et al.*[49] evaluated the antibacterial properties of composite fibers of PP. They suggested the use of twin-screw extruder to promote the reduction of particle agglomeration and to improve antibacterial efficiency against *E. coli* and *S. aureus*.

The use of AgNPs incorporated in PVP promoted in the PP/PP modified blend a unique AgNP distribution on the surface with antibacterial effects.

CONCLUSIONS

The addition of coated AgNPs to a PP matrix during the extrusion process represented an interesting solution for increasing the protection against *S. aureus* and *E. coli*. For instance, AgNPs in the PP film properly hindered the bacterial activity in the bulk, and when appropriated surfactants were used, the overall effect was a high antibacterial efficiency on the surface. The percentage reduction for the CFU assay showed positive biocidal results for *S. aureus* and *E. coli*. The cytotoxicity test for the PP film with AgNPs showed no cytotoxic effects on mammalian cells. The PVP coating presented a favorable medium for ionic silver diffusion and bactericidal effect in the PP blend modified by irradiation.

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REFERENCES

1. Rätzsch, M.; Arnold, M.; Borsig, E.; Bucka, H.; Reichelt, N. *Prog. Polym. Sci.* **2002**, *27*, 1195.
2. Oliani, W. L.; Lima, L. F. C. P.; Parra, D. F.; Dias, D. B.; Lugao, A. B. *Radiat. Phys. Chem.* **2010**, *79*, 325.
3. He, C.; Costeux, S.; Adams, P. W.; Dealy, J. M. *Polymer* **2003**, *44*, 7181.
4. Yeum, J. H.; Park, J. H.; Kim, I. K.; Cheong, I. W. Advances in Nanocomposites—Synthesis, Characterization and Industrial Applications; Edited by Boreddy Reddy; InTech: Croatia, **2011**; p 483.
5. De-Simone, S.; Lombardi, F. A.; Paladini, F.; Starace, G.; Sannino, A.; Pollini, M. *J. Appl. Polym. Sci.* **2015**, *132*, 41623.
6. Brody, A. L.; Strupinsky, E. R.; Kline, L. R. Active Packaging for Food Applications; CRC Press LLC: Boca Raton, FL, EUA, **2002**; p 144.
7. Oliveira, L. A.; Oliveira, P. A. P. L. V. *Braz. J. Food Technol.* **2004**, *7*, 161.
8. Rivero, P. J.; Urrutia, A.; Goicoechea, J.; Zamarreno, C. R.; Arregui, F. J.; Matías, I. R. *Nanoscale Res. Lett.* **2011**, *6*, 1.
9. Liau, S. Y.; Read, D. C.; Pugh, W. J.; Furr, J. R.; Russell, A. D. *Lett. Appl. Microbiol.* **1997**, *25*, 279.
10. Jokar, M.; Rahman, R. A.; Ibrahim, N. A.; Abdullah, L. C.; Pan, C. *Food Bioprocess. Technol.* **2012**, *5*, 719.
11. Kumar, R.; Münstedt, H. *Biomater.* **2005**, *26*, 2081.
12. Nowack, B.; Krug, H. F.; Height, M. *Environ. Sci. Technol.* **2011**, *45*, 1177.
13. Appendini, P.; Hotchkiss, J. H. *Innovat. Food Sci. Emerg. Technol.* **2002**, *3*, 113.
14. Miola, M.; Perero, S.; Ferraris, S.; Battiato, A.; Manfredotti, C.; Vittone, E.; Del-Vento, D.; Vada, S.; Fucale, G.; Ferraris, M. *Appl. Surf. Sci.* **2014**, *313*, 107.
15. Suktha, P.; Lekpet, K.; Siwayaprahm, P.; Sawangphruk, M. *J. Appl. Polym. Sci.* **2013**, *128*, 4339.
16. Morones, J. R.; Elechiguerra, J. L.; Camacho, A.; Holt, K.; Ramírez, J. T.; Yacaman, M. *J. Nanotechnology* **2005**, *16*, 2346.
17. Hwang, E. T.; Lee, J. H.; Chae, Y. J.; Kim, Y. S.; Kim, B. C.; Sang, B. I.; Gu, M. B. *Small* **2008**, *4*, 746.
18. Marambio-Jones, C.; Hoek, E. M. V. *J. Nanoparticle Res.* **2010**, *12*, 1531.
19. Fages, E.; Fenollar, O.; Sanoguera, D. G.; Balart, R. *Polym. Eng. Sci.* **2010**, *51*, 804.

20. Perkas, N.; Shuster, M.; Amirian, G.; Koltypin, Y.; Gedanken, A. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 1719.
21. Rathnayake, W. G. I. U.; Ismail, H.; Baharin, A.; Darsanasiri, A. G. D. N.; Sanath, R. *Polym. Test.* **2012**, *31*, 586.
22. Li, Y. N.; Li, S. C. *Polym. Plast. Technol. Eng.* **2010**, *49*, 725.
23. Rathnayake, W. G. I. U.; Ismail, H.; Baharin, A.; Bandara, I. M. C. C. D.; Rajapakse, S. *J. Appl. Polym. Sci.* **2014**, *131*, 39601.
24. Youssef, A. M. *Polym. Plast. Technol. Eng.* **2013**, *52*, 635.
25. Allahyarzadeh, V.; Montazer, M.; Nejad, N. H.; Samadi, N. *J. Appl. Polym. Sci.* **2013**, *129*, 892.
26. Wei, X.; Yang, Z.; Tay, S. L.; Gao, W. *Appl. Surf. Sci.* **2014**, *290*, 274.
27. Hausman, R.; Escobar, I. C. *J. Appl. Polym. Sci.* **2013**, *128*, 1706.
28. Yoshiga, A.; Otaguro, H.; Parra, D. F.; Lima, L. F. C. P.; Lugao, A. B. *Polym. Bull.* **2009**, *63*, 397.
29. Oliani, W. L.; Parra, D. F.; Lugao, A. B. *Radiat. Phys. Chem.* **2010**, *79*, 383.
30. Otaguro, H.; Lima, L. F. C. P.; Parra, D. F.; Lugao, A. B.; Chinelatto, M. A.; Canevarolo, S. V. *Radiat. Phys. Chem.* **2010**, *79*, 318.
31. Oliani, W. L.; Parra, D. F.; Riella, H. G.; Lima, L. F. C. P.; Lugao, A. B. *Radiat. Phys. Chem.* **2012**, *81*, 1460.
32. ISO 10993-5, 2009; Biological Evaluation of Medical Devices. Part 5: Tests for In Vitro Cytotoxicity; International Organization for Standardization: Geneva, Switzerland, **2009**.
33. Rogero, S. O.; Malmonge, S. M.; Lugao, A. B.; Ikeda, T. I.; Miyamaru, L.; Cruz, A. S. *Artif. Organs* **2003**, *27*, 424.
34. Rogero, S. O.; Lugao, A. B.; Ikeda, T. I.; Cruz, A. S. *Mater. Res.* **2003**, *6*, 317.
35. JIS Z 2801 (2010); Japanese Industrial Standard; Antibacterial Products—Test for Antibacterial Activity and Efficacy; Japanese Standards Association: Tokyo, Japan, **2010**.
36. Oliani, W. L.; Parra, D. F.; Lima, L. F. C. P.; Lugao, A. B. *Polym. Bull.* **2012**, *68*, 2121.
37. Tang, B.; Xu, S.; Jian, X.; Tao, J.; Xu, W. *Appl. Spectrosc.* **2010**, *64*, 1407.
38. Dehnavi, A. S.; Aroujalian, A.; Raisi, A.; Fezel, S. *J. Appl. Polym. Sci.* **2013**, 1180.
39. Afreen, R. A.; Ranganath, E. *J. Environ. Sci.* **2012**, *1*, 1582.
40. Quang, D. V.; Sarawade, P. B.; Hilonga, A.; Kim, J. K.; Chai, Y. G.; Kim, S. H.; Ryu, J. Y.; Kim, H. T. *Appl. Surf. Sci.* **2011**, *257*, 6963.
41. Kim, Y. H.; Lee, D. K.; Kang, Y. S. *Colloid Surf. A* **2005**, *257*, 273.
42. Guzman, M. G.; Dille, J.; Godet, S. *Int. J. Chem. Biomol. Eng.* **2009**, *2*, 104.
43. Wei, Q.; Tao, D.; Deng, B.; Hung, F. *J. Ind. Text.* **2009**, *38*, 1.
44. Sahaa, S. K.; Chowdhurya, P.; Sainib, P.; Babu, S. P. S. *Appl. Surf. Sci.* **2014**, *288*, 625.
45. Zhang, Z.; Zhao, B.; Hu, L. *J. Solid State Chem.* **1996**, *121*, 105.
46. Wang, H.; Qiao, X.; Chen, J.; Wang, X.; Ding, S. *Mater. Chem. Phys.* **2005**, *94*, 449.
47. Behera, M.; Ram, S. *Appl. Nanosci.* **2014**, *4*, 247.
48. Fanelli, M.; Feke, D. L.; Zloczower, I. M. *Chem. Eng. Sci.* **2006**, *61*, 473.
49. Gawish, S. M.; Ramadan, A. M.; Mosleh, S.; Monticello, R.; Breidt, F.; Kotek, R. *J. Biomater. Sci.* **2012**, *23*, 43.