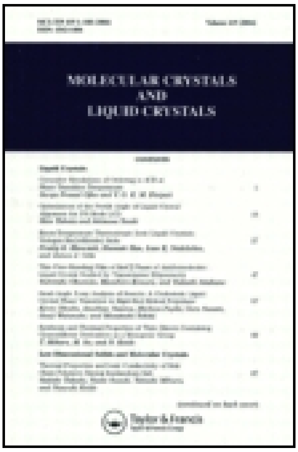

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LDPE/EVA Composites for Antimicrobial Properties

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LDPE/EVA Composites for Antimicrobial Properties

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Composites with antimicrobial activity are of great interest nowadays and the development of titanium dioxide with these functional properties presents interest in academic and industrial sectors.

An approach to develop PE composite containing silver microparticles to have an antimicrobial effect is presented. To obtain such antimicrobial composites, LDPE/EVA were processed with Ag particles on TiO_2 particles as inorganic carrier substance. Titanium dioxide nanoparticles (P-25) were covered with silver particles using Turkevich Method or citrate reduction method. The Ag/TiO_2 particles were dispersed at concentration of 0,8 wt% and 1% wt% in LDPE/ethylene vinyl acetate copolymer (EVA)–(50% w/w) at the melt state in a Haake torque Rheometer. Silver microparticles were characterized with UV-Vis Spectroscopy. The composites thus prepared were characterized through XRD, Ares Rheometer, Scanning Electronic Microscopy (SEM) and JIS Z 2801 antimicrobial tests to study the effects of the addition of particles on rheological properties, morphological behavior and antimicrobial properties. The results showed that incorporation of silver/titanium dioxide particles on composites obtained systems with differents dispersions. The Ag/TiO_2 particles showed uniform distribution of Ag on TiO_2 particles as observed by SEM-EDX and antimicrobial tests according to JIS Z 2801 shows excellent antimicrobial properties.

Keywords Antimicrobial polymers; citrate reduction method; nanocomposite

1. Introduction

Antimicrobial polymers have many applications in medical and packaging industries. The design of antimicrobial properties for a polymer depends on the application field of that polymer. Different types of antimicrobial additives based on silver are available in the market. It can kill the bacterial cell by reacting with sulfur containing functional groups

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in the cell and stops the respiratory function [1,2]. Additives in form of coatings are being used for different application e.g. in refrigerator or in paints and varnishes. Coating plastic part with an antimicrobial material is a cost intensive process. Further disadvantages of such coatings are that these could get scratched easily and lose their antimicrobial effect in that area. Additives containing silver in powder form are also available in the market and these are mainly based on inorganic carrier substance zeolite [3–5]. Sondi and Salopek Sondi [6] investigated the antimicrobial activity of silver nanoparticles with ascorbic acid in the presence of a surfactant agent (Daxad 19) against E.coli. EDAX (energy dispersive spectroscopy) showed that silver nanoparticles were incorporated into the bacterial cell membrane and kill bacterial cells. Yanyan Yao et al. [7] showed that Ag/TiO2-coated silicon catheters possessed significant bactericidal activity against E. coli, P. aeruginosa, and S. aureus.

Blending two or more polymers is an effective strategy to improve plastic material performance. The procedure is to use common polymers and to blend them in the melt to accomplish the required properties. However, most polymer pairs are immiscible and form a multiphase system leading to a more complex rheology [8]. In these systems, interfacial tension has a controlling role on both rheology and morphology since it influences the dispersed particle size as well as particle size distribution. LDPE/EVA shows a finely interconnected morphology at 50 wt% of EVA and the morphological observations can be attributed to the lower viscosity ratio and lower interfacial tension in the LDPE/EVA system. Besides, additive polymers EVA improves solubilization by partially binding the antimicrobial agents in the polymer matrix [9,10].

In this study, a strategy to develop an antimicrobial product on the basis of TiO_2 as inorganic carrier substance is explained. Silver nitrate was reduced by sodium citrate in the presence of poly(vinyl pyrrolidone) (PVP) and titanium dioxide resulting in Ag/TiO_2 stabilized suspension. Each sample was centrifuged and the supernatant was removed, after that, the remains solid was dried then the Ag/TiO_2 particles were dispersed at concentration of 0,8 and 1 wt% in LDPE / ethylene vinyl acetate copolymer (EVA)–(50% w/w) at the melt state in a Haake torque Rheometer.

2. Experimental Details

2.1. Materials

A low density polyethylene homopolymer with a melt flow index of 0,32 g/10min (190°C/2,16 Kg) and tradename of BF-0323 HC with a was supplied by Braskem (Brazil). A EVA copolymer with a content of 9% vinyl acetate by weight and a melt flow index of 2 g/10 min (190°C/2,16 Kg) was supplied as pellets by Triunfo Petrochemical (Brazil) under the tradename of Tritheva® TN 2020.

TiO_2 nanoparticles (Degussa P-25), $AgNO_3$ (HEXIS, ACS Reagent), Sodium Citrate (Synth) and PVP 40 (poly(vinyl pyrrolidone)-Sigma Aldrich) were used as received without further purification.

2.2. Colloidal Synthesis

For a typical procedure at room temperature and under stirring, silver nitrate solution (1×10^{-2} mol/L) were heated until 110°C and after sodium citrate ($3,6 \times 10^{-3}$ mol/L) was added to the boiling solution with vigorous mechanical stirring. After fifteen minutes, PVP (poly(vinyl pyrrolidone) solution was added (3,75 $\times$ 10^{-3} mol/L). Then, commercial Degussa TiO_2 nanoparticles were added in Ag-solution resulting in microparticles Ag/TiO_2 stabilized suspension, characterized by UV-Vis Spectroscopy .Each sample was centrifuged and the supernatant was removed, after that, the remains solid was dried in a vacuum oven. Silver-titanium dioxide powders were characterized by XRD and SEM.

2.3. Nanocomposite Preparation

All materials were vacuum dried for at least 12 hours prior to melt processing. The antimicrobial composites were prepared in a Haake torque Rheometer model Rheomix 600 p with CAM rotors at 190 degree celsius. The Ag/TiO_2 particles were dispersed at concentration of 0,8 and 1 wt% in LDPE / ethylene vinyl acetate copolymer (EVA)–(50% w/w) at the melt state in a Haake torque Rheometer. Thick films were obtained for antimicrobial test and reological analysis.

2.3.1. Nanoparticle and Nanocomposite Characterization

2.3.1.1. UV-Vis Spectroscopy. Using the spectrometer VARIAN Caryn Scan 50, were taken from the spectra of UV-Vis of suspension of silver particles.

2.3.1.2. XRD. The X-ray diffraction patterns were obtained in a SIEMENS D5005 diffractometer using copper Kα the radiation, sweeping the sample from 50 to 90°C, a step of 2°C per minute.

2.3.1.3. Scanning Electronic Microscopy. Scanning electronic microscopy images were performed on a PHILIPS XL30 FEG. The samples were covered with gold and silver paint for electrical contact and to perform the necessary images.

2.3.1.4. Ares Rheometer. A Rheometrics ARES rheometer with a convection oven purged with nitrogen gas was used. The frequency range used was 0.01–10 Hz. The oven was preheated, and the rheological measurement was started 120 s after the sample was placed in the apparatus. Time sweep measurements were performed at a frequency of 1 Hz.

2.3.1.5. Antimicrobial Test (JIS Z 2801). Antibacterial activity is measured by quantifying the survival of bacterial cells which have been held in intimate contact for 24 hours at 35°C with a surface that contains an antibacterial agent. The antibacterial effect is measured by comparing the survival of bacteria on a treated material with that achieved on an untreated material.

3. Results and Discussion

3.1. UV-Vis Spectroscopy

Using the spectrometer VARIAN Caryn Sacan 50, were taken from the spectra of UV-Vis of suspension of silver particles.

The absorption spectra of the silver particles are presented in Fig. 1. A weak band near to 450 nm corresponding to the signal of silver nanoparticles [11–13].

3.2. XRD

Silver/titanium dioxide nanoparticle and microparticle powder were characterized with XRD. Figure 2 illustrates the x-ray analysis performed on a sample of the reaction. The detection of two types of titanium dioxide in Fig. 2 is due to the fact that titanium marketed by Evonik Industries has a mixture of anatase titanium dioxide (70%) and rutile (30%) in

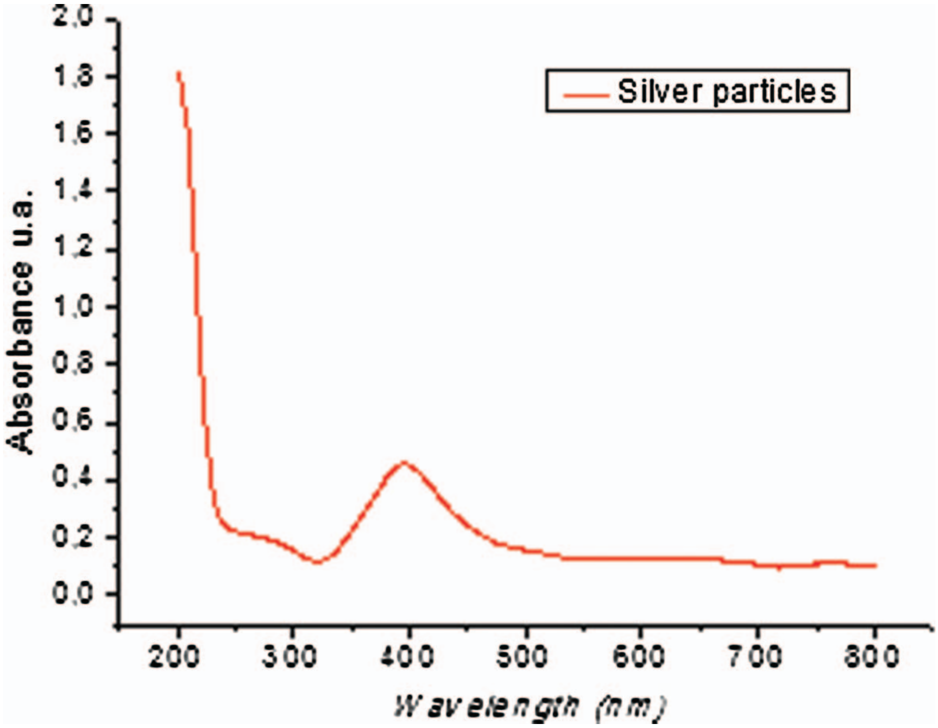

Figure 1. Electronic Spectra (UV-Vis): Suspension of Ag particles (red line).

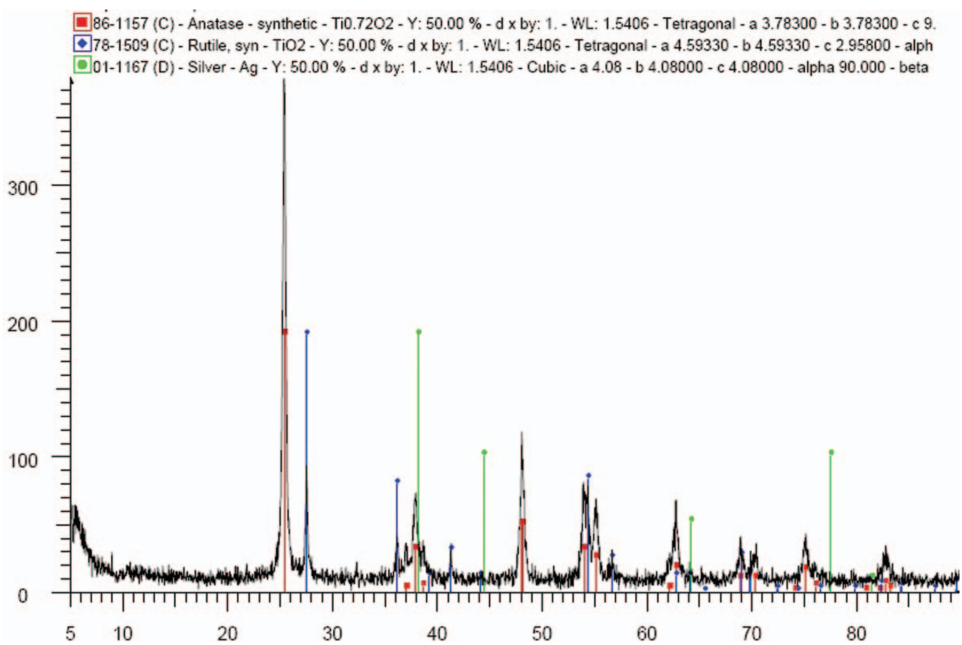

Figure 2. XRD analysis of the powder with silver/dioxide titanium particles.

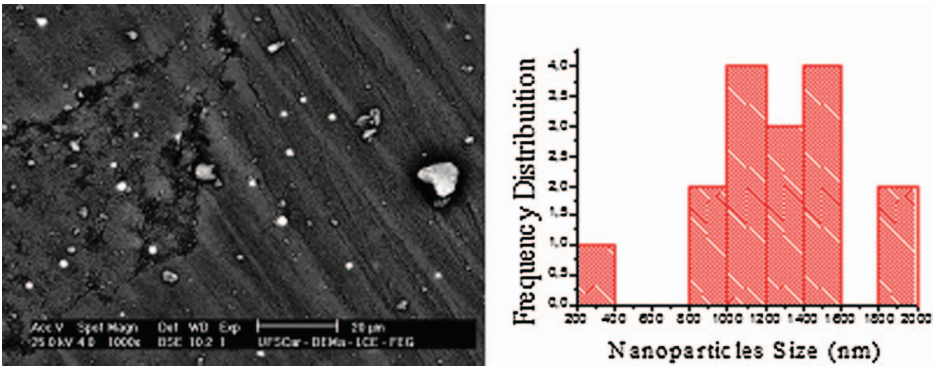

Figure 3. (a) Silver particles on titanium dioxide; (b) Size distribution of silver particles on titanium dioxide nanoparticles.

its formulation. It can be observed that silver particles was detachment completely on TiO_2 nanoparticles, in Fig. 2, peaks from silver, anatase and rutile titanium dioxide are observed by XRD from silver-titanium dioxide powders obtained by colloidal synthesis.

3.3. Scanning Electronic Microscopy (SEM)

Silver/titanium dioxide microparticles were synthesized with sodium citrate like reductor agent and poly(vinyl pyrrolidone) like surfactant. With the help of a software image analyzer (IMAGEJ) we can draw graphs of the distribution of silver particles on titanium dioxide particles. The figure illustrates silver particles with different shapes, triangular, square and with a broad distribution, with most frequencies between 200 and 400nm and between 1200 and 1400 nm as shown in Fig. 3. PVP (polyvinyl pyrrolidone) has some interesting and unique features, it donating their free electrons from atoms of oxygen and nitrogen to the sp orbital of silver ions, and thus form a complex of PVP-silver ions in aqueous solution and this promotes nucleation of metallic silver because the complex formed is more easily reduced by reducing agent (sodium citrate) than silver ions allowing silver ions receive more electron clouds of PVP that water [14,15].

3.4. Ares Rheometer

We tested silver/titanium dioxide particles in LDPE/EVA polymer blends with oscillatory rheological analysis. When we put inorganics particles in the system, we observed in Fig. 4(a) that increase elastic and viscous modulus in the LDPE/EVA blends, because inorganics particles(silver/titanium dioxide particles) prevent oscillatory macromolecular moviments perfomed by rheometer shear thinning.Thus, silver/titanium particles addition on polymer system (LDPE/EVA) makes the system more strenght to industrial applications. In Fig. 4, all systems has the inclination curves (G', G'') proportional to w (rad/s), every behaviors can be characterized as pseudo-solid, which may be related to an inappropriate level of dispersion of the dispersed phase, mainly because LDPE/EVA is a immiscible blends but compatible too, which was worsened because of processing of the composite with Haake rheometer, where the shear rate is low compared to the extrusion and injection, affected the dispersion of the system. It can be note in Figs 4(b) and 4(c) are similars, then,

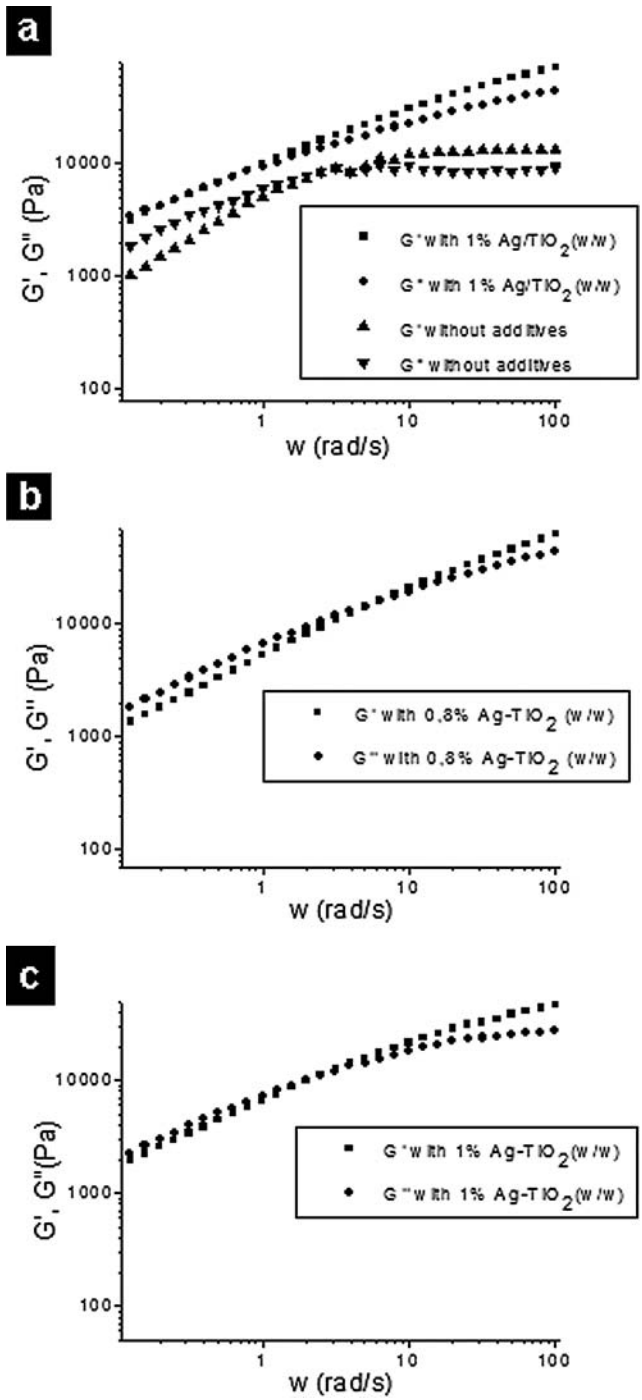

Figure 4. (a) G′(elastic modulus) and G″ (viscous modulus) versus oscillatory shear (rad/s); (b) LDPE/EVA/Ag-TiO_2 (0,8% w/w); (c) LDPE/EVA/Ag-TiO_2 (1% w/w).

Table 1. Antimicrobial Test (JIS Z 2801) in LDPE/EVA/Ag-TiO_2 composites

Samples	Colony formation units in zero time *Staphylococcus aureus* (ATTC n°6538)	Colony formation units after contact for 24 h	Logaritmic Reduction	% Reduction
01 (0,8% Ag/TiO_2/ LDPE/EVA)	3,7 × 105	$7,6 \times 10^4$	0,69	79,46%
02 (1% Ag/TiO_2/ LDPE/EVA)	$3,7 \times 10^5$	$3,2 \times 10^4$	1,06	91,35%
03 (LDPE pure)	$3,7 \times 10^5$	$3,4 \times 10^5$	0,04	8,11%

differents addition of fillers or the effect of the synthesis of particles has generated equal rheological systems.

3.5. Antimicrobial Test (JIS Z 2801)

In antimicrobial test, *Staphylococcus aureu* bacterial colony were tested. *Staphylococcus aureu* is is a species of Staphylococcus coagulase-positive. It is one of the most common pathogenic species, along with the Escherichia coli. It is the most virulent species of its genus. Is spherical (cocci are) about 1 micrometer in diameter, and form groups with the appearance of bunches of grapes on a yellowish color, due to the production of carotenoids, and hence the name "golden staph". It grows well in saline environments In Table 1, we can observed that *Staphylococcus aureu* isn't resistant to polymer composite and that a larger amount of antimicrobial agent is better in kill superficial bacteria.

4. Conclusions

In this study, an approach to develop a process for the preparation of antimicrobial polyethylene composites is discussed. Morphological analysis of the compounded materials (silver-titanium dioxide particles) showed partial dispersion of silver particles and the detachment of silver particles from the TiO_2 particles at different parts of the compounded materials as observed by SEM and XRD. UV-vis Spectroscopy analysis confirm the presence of silver in the form of Ag^0 obtained of colloidal synthesis.

The effect of different parameters on the antimicrobial composites which are compounded in a Haake rheometer was analyzed. Ares rheometer showed rheological instability systems characterized as pseudo-solid, which may be related to an inappropriate level of dispersion of the dispersed phase. In antimicrobial test, a large amount of antimicrobial fillers showed linear increase of antimicrobial properties. In future work, an ideal filler amount will be studied to obtained an economic and excellent antimicrobial composites.

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