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Fabrication of polypropylene/silver nanocomposites for biocidal applications

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ABSTRACT

This paper presents a study on biocidal effect of polymer nanocomposite films of gamma irradiated polypropylene (PP) and silver nanoparticles. The modified polypropylene was obtained from isotactic polypropylene (iPP) in pellets form by irradiation with gamma rays in the presence of acetylene. A new morphology with long chain branching of PP and distinct rheology is obtained by this process. The blend of 50/50 wt% neat PP and PP modified by gamma radiation were further mixed using a twin screw extruder. The AgNPs were infused into this polymer blend at different concentrations of: 0.1%; 0.25%; 0.5%; 1.0%; 1.0% (PVP), 2.0% and 4.0% by wt%. These polymer nanocomposites were characterized by Raman spectroscopy, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), thermogravimetric analysis (TG), differential scanning calorimetry (DSC), X-ray diffraction (XRD), transmission electron microscopy (TEM), cytotoxicity test and Kirby-Bauer disk diffusion techniques. The bactericidal effect of *Pseudomonas aeruginosa* (*P. aeruginosa*) and *Staphylococcus aureus* (*S. aureus*) were assessed in detail.

1. Introduction

Polypropylene (PP) has emerged as an environmentally friendly polymeric material because its low cost and high chemical resistance coupled with ease of fabrication, high versatility in applications and recycling [1,2]. PP is the fastest growing commodity resin in the thermoplastic polymers world market [3].

PP has low melt strength, low elasticity, and a narrow processing window because of its linear macromolecular architecture and semi-crystalline nature. As a result, upon heating PP to its melting temperature, it undergoes sharp transition from a semi crystalline solid to a melt that has no appreciable rubbery plateau. Hence, PP cannot be easily used in melt processing operations such as deep draw thermoforming, upward film blowing and extrusion coating, which involve free surfaces undergoing extensional deformation [3–5].

An effective approach to achieve high-melt-strength-polypropylene (HMSPP) is to add long-chain-branches (LCB) into linear PP, onto backbone, using gamma radiation and acetylene. The grafting and branching result from macroradicals combinations during the irradiation process [6–9]. The strain hardening effect of the HMSPP represents an important role in many processing operations like film blowing, blow molding, foam expansion, fiber spinning and thermoforming [10].

Extrusion process has been one of the important basic processing technologies for producing polymer based compounds. The extrusion technology has been divided into two major streams. The first stream goes towards higher efficiency using lager scale processing lines, and the other towards the production of functional products with special properties, such as nanocomposites and/or polymer blends with specified nanoscale morphology [11].

The modification of polypropylene with inorganic nanoparticles (AgNPs) nanocomposites prepared by melt mixing may provide some functionality to the polymer. Applications such as household, automotive, and packaging materials depend on the properties of the inorganic nanoparticles. The presence of Ag nanoparticles increases the crystallization temperature of iPP even at very low Ag content, which represents a high efficiency of the heterogeneous nucleation [12,13]. The dispersion of particle agglomerates is a key processing step in many industrial applications. Solid particle clusters are subjected to shearing forces while flowing through the process streams. They are broken down into smaller components and are distributed [14]. Although the properties of the dispersing fluid and the particulate material can be very diverse, depending on the application, the same fundamental principles are apply to control the dispersion process and the properties of the

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Table 1
Samples of PP-nanocomposites with addition AgNPs (wt%).

Sample	A	B	C	D	E	F	G	H
PPAgNPs/wt%	PP0	PP0.1	PP0.25	PP0.5	PP1.0	PP1.0PVP	PP2.0	PP4.0

*HMSPP obtained at 12.5 kGy was used as control: PP0.

final product [15]. In spite of antimicrobial activity, active substances can be incorporated directly into polymeric materials or previously encapsulated by organic coating for follow polymer incorporation.

Thermal processing such as melt blending, extrusion and injection molding have also been applied to incorporate the antimicrobials into polymers. The thermal stability of active component and chemical compatibility of polymer matrix and antimicrobials should be considered in order to evenly distribute antimicrobial substance [16]. Silver is particularly attractive because its high toxicity against bacteria at exceptionally low concentrations and a very low toxicity for humans [17,18].

Colloidal silver and silver nanoparticles are increasingly used as antimicrobial agents, stimulated by its depot function for silver ions and its high specific surface area [19].

Recently, silver nanoparticles (AgNPs), metallic silver obtained in nanosize are stabilized with different surfactants such as, polyvinyl pyrrolidone (PVP) or oleic acid (OA) for better dispersion [20].

These polypropylene-AgNPs compounds were prepared by melt mixing, and the effects of the processing conditions on nanoparticles dispersion were investigated, as well as, antimicrobial properties of polypropylene filled with coated AgNPs [20].

The mechanisms behind the activity of nano-scaled silver on bacteria are not fully elucidated yet. The three most common mechanisms of toxicity proposed to date are: (1) uptake of free silver ions followed by disruption of ATP production and DNA replication, (2) silver nanoparticles and silver ion generation of ROS, and (3) direct damage to cell membranes by silver nanoparticles [21–23].

In our recent study we developed a method for branched PP, based on the grafting of long chain branches on PP backbone using acetylene as a crosslink promoter under gamma radiation process [24]. In the current study we extended the branched PP to incorporate AgNPs. Films of polypropylene nanocomposite with silver nanoparticles were obtained by extrusion process and evaluated for biocidal effect of bacteria *P. aeruginosa* and *S. aureus*.

2. Experimental

2.1. Materials

The isotactic Polypropylene (iPP) with MFI = 1.5 dg min^{-1} and Mw = 338,000 g mol^{-1} from Braskem – Brazil, was supplied in pellets. Acetylene 99.8% supplied by White Martins. Silver nanoparticles (AgNPs) was purchased from Sigma Aldrich, reference 576832, lot MKBF5701V. The AgNPs particle sizes are in the range of 26–41 nm with 99.9% of purity originally coated with 0.1 wt% of PVP as a surfactant. The PVP (K90) (average molecular weight = 1,300,000 g mol^{-1}), was purchased from Plasdone.

Antioxidant Irganox®B215 ED, 67% tris(2,4-ditert-butylphenyl)phosphite and 33% pentaerythritol tetrakis[3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionate] from BASF.

2.2. Methods

2.2.1. Radiation process

The irradiation process of the polymer pellets was carried at room temperature and at dose rate of 5 kGy h^{-1}, using a multipurpose ^{60}Co gamma irradiator. The polypropylene irradiation was performed at 12.5 kGy dose monitored by a Harwell Red Perspex 4034 dosimeter. After irradiation, the samples were heated for 1 h at 90 °C to promote the recombination and annihilation of residual radicals [25,26].

2.2.2. Preparation of the nanocomposites

The blend of iPP and PP 12.5 kGy (50/50 wt%) were mixed with Irganox® B 215 ED, long-term thermal stabilizer, in a rotary mixer for 12 h. The PP-nanocomposites were prepared by addition of AgNPs at different concentrations of 0.1%; 0.25%; 0.5%; 1.0%; 1.0% (PVP), 2.0% and 4.0% in wt%. The sample with 1.0% of AgNPs added with PVP as surfactant was mixed with ultrasonic mixer equipment, Quimis - Brazil, at 2000 rpm for 20 min. The polypropylene composite was processed in a twin-screw extruder (Haake co-rotating, Model Rheomex PTW 16/25), with the following processing conditions: the temperature profile (feed to die) was 180 to 195 °C, with a speed of 100 rpm. After mixing, the nanocomposites were granulated in a granulator Primotécnica W-702-3. The PP-AgNPs nanocomposite 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 these films were cooled at room temperature before

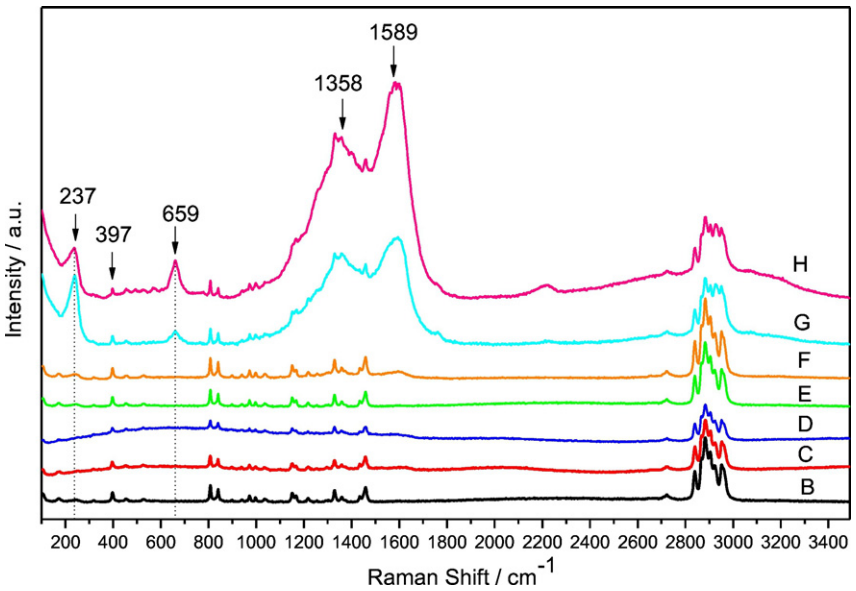

Fig. 1. Raman spectrum of polypropylene films with AgNPs: B) PP0.1% AgNPs; C) PP 0.25% AgNPs; D) PP 0.5% AgNPs; E) PP 1.0% AgNPs; F) PP 1.0% AgNPs PVP; G) PP 2.0% AgNPs; H) PP 4.0% AgNPs.