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Study of the effects of ionizing radiation on calcium carbonate-modified polypropylene loaded with silver nanoparticles

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ABSTRACT

Mineral calcium carbonate is the most important and abundant of all sedimentary rocks used commercially. There are several studies on the influence of the addition of calcium carbonate on the physical and rheological properties of the materials. The chicken egg shell, which contains at about 40% Ca in the form of calcium carbonate ($CaCO_3$), is a low-cost, easy-to-obtain and option to achieve the purpose of this study. In order to obtain eggshell powder, the peels were washed, sanitized, dried in an oven, ground in a mill and characterized for use in the present work. High melt strength polypropylene (HMSPP) has been recently developed and marketed by leading polypropylene producers. One way to improve melt strength and extensibility is to add polypropylene backbone strands using gamma radiation. The objective of this work is to evaluate the influence of the addition of calcium carbonate with silver nanoparticles in different proportions in the properties of films and pellets of HMSPP 12.5 kGy with concentrations of 0.1 and 0.3%.

1. INTRODUCTION

Polypropylene (PP) is a versatile material and its use is directly connected with countless manufacturing sectors, in medicine and in the packaging industry. For this work HMSPP - High Melt Strength Polypropylene, or Polypropylene with High Strength of Melt was obtained using the process developed by the group of polymers of IPEN [1]. In this process ionizing radiation is used under an acetylene atmosphere, which leads to various physico-chemical changes, some of which include, splits and / or branching, oxidation, generation of fragments with low molecular weight. In order to develop the product and add values to the irradiated polypropylene (HMSPP), calcium carbonate was added with silver nanoparticles via extrusion in two concentrations in order to study its properties and morphology of this nanocomposite polymer. Eggshell is a biologically derived metallic carrier, utilized for this study.Generally, egg shell is a reinforcing component in structural materials that helps in mitigating challenges while providing other societal needs. Few technologies are available for the processing of eggshells into useful products. More innovations in recovery technologies for turning eggshells into resource materials are currently need to convert such natural and rich source of $CaCO_3$ into other forms that are useful for functional and sustainablematerial design. Past findings show that eggshell contains about 95% $CaCO_3$ which can be used to modify the weak properties of polymers [1]. There are several studies on the influence of the addition of calcium carbonate on the physical and rheological properties of the materials. In order to obtain eggshell powder, the peels were washed, sanitized, oven dried, milled in a mill and characterized for use in the present work. The objective of this work is to evaluate the influence of the addition of calcium carbonate with silver nanoparticles in different proportions in the properties of films and pellets of HMSPP 12.5 KGy with concentrations of 0.1 and 0.3%. Gamma radiation was used in the preparation of HMSPP at a rate of 12.5 KGy.[1-6]

2. METHODOLOGY

2.1 Synthesis of HMSPP by gamma ionizing radiation

To obtain the HMSPP by irradiation of PP: the sample of isotactic polypropylene pellets (H603—Braskem) was placed in plastic container and irradiated by gamma (60Co) in acetylene atmosphere in order to obtain the HMSPP, dose of 12,5 kGy and dose rate 5kW/h. The melt processing of HMSPP was made in single-screw extruder—Thermo Haake Polymer, in the range of temperature of 160–210 °C. The extruded material in pellets form was divided and mixed with different concentrations wt% of $CaCO_3$/Ag°Np.

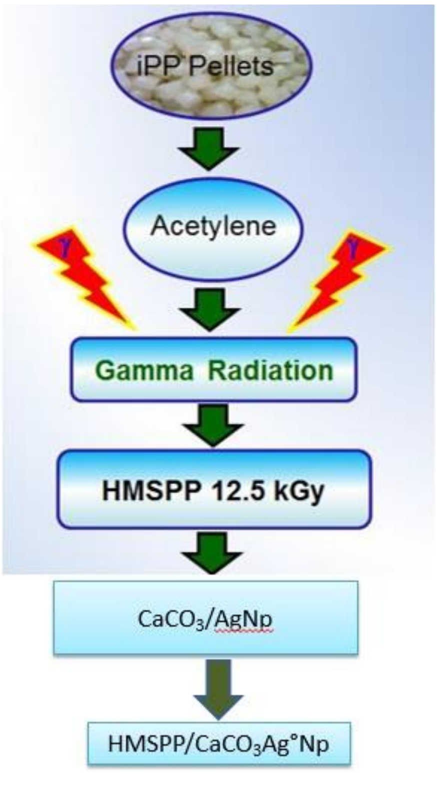

Figure 1: Synthesis of HMSPP by gamma ionizing radiation

2.2 Extraction of Calcium Carbonate from Eggshells

The eggshells were boiled in distilled water for 4 h and dried at 50 °C until constant weight. The eggshells were mechanically triturated using ball milling for 8 h. The sample was washed with distilled water (three times) and (one time) with alcohol and centrifuged I the sequence. The supernatant was discarded, and the calcium carbonate sediment was dried at 60 °C. The calcium carbonate was characterized by dynamic lighting scattering (DLS).

2.3 Synthesis of $CaCO_3$/Ag Nanoparticles

The eggshell powder was prepared with the $AgNO_3$(1/1), and ethyleno glicol was ball- milled for 8 h. The sample was washed with distilled water three times to remove chemical surplus and centrifuged and dried in a desiccators. The $CaCO_3$/AgNp was characterized by dynamic lighting scattering (DLS).

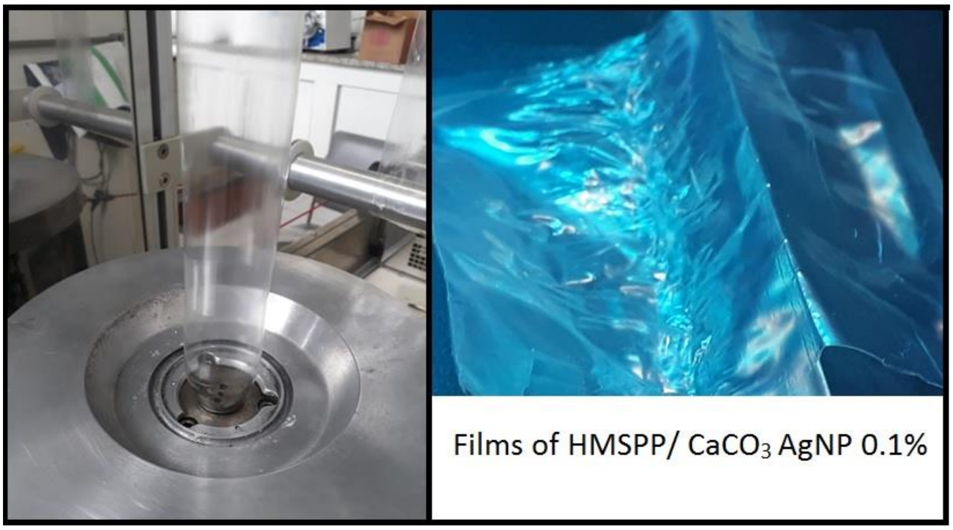

Figure 2: Films of HMSPP/ $CaCO_3$ AgNP 0.1%

3. RESULTS AND DISCUSSION

3.1 Dynamic Lighting Scattering (DLS) and X-Ray Diffraction (XRD)

From DLS analysis, the particles of $CaCO_3$ and $CaCO_3$/Ag showed the particle size of 1795.5 and 1752.3 nm, respectively. Themicrometric size of the synthesized particles can be justified by the time used to process then in the ball milling. $CaCO_3$/Ag showed a particle size approximately equal to neat $CaCO_3$ particle. Is expected that Ag nanoparticleswere formed on the surface of $CaCO_3$ due to porosity of the surface. It was not possible to detect the Ag by XRD analysis, as shown in Fig. 3. In the nanoparticles concentration of 1% was identified $CaCO_3$eggshell by DRX directly on films of blow extruded materials

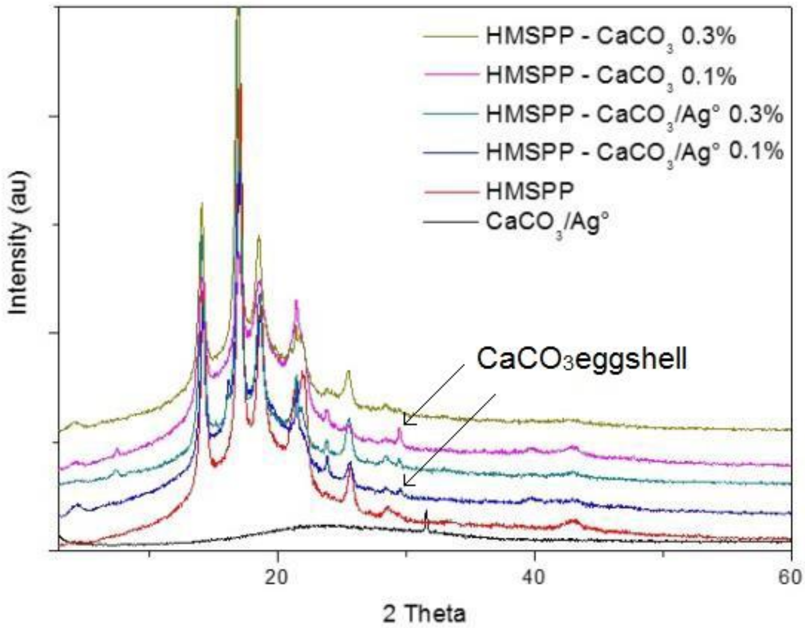

Figure 3: DRX results for films of HMSPP/ nanoparticles

3.1 FTIR Spectroscopy Analysis

Analyzes were performed in accordance with the AMERICAN SOCIETY FOR TESTING OF MATERIALS standard (2013) on a Perkin Elmer Spectrum One spectrophotometer coupled with a universal ATR ("Sampling Accessory") device in medium frequency transmittance (MIR) mode. and $2cm^{-1}$ resolution.

The results indicated the presence of $CaCO_3$-Ag in the polymer films by FTIR absorption. Large peak at 1720 cm^{-1} , which is related to the C=O stretching vibration of the carbonyl group. The second band around 3400 cm^{-1} is related to the hydroxyl group, which indicates the generation of hydroperoxide

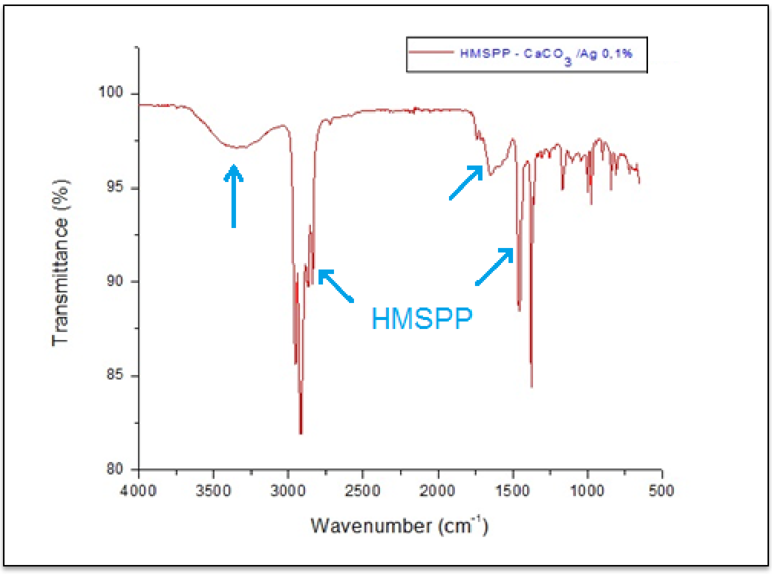

Figure 4: FTIR spectroscopy identifies presence of Ca CO_3

3.3 Thermogravimetric Analysis (TGA)

The TGA analysis was carried out in Mettler Toledo TGA/851 equipment, in heating program of 25–650 °C and heat rate of 10 °C min^{-1} under N2 (50 mL min^{-1}) atmosphere. The TGA analysis indicated for both films samples, in different $CaCO_3$/Ag concentrations, the same decomposition perfil, showing no influence of the radiation or [$CaCO_3$/Ag] in the thermal stability of the nanocomposites. The particles like $CaCO_3$/Ag or $CaCO_3$ can act on the polymers as nucleant agent, increasing the crystallinity of material. However, this effect was not possible to observe in the present case. Onthe other hand, it was possible to observe the formation of the two Tonset on TGA, indicating the presence of each polymer.

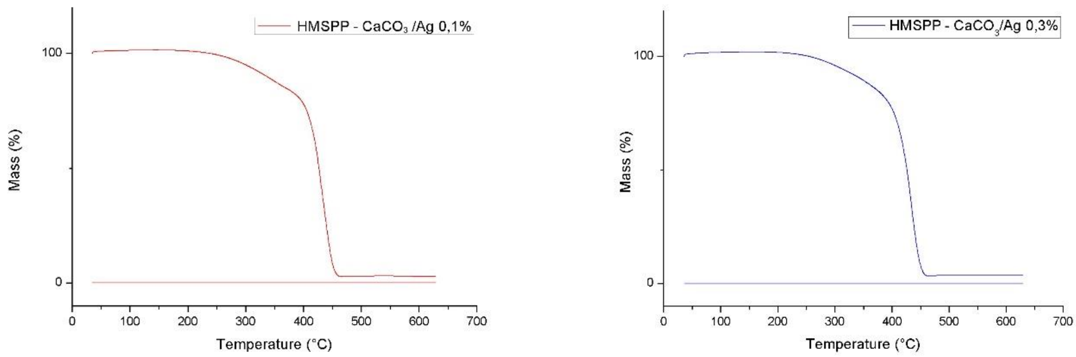

Figure 5: Thermogravimetric analysis of HMSPP $CaCO_3$ / Ag samples 0.1% and 0.3%

The presence of silver nanoparticles carried by $CaCO_3$ from eggshell natural source not influenced in the thermal stability of the material. The $CaCO_3$/AgNP x% had not influence on the Tm1 of the material.

Tabela 1: Thermal analysis characterization

	Tm_1 beta phase (°C)	Tm_1 (°C)	T_{onset} of decomposition under N_2 (°C)	Crystallinity (%)
HMSPP	--------	164.0	420.0	46.0
HMSPP/$CaCO_3$Ag°0.1%	--------	165.1	419.4	45.0
HMSPP/$CaCO_3$Ag°0.3%	150,5	164.6	416.8	45.4

2.2 Differential scanning calorimetry (DSC)

The thermal behavior of the films was monitored in the program: (1) heating from 25 to 280 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere, (2) holding for 5 min at 280 °C, and (3) then cooling to 25 °C and reheating to 280 at 10 °C min^{-1}, according to ASTM D 3418-08. DSC result indicated that the presence of $CaCO_3$/Ag in the films not changed the melting Tm2 (156.0°C/$CaCO_3$-Ag 0,1%; 156.1/$CaCO_3$-Ag 0.3 %) or the crystallinity of the polymer (31.9% and 32.2%) respectively.

3. CONCLUSIONS

The initial results of the use of HMSPP 12.5KGy in calcium carbonate with silver nanoparticles demonstrate the presence of $CaCO_3$/Ag, but there was no significant change in the thermal properties of the composite. Thus, for future work, the increase of radiation dose in composite samples already prepared for further studies on composite morphology, microscopic tests to observe silver dispersion in carbonate and bactericidal activity.

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