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Processing and antimicrobial efficacy of polypropylene/montmorillonite/silver nanocomposites as food packaging films

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Abstract - The aim this study was to use nanocomposites of polypropylene (PP), montmorillonite (MMT) and silver nanoparticles (AgNPs), prepared by melt intercalation in a twin-screw extruder, as a food packaging bactericide material. The use of nanoclay and nanosilver as additives for polymer matrices requires, in some cases (with non-polar matrices) the use of a compatibilizer agent which will act as a bridge or permanent buffer for nanoclay-nanosilver-matrix interaction. As compatibilizer agent it has been used a propylene graft maleic anhydride copolymer (PP-g-MA). The nanocomposites were evaluated by differential scanning calorimetry (DSC), X-Rays diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and determination of antibacterial activity. The results indicate the formation of microstructures predominantly exfoliated. Further, the antibacterial properties of the films were investigated against *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive) bacteria.

Keywords: polypropylene, nanocomposites, nanoclay, silver nanoparticles

1. INTRODUCTION

The field of nanotechnology is one of the most attractive areas for current research and development in basically all technical disciplines. Even in the field of nanocomposites, many diverse topics exist including composite reinforcement, barrier properties, flame resistance, electro-optical properties, cosmetic applications, bactericidal properties. Nanoscale is considered where the dimensions of the particle, platelet or fiber are in the range of 1–100 nm¹. The possibility of manufacturing nanocomposites materials with tailored properties at low cost has gained much interest. In fact, there is already more than two decades of research on those materials. Particular interest has been paid to clay nanoplatelets and their composites with non-polar thermoplastic polyolefin matrices, namely polypropylene (PP)². Polypropylene (PP) is a versatile material which use has significantly penetrated in numerous sectors of the manufacturing, medical, and packaging industries. Polymer clay nanocomposites are multiphase organic/inorganic hybrid materials pioneered by researchers at Toyota^{3,4,5}, which may exhibit significantly improved mechanical, flammability, and permeability properties relative to the base polymer matrix at very low clay loading. Although first demonstrated for nylon, polymers clay nanocomposites have since been prepared for a lot of thermoplastic and thermoset polymers. However, the development of PP/clay nanocomposites poses special challenges because of polypropylene's hydrophobicity². As exfoliated nanocomposites have higher phase homogeneity than the intercalated counterpart the exfoliated structure is more desirable in enhancing the properties of nanocomposites⁶. Silicate layer exfoliation in polyolefins such a PP and polyethylene is achieved by the introduction of small amounts of polar groups to nonpolar polyolefins⁶. Polypropylene-clay nanocomposites are still attractive for applications as packaging materials where enhanced barrier properties are desired⁷. The modification of poly(propylene) (PP) with inorganic nanoparticles (Ag) nanocomposites prepared by melt mixing, may provide some functional properties to the polymer for use in applications such as household, automotive, and packaging materials, depending on the feature 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 nucleation⁸. As solid particle clusters are subjected to shearing forces while flowing through process streams, they break down into smaller components and are distributed in surrounding medium⁹. The dispersion of particle agglomerates is a key processing step in many industrial applications. Although the properties of the dispersing fluid and the particulate material can be very diverse, depending on the application, the same fundamental principles apply to controlling the dispersion process and the properties of the final product¹⁰. In spite of antimicrobial activity, substances can be incorporated directly into polymeric materials coated onto polymer surface or immobilized into the polymers. Thermal processing such as melt blending, extrusion, and injection molding have been applied for incorporate the antimicrobials into polymers, but the thermal stability of active component and chemical compatibility of polymer matrix and antimicrobials should be considered in order to evenly distribute antimicrobial substance¹¹. Silver is particularly attractive because it combines the high toxicity for bacteria with a low toxicity for humans¹². Important research used silver nanoparticles (AgNPs) with different surfactants, polyvinyl pyrrolidone (PVP) and oleic acid (OA) to facilitate dispersion. The 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 AgNPs¹³. The exfoliated clay should be an important factor for the barrier effect and hence attenuate the penetration of oxygen in food packaging and increase the shelf life of various products of this class. Associated with this issue is the idea to add an amount equal to or less than 1% by weight of silver nanoparticles with aim to preserve food as the proliferation of bacteria and fungus. The aim this study was to use nanocomposites of polypropylene (PP), montmorillonite (MMT) and silver nanoparticles (AgNPs), prepared by melt intercalation in a twin-screw extruder, as a food packaging bactericide material.

2. MATERIALS AND METHODS

2.1. Materials

Isotactic polypropylene (iPP) with a melt flow index (MFI) of 1.5 dg min^{-1} ($230 \text{ }^\circ\text{C}/2.16 \text{ Kg}$) and $M_w = 338,000 \text{ g mol}^{-1}$, was purchased from Braskem S.A., Brazil. The compatibilizer agent, propylene maleic anhydride graft copolymer (PP-g-MA) was supplied by Chemtura (Polybond 3200). The nanoclay mineral used was the MMT Cloisite 20A, group of smectites, organically modified with a salt of alkyl quaternary ammonium, from Southern Clay Products. The polymeric material (nanocomposite) was stabilized with IRGANOX B 215 ED (BASF) at concentration around 0.1%wt. The silver nanoparticles (AgNPs) were supplied by Sigma Aldrich.

2.2. Preparation of the Nanocomposites

The iPP (pellet) was mixed with Irganox B 215 ED and PP-g-MA in a rotary mixer and maintained under this condition for 24 hours. Then the mixture was processed with the addition of clay (MMT 1% by weight) and silver nanoparticles (AgNPs 0.1% by weight) in a twin-screw extruder Haake co-rotating, model Rheomex PTW 16/25, Figure 1, with the following processing conditions: the temperature profile (feed to die) was $165\text{-}200 \text{ }^\circ\text{C}$, with a speed of 100 rpm. After processed, the nanocomposites were granulated in a granulator Primotécnica W-702-3. The PP/MMT-AgNPs films were produced in planar sheet extruder and the material was placed directly into the hopper of the extruder with a temperature profile (feed to die) of $165\text{-}210 \text{ }^\circ\text{C}$, screw speed of 20 rpm and torque of 40-100 Nm. The films were produced with a thickness of $\sim 0.05 \text{ mm}$.



Figure 1. Extruder Haake-Rheomex device used to process the polymeric films. Polymer Laboratory at Chemistry Centre and Environment (CQMA) / Nuclear and Energy Research Institute (IPEN).

3. CHARACTERIZATION

3.1. Differential scanning calorimetry

Thermal properties of specimens were analyzed using a differential scanning calorimeter DSC 822, Mettler Toledo. The thermal behavior of films was obtained by: (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 °C at 10 °C min⁻¹. Melting enthalpy value for 100% crystalline PP is 209 kJ kg⁻¹^{14, 15}.

3.2. X-rays diffraction

X-rays diffraction (XRD) measurements were carried out in the reflection mode on a Rigaku diffractometer Mini Flex II (Tokyo, Japan) operated at 30kV voltage and a current of 15mA with CuK α radiation ($\lambda = 1.541841 \text{ \AA}$).

3.3. Scanning electron microscopy and Energy dispersive spectroscopy

Details of the nanocomposite morphology was investigated using scanning electron microscopy, EDAX equipment brand Philips Model XL-30. The samples were fixed on metal support adequate and coated with gold by sputtering technique. The EDS spectrums of polypropylene-AgNPs films were also obtained.

3.4. Determination of antibacterial activity

An aliquot (400 μL) of a cell suspension of either *Staphylococcus aureus* ATCC 27853 (10^6 cells mL⁻¹) or *Escherichia coli* ATCC 25922 (10^6 cells mL⁻¹) prepared using the method described in JIS Z 2801¹⁶ were held in intimate contact with each of the 2 replicates of the test surfaces supplied using a 45 x 45 mm² polypropylene film for 24 hours at 37°C under humid conditions. The size of the surviving population was determined using a method based on JIS Z 2801. The viable cells in the suspension were enumerated by viable cell counts on MacConkey Agar after incubation at 37°C for 24 hours using a 100 μL sample taken from the test surfaces.

4. RESULTS AND DISCUSSION

The DSC results are shown in Figure 2 and X-Rays diffraction in Figure 3.

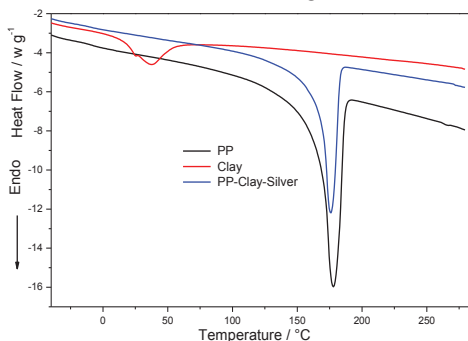


Figure 2. DSC curves of the second heating run of Clay, PP and PP-Clay-Ag

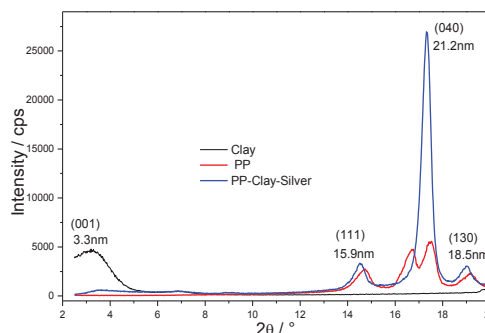


Figure 3. X-Rays diffraction patterns of Clay, PP and PP-Clay-Ag nanocomposite

Table 1. DSC characteristics of Clay, PP and PP-MMT-Ag

| Samples | $T_{m1} / ^\circ\text{C}$ | $T_c / ^\circ\text{C}$ | $T_{m2} / ^\circ\text{C}$ | $X_C / \%$ |
|------------|---------------------------|------------------------|---------------------------|------------|
| Clay (MMT) | 44.7 | | | |
| PP | 179.1 | 126.8 | 177.7 | 52.0 |
| PP-MMT-Ag | 117.3 | 127.7 | 176.1 | 40.2 |

As shown in Table 1 the value of the crystallinity of the PP film is much larger than that nanocomposite film, which is due to the absence of antioxidant on the sample and consequent degradation.

In X-rays analysis at high diffraction angles, Figure 3, showed diffraction peaks corresponding to interplanar distance of (PP-Clay-silver): $d_{(110)}=6.1\text{ \AA}$, $d_{(040)}=5.1\text{ \AA}$, $d_{(130)}=4.6 \text{ \AA}$. Considering the diffraction peaks related to the (001) reflexions, Cloisite 20A showed a basal spacing $d_{(001)}= 26.2\text{ \AA}$ according to the Bragg equation ($2d\sin\theta=n\lambda$, $\lambda=1.541841\text{ \AA}$), and crystallite size of 3.3nm. The crystallite size obtained was estimated to be in the range 3.3 – 21.2 nm using Scherrer equation, which may indicate to volume ratio of the nano-crystals. The equation is written below:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad \text{Equation 1}$$

Where K, known as Scherrer's constant (shape factor), ranges from 0.9 to 1.0, λ is the wavelength of the X-Ray radiation source, β is the width of the XRD peak at half height and θ is the Bragg angle. Disappearance of the nanoclay interlayer diffraction Peak (d_{001}) indicates possible exfoliation of the nanoclay platelets and broadening of the peak is considered to be the result of partial exfoliation¹⁸. The results indicate the formation of microstructures predominantly exfoliated in film PP-clay-Ag. The ideal nanocomposite structure is thought to be composed of disordered, completely exfoliated clay layers dispersed in the polymer matrix. The resulting composites should be stiffer and harder but not brittle, which is one of the disadvantages of conventionally filled polymers. The reason for this different behavior from conventional composites is expected to be the enormous interfacial area, which is accessible only in the intercalated or better exfoliated state. But so far, especially with non-polar polymer matrices such as PP, there are many difficulties impeding a market launch of nanocomposites, although some companies announced the preparation and application of nanocomposites¹⁷.

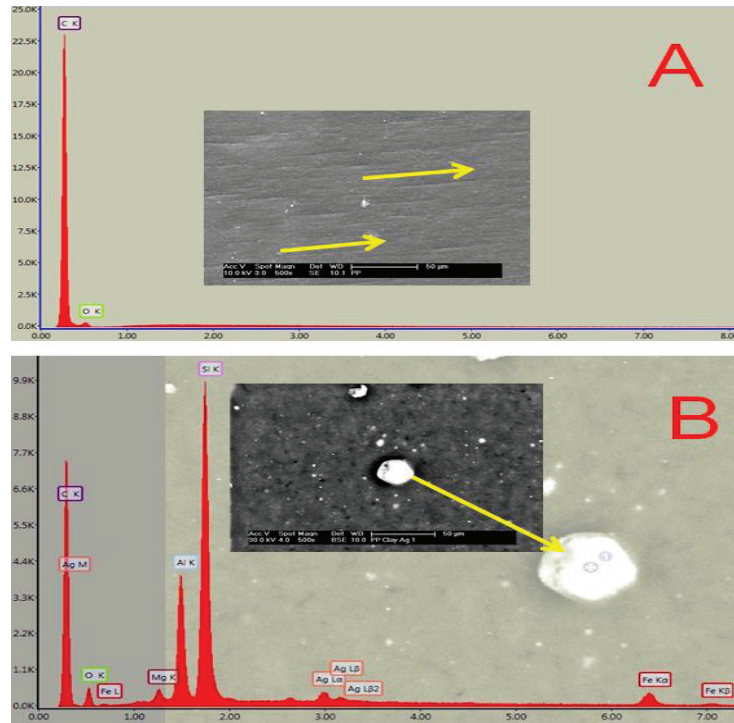


Figure 4. (A) SEM-EDS of the polypropylene film and (B) Nanocomposite PP-MMT-AgNPs.

The micrograph of the polypropylene film Figure 4A shows the surface of the film and the alignment by this processing. Since the polypropylene nanocomposite film, Figure 4B, there is a micrometer agglomerated clay and the incidence of nanosilver, characterized by EDS. In Figure 5 are presented the results of films without silver and Figure 6 are presented the results of films with silver nanoparticles.

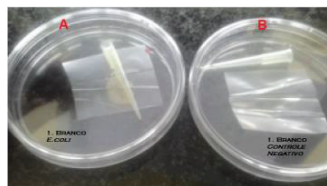


Figure 5. Films without silver in duplicate

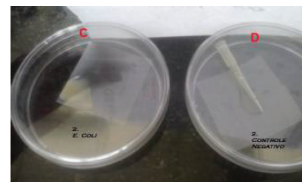


Figure 6. Antibacterial effects of plastic film on *Escherichia coli*.

The Petri plate (A) shown turbidity, indicating bacterial growth and no antimicrobial activity. At the plate (B) the film also without silver with negative control shows no turbidity due to absence of bacteria.

The film 2, in the Petri plate (C) shows turbidity, indicating the occurrence of bacterial growth and proving no antimicrobial activity and at the plate (D) the film without silver as negative control shows no turbidity because no bacteria are present.

5. CONCLUSIONS

PP/MMT/Silver nanocomposite was prepared by melt processing in a twin-screw extruder up to 1wt%(MMT) and 0.1wt% (AgNPs), to develop food package films with barrier and biocide properties. The nanocomposite films exhibit good exfoliation of clay found by X-Ray, but the antibacterial properties were not observed in the samples.

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