Report on the outcomes of a Short-Term Scientific Mission[1]

Action number: CA20126

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Details of the STSM

Title: Biodegradable potato starch-based films integrated with porous clay composites for active fruit packaging applications

Start and end date: 15/05/2022 to 11/06/2022

Description of the work carried out during the STSM

This proposal aimed to develop biodegradable potato starch-based films containing porous clay/ZnO composites with ethylene adsorption capacity for active food packaging application. To fulfil this objective, five different tasks were developed, as described below:

1) Modification of natural clays by microwave (MW) and hydrothermal (HT) treatments

Commercial sepiolite was dispersed into an aqueous acid solution in Pyrex microwave's tubes and irradiated with 300 W irradiation power during 30 min, 45 min, 60 min, and 75 min, under stirring, using a dynamic program that guaranteed a maxim temperature of 95 ºC. After the MW treatment, the powders were recovered, neutralized to pH ≈ 7.0 with successive distilled water centrifugations, and dried at 60 ºC for xx h. Alternatively, commercial sepiolite was dispersed into aqueous acid solution or basic acid solution and then the dispersions were transferred to a Teflon-lined stainless-steel autoclave (60 mL) and heated in an oven at 100 ºC for 2 h. The produced precipitates were collected, washed/centrifuged with distilled water till pH ≈ 7.0, and dried, similarly to the MW-treated sepiolite samples. All the obtained powders were chemically and morphologically characterized and their efficiency to absorb ethylene was measured.

2) Chemical characterization of modified clays

The chemical profile of neat sepiolite, MW- and HT-treated sepiolite samples was obtained through ATR-FTIR spectroscopy in the region of 4000 cm^{-1} – 400 cm^{-1} with 32 scans and a resolution of xx. The FTIR spectra were collected in Absorbance mode. X-ray diffraction (XRD) was used to identify the crystalline phases of the obtained solids. These experiments were performed on a

[1] This report is submitted by the grantee to the Action MC for approval and for claiming payment of the awarded grant. The Grant Awarding Coordinator coordinates the evaluation of this report on behalf of the Action MC and instructs the GH for payment of the Grant.

Panalytical Empyrean X-ray diffractometer (Malvern Panalytical, Marvern, UK) with Cu-Kα radiation (λ = 1.54178 Å). The diffractograms were recorded in a reflection mode with the scanning angle ranged from 5 to 60 2θ.

3) **Morphological characterization of modified clays**

Specific surface area and porosity of the samples were determined by N_2 adsorption/desorption isotherms at −196 °C using a static volumetric apparatus, Micromeritics Instrument Corp. Gemini V 2.00 instrument model 2380. Previously to the analysis, each sample was outgassed at 100 °C overnight and then cooled down to room temperature prior to the N_2 adsorption.

4) **Measurement of ethylene adsorption capacity**

Ethylene adsorption capacity of each modified sepiolite sample was determined by analysing the gas evolution over time in a sealable chamber using a Bruker Tensor 37 instrument Fourier Transform Infrared (FTIR) spectrometer. The used measuring cell has a volume of 393.7 mL. The disks used as chamber windows made of sodium chloride were replaced by polymeric disks. For the analysis of the modified sepiolite samples, the powder was weighed before the start and storage inside the FTIR gas chamber. Then, 40 µL – 100 µL of ethylene was injected and ATR-FTIR spectra were collected over the time in order to infer the evolution of ethylene levels in the presence of each material. A calibration curve was prepared with 10 µL, 40 µL, 70 µL, and 100 µL of pure ethylene.

5) **Development of starch/clays-based bioplastic composites**

Targeting to develop biobased packaging systems with ethylene scavenging activity, in a first instance, the best procedure to incorporate the commercial sepiolite into starch-based formulations without compromising its adsorption capacity was studied. Two different approaches were initiated: (1) the commercial sepiolite was incorporated into the starch-based formulation during the melt-mixing step and the bioplastic was obtained by thermocompression, and (2) commercial sepiolite was spread onto the starch-based bioplastics surface by coating with polydimethylsiloxane. Although it was planned to evaluate the impact of porous clays in morphology, mechanical, and ethylene adsorbing properties of the starch-based bioplastic, there was no more time to finish this task, so the work will continue at University of Aveiro.

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Description of the STSM main achievements and planned follow-up activities

Results

1) **Chemical composition of modified clays**

FTIR spectra of MW- and HT-treated samples (Figure 1) revealed the progressive loss of bands attributed to magnesium species coordinated with -OH and H_2O located between 3700 cm^{-1} and 3550 cm^{-1}. This modification attributed to Si-O stretching mode, leading to a broad band between 1325 cm^{-1} and 1000 cm^{-1}, which confirms the changes on the sepiolite structure during MW- and HT-treatments. Moreover, MW-treatments revealed to have higher impact on sepiolite modification than HT-treatments.

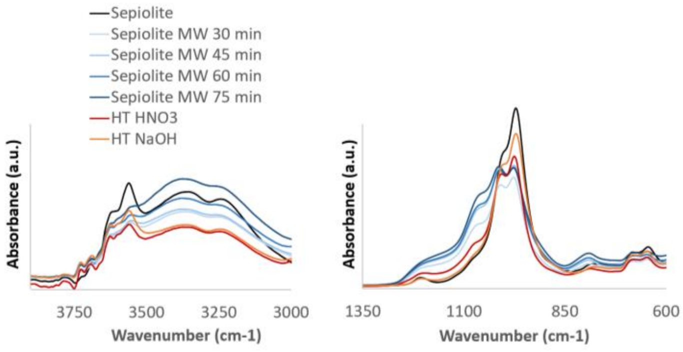

Figure 1: FTIR spectra of neat, MW-treated, and HT-treated sepiolite powders.

2) Crystallinity of modified clays

The MW-assisted acid treatment caused significant changes in the sepiolite's X-ray diffraction pattern (Figure 2), mainly in the d110 reflection, located at about 2θ = 7.3, being the MW-treated powders more amorphous than initial sepiolite. Despite having a minor impact, the HT-assisted acid or basic treatments also generated a structural change in sepiolite, with the acid treatment giving rise to more SiO_2-rich and amorphous powders than the basic HT treatment.

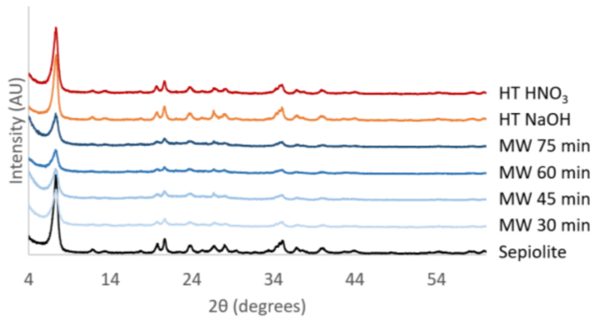

Figure 2: X-ray diffraction pattern of neat, MW-treated, and HT-treated sepiolite powders.

3) Surface area and porosity of modified clays

The MW-assisted treatment increased the sepiolite's surface area and pore volume, while decreasing its pore size (Table 1), when compared with neat sepiolite, being these differences dependent of MW treatment time. The MW-treated powder for 75 min seems to be more promising for ethylene adsorption. The HT-assisted treatments did not show potential to increase the sepiolite's porosity.

Table 1: Surface area, pore volume, and pore size of neat, MW-treated, and HT-treated sepiolite powders.

	Surface area (m^2/g)	Pore Volume (cm^3/g)	Pore size (nm)
Sepiolite	337.6	0.404	7.9
MW 30 min	435.2	0.734	8.7
MW 60 min	453.5	0.664	7.4
MW 45 min	459.5	0.686	7.5
MW 75 min	519.0	0.769	7.2
HT NaOH	261.0	0.315	7.7
NT HNO_3	324.0	0.535	8.5

4) Ethylene adsorption capacity

FTIR system showed to be able to measure ethylene levels between 10 μL and 100 μL, being the obtained ethylene peak area linear in accordance with the amount of injected ethylene. When Sepiolite MW 30 min and Sepiolite MW 60 min were introduced in the chamber (separately) and ethylene was injected, there was a decrease of ethylene in the chamber over the time. However, it was verified that the chamber was not gas-tight, so the results were not conclusive.

5) Development of starch/clays-based bioplastic composites

For the development of starch bioplastic/clay composites, two different approaches were initiated: (1) neat clay was incorporated into potato starch-based formulation during the melt-mixing step and the bioplastics was obtained by thermocompression (Figure 3A) and (b) neat clay was spread onto the starch-based bioplastics' surface by coating with polydimethylsiloxane and a curing agent, without using solvent or using acetone as solvent (Figure 3B). These films will be characterized in terms of morphology, mechanical, and ethylene adsorbing properties at University of Aveiro.

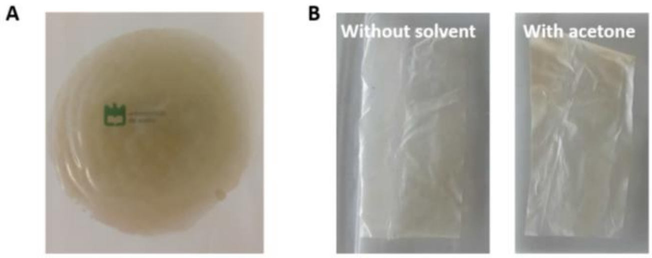

Figure 3: Starch/clays-based bioplastic composites obtained by melt-mixing/thermocompression (A) and by coating (B).

Conclusion

Microwave-assisted acid treatment revealed to be a methodology that induces morphological and chemical changes on sepiolite, which opens an opportunity to develop porous clays with ethylene scavenging activity.

Future experiments

- To explore a more accurate and efficient methodology for ethylene adsorption evaluation.
- To evaluate the ethylene adsorption capacity of the developed MW-modified clays and starch/clays-based bioplastic composites

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