

# Analysis of the Poly(Butylene Succinate-Co-Lactate)/Montmorillonite-Kaolinite Nanocomposite in the Formation of Microcapsules

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**Abstract:** A nanocomposite system comprised by a biodegradable polymer, poly(butylene succinate-co-lactate) (PBSL), and a Brazilian nanoclay (VMF1) containing montmorillonite (MMT) and kaolinite (K) is used to prepare microcapsules by solvent diffusion method. The nanocomposite PBSL/MMT-K and the microcapsules were characterized by wide angle X-ray diffractometry (XRD), scanning electron microscopy (SEM), stereomicroscopy, and Fourier transform infrared spectroscopy (FTIR). The overall results show that PBSL/MMT-K presents intercalated nanostructure of montmorillonite and kaolinite, both PBSL and PBSL/MMT-K proved to be very effective as matrix for production of uniform spherical microcapsules, as surveyed by scanning electron microscopy and stereomicroscopy. The spherical microcapsules prepared from PBSL/MMT-K nanocomposite presented diameters smaller than 50µm, and can probably be used as delivery systems.

**Keywords:** Microcapsules, delivery systems, MMT, K, biodegradable polymer.

## 1. INTRODUCTION

Biodegradable delivery systems are important in many technological applications, such as agriculture, pharmaceuticals and cosmetics areas, because they protect the active substances from premature degradation and regulate their release through a pre-established fashion.

Microcapsules obtained from nanocomposite materials using biodegradable polymers are currently a promising vehicle, leading to systems with improved performance and contribute to guarantee the dispersion of particulate clays. Nanostructured materials usually present higher thermal stability, mechanical resistance and superior barrier properties [1]. Nanocomposites having montmorillonite (MMT), a layer silicate with a 2:1 structure, is widely utilized for this goal [2], and so are those containing kaolinite (K), with 1:1 structure [3]. The structural difference between these two clay minerals, allows better dispersion of the particles of MMT in the polymeric matrices by intercalation or exfoliation [4]. Montmorillonite, especially as modified clay, is the most used clay

mineral as filler to obtain nanocomposites generally described as polymer-clay.

The use of biodegradable polymeric microcapsules as delivery systems has been reported to improve the chemical substances delivery systems in several aspects, mainly regarding the stability of the active chemical, toxicity management, delivery rate profile and variable quantity allocation, among others [5, 6].

Poly(butylene succinate co-lactate) (PBSL) is a biodegradable polyester [7], commercially available as GS Pla<sup>®</sup>, from Mitsubishi Chemical Corporation. PBSL may be prepared from renewable resources, such as fermentation of starch. Blend of PBSL with poly (L-lactide) (PLLA) according to Shibata *et al.* (2006) [8] presents good mechanical properties.

The preparation of microcapsules from PBSL and Brazilian clay was successfully carried out previously [9]. In this work, we investigated the characteristics of the nanocomposite and its contribution to the preparation of microcapsules.

## 2. EXPERIMENTAL

### 2.1. Materials

Natural Brazilian polycationic clay from Vitoria da Conquista, Bahia, pink powder, labeled as VMF1 and characterized as a mixture of montmorillonite and

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kaolinite was used in the composites. PBSL, in pellet form, GS Pla AZ-type (lactate unit ca. 3 mol%, melt flow index (190°C, 2.16Kg) 25g/10 min, specific gravity 1.26), was acquired from Mitsubishi Chemical Corporation, Japan. Dichloromethane P.A. (CH<sub>2</sub>Cl<sub>2</sub>) (Synth, Brazil) was used as solvent.

## 2.2. Nanocomposite Preparation

A solution of PBSL-5% in CH<sub>2</sub>Cl<sub>2</sub> and a dispersion of VMF1-0.5% in CH<sub>2</sub>Cl<sub>2</sub> were previously prepared by magnetic stirring (500rpm) at 25°C for 20 minutes. The nanocomposite dispersion was obtained by adding the PBSL-5% solution to the VMF1-0.5% dispersion under magnetic stirring (800rpm) at 25°C, followed by vigorous stirring for 3h and resting for 20h.

## 2.3. Microcapsules Preparation

PBSL/MMT-K microcapsules were prepared using an emulsification-diffusion [10]. The preparation was carried out by transferring the nanocomposite dispersion into an aqueous 0.5% polyvinyl alcohol solution (1/2, v/v) in a beaker under vigorous mechanical stirring (1,500rpm) [9]. After the addition, the mixture thus formed was left to rest for one hour for complete deposition of the microcapsules on the bottom of the beaker. Then, the supernatant was withdrawn and the microcapsules were washed with distilled water (three times), gently, in a proportion of three times the volume of microcapsules. After washing, the microcapsules were transferred to an agate container and were air-dried, overnight. The same method was used to prepare PBSL microcapsules from a solution of PBSL-5%.

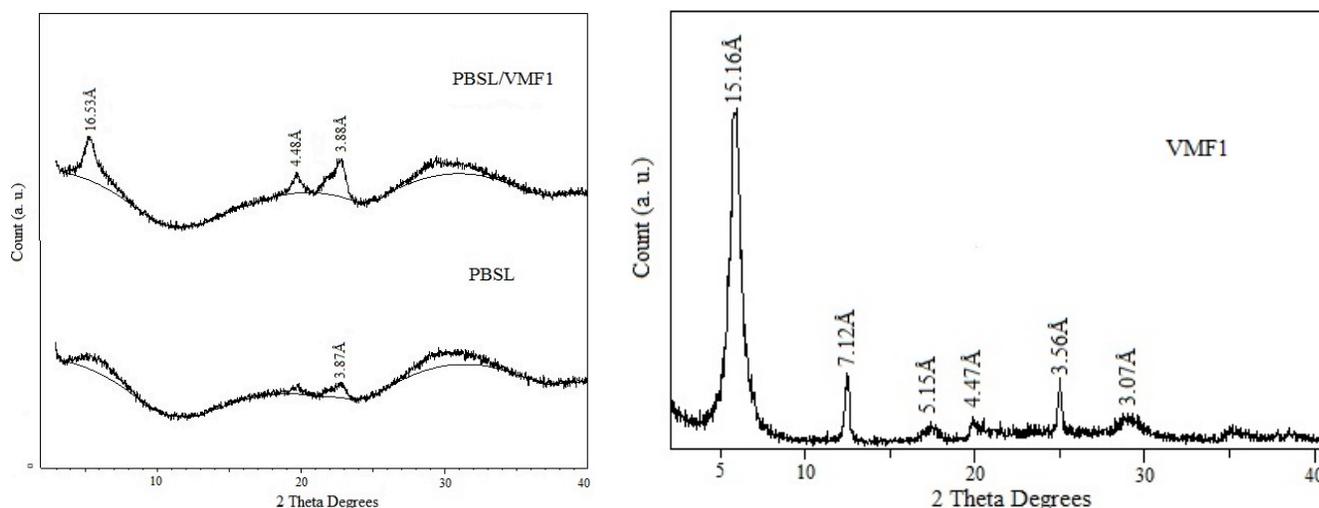
## 2.4. Characterization

The crystalline structure of VMF1, PBSL and PBSL/VMF1 nanocomposite microcapsules were analyzed by X-Ray Diffractometer using a Philips X'Pert MPD diffractometer with CuK $\alpha$  radiation, operating at 40 kV and 20 mA, at 2 $\theta$  step scan of 0.1°/s. The morphology, sizes and homogeneity of dried microcapsules were observed by a Zeiss Stemi 2000-C Stereo Microscope at 100x magnification, and further investigated by using Scanning Electron Microscopy (SEM), by Inspect F50 microscope. Attenuated Total Reflectance-Fourier Transformed Infrared (ATR-FTIR) spectra of the samples were collected in the range of 4000-400cm<sup>-1</sup>, using a Thermo Nicolet iS5 spectrometer.

## 3. RESULTS AND DISCUSSION

### 3.1. X-Ray Diffraction

VMF1 was shown to be a clay comprised mainly by montmorillonite and kaolinite with characteristic peaks at  $d_{001}=15.16\text{\AA}$  and  $d_{001}=7.12\text{\AA}$ , respectively (Figure 1) [11]. PBSL/MMT-K nanocomposite showed a diminished peak assigned to montmorillonite from  $d_{001}=16.53\text{\AA}$ , which does not appear in the diffractogram of PBSL. However, the characteristic kaolinite peak ( $d_{001}=7.12\text{\AA}$ ), observed for VMF1, is not observed in the diffractogram of the nanocomposite, suggesting that both kaolinite and/montmorillonite were intercalated to PBSL matrix to form the PBSL/MMT-K nanocomposite. The intercalation of these two clay minerals occur probably because VMF1, a mixture of MMT and K, contains kaolinite in high concentration (ca. 30%) [11]. Montmorillonite and



**Figure 1:** Show diffractograms of PBSL, PBSL/MMT-K, and VMF1.

kaolinite, separately, has been reported as nanometric reinforcing filler for polymer matrices [1, 3], however the simultaneous use of both clay minerals has not yet been described in the preparation of polymer nanocomposites.

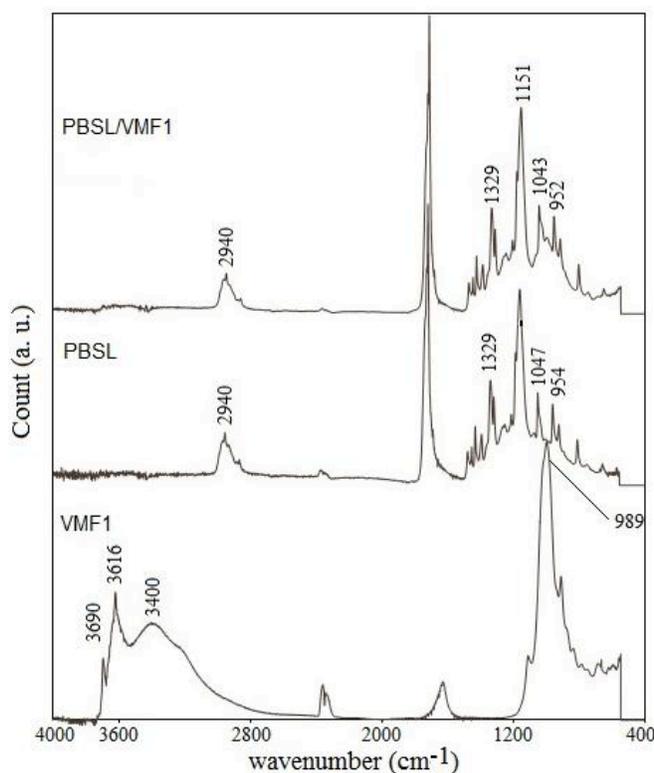
### 3.2. ATR-FTIR Spectra

The infrared spectra of VMF1 clay, PBSL microcapsules, and PBSL/MMT-K nanocomposite microcapsules are shown in Figure 2. According to Farmer (1974) [12], the ATR-FTIR spectra of layered silicates present characteristic bands due to OH stretching and OH bending vibrations in the 3400-3750 $\text{cm}^{-1}$  and 600-950 $\text{cm}^{-1}$  range, respectively. VMF1 is comprised by kaolinite and motmorillonite. The kaolinite fraction, among other clays, is distinguished by presenting structural hydroxyl groups that are responsible for strong absorption peaks in the former region, more specifically, at 3616 $\text{cm}^{-1}$ , due to inner hydroxyl groups, lying between the tetrahedral and octahedral sheets, and at 3690 $\text{cm}^{-1}$ , symmetrical stretching of hydroxyl group at the octahedral surface [12, 13]. In contrast, the motmorillonite fraction is characterized by a sole broader absorption at 3620 $\text{cm}^{-1}$  associated to dioctahedral smectites with high amount

of Al in the octahedral [13], here superposed by the kaolinite peak at 3616 $\text{cm}^{-1}$ . The broadest band exhibited near 3400 $\text{cm}^{-1}$  is due to stretching vibrations of structural hydroxyl groups from adsorbed water, and is also typical of smectites [12, 14].

VMF1 presents a strong broad peak around 989 $\text{cm}^{-1}$  which is attributed to motmorillonite Si-O stretching mode, while for kaolinite the same bond deformation is observed as a well resolved peak at 1125 $\text{cm}^{-1}$ .

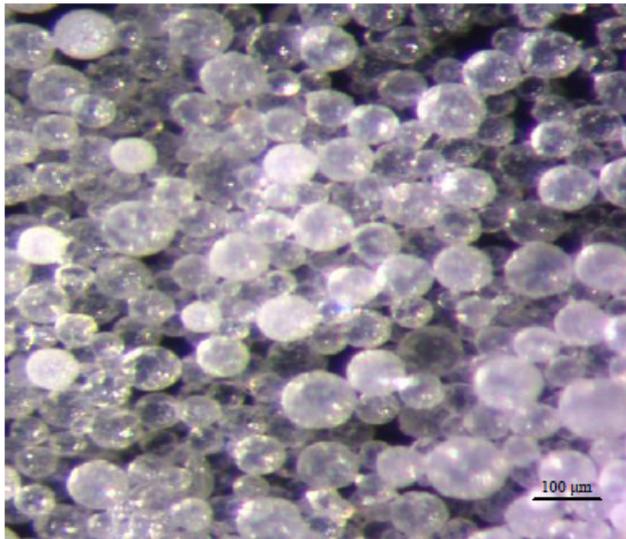
The infrared spectra of the polymer and nanocomposite are similar, except for the small peak near 989 $\text{cm}^{-1}$  attributed to nanocomposite spectrum (Figure 2), which also was assigned as intense peak in the VMF1 spectrum, and is related to Si-O stretching vibration. This peak was not observed in the polymer spectrum, and is an indicative of the formation of the nanocomposite. In addition, PBSL and PBSL/MMT-K are characterized by absorptions due to PBSL, exemplified by bands at 2940 $\text{cm}^{-1}$ , C-H stretching, 1720 $\text{cm}^{-1}$ , carboxyl stretching, while 1330 and 1150 $\text{cm}^{-1}$  are related to the C-O stretching vibrations from succinate ester group; in lactate these same vibration bands are observable at 1180 and 1090 $\text{cm}^{-1}$ . Thus, in both spectra, it is possible to point that the relative concentration of succinate units overcomes by far the lactate units [15]. The main peaks attributed to samples are listed in Table 1.



**Figure 2:** ATR-FTIR spectra of VMF1, PBSL and PBSL/MMT-K.

**Table 1: Main Peaks Observed in the Infrared Spectra of the Samples**

VMF1 ( $\text{cm}^{-1}$ )	PBSL ( $\text{cm}^{-1}$ )	PBSL/MMT-K ( $\text{cm}^{-1}$ )
3690 ( $\nu$ O-H)		
3616 ( $\nu$ O-H)		
3400 ( $\text{H}_2\text{O}$ )		
	2940 ( $\nu$ C-H)	2940 ( $\nu$ C-H)
	1720 ( $\nu$ C=O)	1720 ( $\nu$ C=O)
	1329( $\nu$ C-O)	1329( $\nu$ C-O)
	1151 ( $\nu$ C-O)	1151 ( $\nu$ C-O)
	1047 ( $\nu$ H)	1043 ( $\nu$ H)
989 ( $\nu$ Si-O)		989 ( $\nu$ Si-O)
	954 ( $\nu$ CO)	952 ( $\nu$ CO)

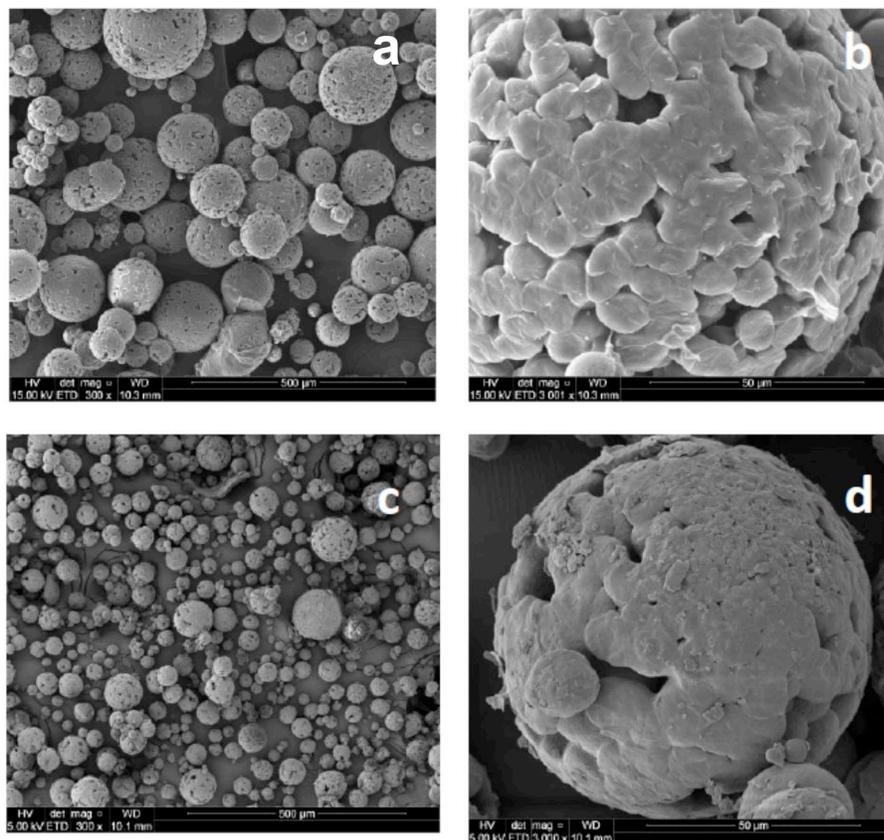


**Figure 3:** Image by stereomicroscopy of PBSL/VMF1 microcapsules (100x).

### 3.3. Stereomicroscopy and SEM

The analysis of PBSL and PBSL/MMT-K microcapsules by stereomicroscopy indicated that after drying, the spherical shape of that particles were preserved (Figure 3). These data were confirmed by

SEM analysis. Moreover, detailed analysis by SEM revealed that the PBSL microcapsules presented roughened surface and average size diameters of 50-150 $\mu\text{m}$ , prevailing capsules with diameter larger than 89 $\mu\text{m}$  (ca. 65%) (Figure 4a-4b). PBSL/MMT-K microcapsules are likely to present moderately smoother surface, and average diameters in 50-150  $\mu\text{m}$  range, but showing the influence of VMF1 presence on the microcapsules formation as the particles became considerably smaller than 50 $\mu\text{m}$  (Figure 4c-4d) (ca. 69%). Brunner *et al.* (2011) [16] used poly(butylene succinate) (PBSu), poly(butylene succinate-co-adipate) (PBSA) and poly(butylene terephthalate-co-adipate) (PBTA) in the preparation of microcapsules, and they observed that larger particles resulted from the more concentrated polymer solutions. This result is associated to higher concentration of polymer. In our study, we observe the similar result by utilizing a polymer nanocomposite in comparison to the original polymer. We have successfully prepared microcapsules with spherical shape by using a PBSL/MMT-K nanocomposite. The dispersion of both montmorillonite and kaolinite is responsible for the morphologic stability of the particles, observed by SEM, demonstrating that nanocomposite was effectively



**Figure 4:** Micrographs by SEM of, (a) PBSL microcapsules (500x), (b) PBSL microcapsules (3000x), (c) PBSL/MMT-K microcapsules (500x) and (d) PBSL/MMT-K microcapsules (3000x).

formed which causes a decrease in the average size diameter of the microcapsules.

## CONCLUSIONS

PBSL/MMT-K nanocomposite comprised by a biodegradable polymeric matrix and two clay minerals, montmorillonite and kaolinite, from single clay, was prepared and characterized. The presence of MMT and K in the nanocomposite structure is supported by XRD and ATR-FTIR, besides SEM. The preparation of microcapsules by solvent diffusion technique was straightforward, originating reasonable uniform spherical particles with average size diameter smaller than 50µm. The results suggest that PBSL/MMT-K microcapsules may be applied as promising delivery systems.

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