

Development and characterization of sodium polyacrylate/bentonite hydrogel with epoxy resin coating

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Abstract

Composites are relevant to high-performance materials in the aerospace sector and have attracted the attention of the scientific and technological communities. Bentonites present very fine granulometry which enables their use in composites. This study showed the development of water absorbent composite based on sodium polyacrylate, bentonite coated by epoxy resin. Since there are gaps in the quantification of composite materials by near-infrared spectroscopy, especially by reflectance analysis (NIRA), this paper shows a quantification methodology (A_{7200}/A_{5202}) of sodium polyacrylate and bentonite. The methodology error found was 1.45% (95% of coefficient of determination). The effectiveness of the developed infrared methodology was verified showing that values are close to the nominal, especially for lower bentonite content. Besides, scanning electron microscopy (SEM) and universal attenuated total reflection (UATR) analysis evidenced the coating with the epoxy resin. Such development ensures rapid and precise methodologies that can be applied to the quality control of composite materials.

Keywords: *bentonite, near-infrared spectroscopy, sodium polyacrylate.*

How to cite: Takematsu, M. M., Baruel, A. F., Cassu, S. N., Diniz, M. F., Graves, D. A., & Dutra, R. C. L. (2023). Development and characterization of sodium polyacrylate/bentonite hydrogel with epoxy resin coating. *Polímeros: Ciência e Tecnologia*, 33(2), e20230021. <https://doi.org/10.1590/0104-1428.20230029>

1. Introduction

Basically, hydrogels are made up of the chemical or physical cross-linking of molecules and are a special class of polymers that absorb a considerable amount of water while maintaining their overall shape. Hydrogels are considered one of the most promising materials due to their unique properties and wide range of applications^[1]. According to Agrawal et al.^[2], resistant hydrogels have shown strong potential as structural biomaterials, including laponite clay-reinforced nanocomposite hydrogels. However, these materials alone have limited mechanical properties because synthetic hydrogel is weak and brittle.

Therefore, hydrogels consist of hydrophilic materials, more precisely, polymers formed by cross-linking, that can absorb a large mass amount of water or aqueous solution (more than 100 times their mass value). Superabsorbent polymers are polymers that are basically made up of the cross-links of monomers such as acrylamide and acrylate. Technological advances include the addition of materials to form superabsorbent composites. Clays, such as kaolinite, diatomite, vermiculite, alumina, and mica are added to the matrix polymer. The presence of minerals improves mechanical properties, water absorption capacity, and biodegradability. Bentonite is an abundant mineral, found in Brazil, is constituted of expandable clay, and can be used in these compositions^[3].

In 2021, Wang et al.^[4] reported a study about the preparation and characterization of GO (graphene oxide) / UHMWPE (ultra-high molar mass polyethylene) and a hydrogel based on polyacrylamide (PAAm) and GO composites for lubricant reinforcement of the UHMWPE polymeric material. It was observed that the UHMWPE polymer modified with the PAAm/GO hydrogel layer showed an improved ability to provide reinforcing effects. All abbreviations in this article are listed in Appendix A.

Additionally, new developments are pursued by Chen et al.^[5], based on a binder of sodium polyacrylate and sodium silicate, used as an oxidation-resistant coating on titanium alloy, a material widely used in aerospace field, due to the attractive combination of properties such as high strength, low density, and good corrosion resistance.

In the last century, organic and inorganic compounds combining the advantages of both parts have attracted considerable attention of the scientific community and are widely applied in the fields of multi-functional and high-performance materials design in biomedicine, new batteries and sensors, automotive and aerospace design, and drug delivery^[6].

It is known that the absorptive capacity of superabsorbent polymers is further increased when the acrylic acid is neutralized with a base such as sodium hydroxide (NaOH).

The sodium ions neutralize the carboxylate groups. Thus, a large amount of moisture can be absorbed through osmosis. As the sodium ions are also hydrated, the distance between the carboxylate groups increases. The free carboxylate groups will repel each other once again in the crosslinking process, providing more space for water absorption^[7].

Superabsorbent polymers such as sodium polyacrylate have the ability to absorb and retain large amounts of water and release it in a controlled manner under drought circumstances. These materials have been widely applied in many sectors, such as, hygiene, agriculture, personal care, engineering, and aerospace^[8]. Also popularly known as absorbent gels or flocc gel, sodium polyacrylate revolutionized the market, especially for diapers, by reducing the average mass of diapers by 50% and also by its great capacity to absorb aqueous liquids^[9].

According to Santos^[10], potassium persulfate or ammonium persulfate is used as an initiator for the polymerization of superabsorbent polymers in aqueous media (Figure 1).

Moini & Kabiri^[12] developed a superabsorbent polymer based on polyacrylates and crosslinking agents, such as diglycidyl ether of bisphenol A (DGEBA) and CAE (cycloaliphatic diepoxide), and used concentrations of 0.25% to 2.5% of two types of epoxy resins in a mixture of acetone and water (90:10) to surface cross-linking acrylic-based water absorbent particles. The resins used in Moini & Kabiri^[12]'s research were diethylene glycol diglycidyl ether and 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate.

In 2017, Huang et al.^[13] published research on a new class of composite called FRSC (Fiber-reinforced soft composites) using hydrogel in applications that require higher material strength and mechanical properties. This new material design has revolutionized the hydrogel field due to the synergistic effect provided by the flexibility of the hydrogel and the tensile strength of the synthetic fibers, resulting in a hydrogel component with extraordinary fracture toughness capability.

It is known that the manufacturing process of composites composed of fibers or inorganic materials constitutes the state of art regarding the application of highly resistant composites with hydrogels, which may have applicability in the aerospace sector since both constituent materials are already widely used in this sector's technology. During the development of these composites that can be applied as water absorbers to prevent corrosion on the metal

structures of rocket engines and airplanes, variations in the composition of hydrogel polymers and minerals can be studied, as applications of reinforcements with epoxy resin, besides the appropriate characterization/quantification of these components in the manufactured material. In this context, the development of instrumental, fast, and precise methodologies addresses this objective.

Regarding instrumental techniques, there are studies in literature^[3] which describe the use of Fourier transform infrared spectroscopy (FT-IR), among others for the characterization/quantification of superabsorbent hydrogels based on acrylamide and acrylate composite with bentonite or dolomite. However, only in the mid-infrared region (MIR) and with the samples analyzed by transmission mode and prepared by potassium bromide pellet, that means through a conventional methodology, demanding a longer analysis time. Nevertheless, there are reflection and reflectance/transmittance techniques that can be used for this purpose, and the application of these techniques is one of the objectives of this study. Wen et al.^[14] studied the development of a smart coating for corrosion protection of steel based on a hydrogel pre-loaded with the corrosion inhibitor benzotriazole (BTA). The morphology and composition of BTA and hydrogel were characterized by SEM (scanning electron microscopy), FT-IR, thermogravimetric analysis and differential exploratory calorimetry. The skeleton of this hybrid hydrogel contains organic and inorganic parts, in which the latter stabilizes the hybrid system, while the organic segments respond to external pH changes.

Concerning the research in composite materials, there are opportunities regarding the development, characterization, and quantification through instrumental techniques, among them, the FT-IR spectroscopy by reflection in the MIR and reflectance, which presents gaps in studies, especially in the near-infrared region (NIR). Therefore, this paper describes the development of different samples of hydrogels based on sodium polyacrylate and bentonite, forming a composite material with physicochemical properties for industrial and aerospace use, characterizing and/or quantifying its main components through methodology, involving less conventional techniques. Additionally, this study aimed to develop an epoxy resin coating in the sodium polyacrylate and bentonite water absorbent particles by virtue of ensuring appropriate coating material for aerospace application.

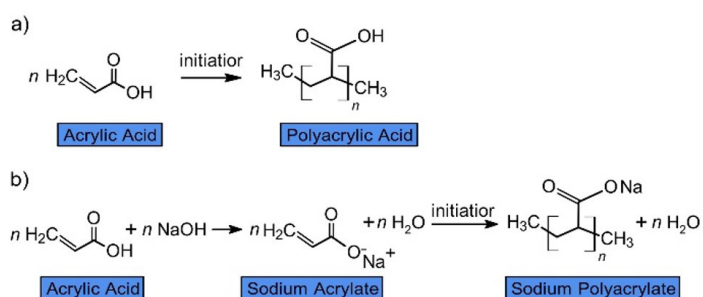


Figure 1. Synthesis reactions of (a) polyacrylic acid and (b) sodium polyacrylate^[11].

2. Materials and Methods

2.1 Materials

Preparation of sodium polyacrylate with different bentonite contents with potassium persulfate (thermal initiator) for quantitative assay by FT-IR/NIRA (near-infrared reflectance analysis) was carried out with the following reagents: acrylic acid, supplied by Sigma Aldrich; NaOH solution 50% (w/w), prepared with NaOH PA supplied by Merck; potassium persulfate, supplied by Synth, and commercial bentonite - Bentone® 38 V CG, supplied by Elementis. Aradite GY260 with 182-196 g/Eq epoxide equivalent and amine curing agent (Ancamine DETA - diethylenetriamine) supplied by Weg, and acetone supplied by J T Baker were used to coat the sodium polyacrylate and bentonite composite. Deionized water was obtained from an 18 Ω Milli-Q Integral ultrapure water system.

2.2 Preparation and qualitative characterization of composite

Composite samples were prepared by reacting the 50% NaOH solution with an aqueous solution of acrylic acid under stirring at 450 rpm. After complete homogenization of the solution, an aqueous solution of potassium persulfate was incorporated into the sodium polyacrylate solution. Each mixture was placed in an oven at 80°C to carry out the polymerization process. The composition of samples was based on literature that indicates the use of bentonite in the range about 5 to 25% in a sodium polyacrylate solution^[15]. The samples prepared for the quantification studies by FT-IR comprehended the composition from 100% to 85% of sodium polyacrylate and 0% to 15% of bentonite. Also, “Test 1” sample (95% of sodium polyacrylate and 5% bentonite) and “Test 2” (88% of sodium polyacrylate and 12% bentonite) were prepared to verify the FT-IR methodology. Figure 2 shows the sequence of the preparation of samples of composites reinforced with and without bentonite.

After the polymerization step, the superabsorbent material with and without bentonite were submitted to the coating process with the epoxy resin, using the epoxy resin Aradite

GY260 (Hunstman) with 182-196 g/Eq epoxy equivalent and an amine curing agent (Ancamine DETA), kindly provided by the company Weg, which are solubilized in a medium of acetone: water (90:10), v/v, at concentrations of 0.5% and 2.5%. This second step of the prototype development procedure follows as shown in Figure 3.

The specimens with the epoxy resin modified surface prepared as described above were analyzed by FT-IR spectroscopy using a PerkinElmer Spectrum One spectrometer with the Universal Attenuated Total Reflection (UATR) accessory, in the MIR region comprising 4000-400 cm^{-1} , resolution 4 cm^{-1} , gain 1 and 20 scans. The samples were ground in an agate mortar and pestle.

Sodium polyacrylate without bentonite and with 10% bentonite, both coated with 0.5% and 2.5% epoxy resin, were analyzed by SEM microscopy as received. No thin coating of conductive material (carbon/gold) was required. The samples with and without epoxy resin coating were mounted on carbon tape and examined by secondary electrons imaging, respectively, with a scanning electron microscope model LEO 435 VPi - ZEISS and model MIRA 3 - TESCAN. The use of different SEM microscopes did not impact in the results of images, once the same parameters were established for the images acquisition.

2.3 FT-IR analysis conditions and quantification methodology

The samples were analyzed by FT-IR equipment (PerkinElmer Frontier FT-IR spectrometer) with the NIRA reflectance accessory between 12000 and 4000 cm^{-1} , 4 cm^{-1} resolution, gain 1 and 120 scans. The sample was homogenized in an agate mortar with a pestle and then placed in a glass sample holder of NIRA accessory and a metal support that performs the reflectance on the detector was positioned on the sample. Each sample of composite and control (100% sodium polyacrylate) was analyzed 5 times following the procedure above. Each spectrum was obtained with the registration of transmittance measurement by FT-IR NIRA bands indicated by the wavenumber, thus comprising a total of 25 spectra measured by Frontier's Spectrum software.

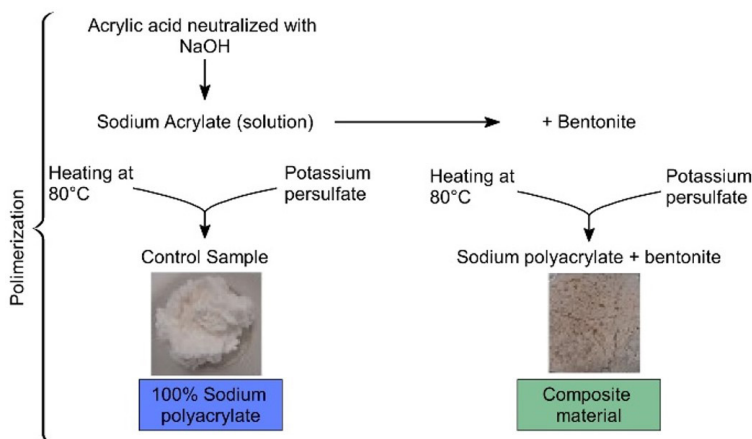


Figure 2. Solution polymerization with and without bentonite.

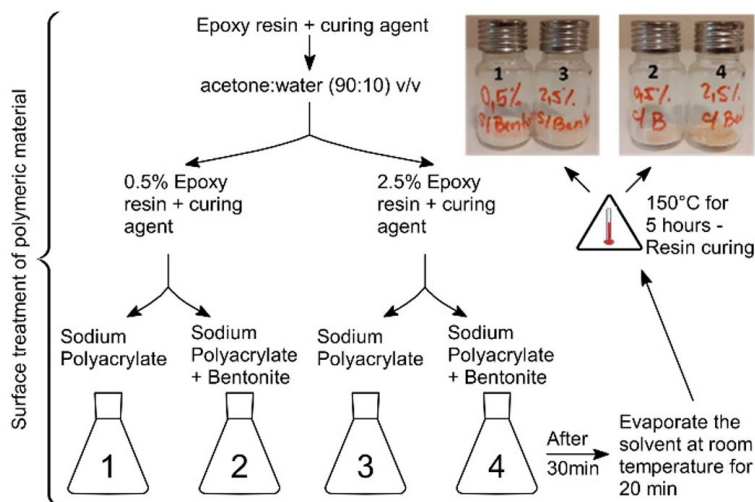


Figure 3. Coating of composite material with epoxy resin.

According to Lambert-Beer’s law, Equation 1 which rules quantitative infrared analysis was used to determine the calibration or analytical curves, relating the absorbance bands of composite obtained by FT-IR analysis^[16]:

$$A = \epsilon bc \quad (1)$$

Where: A= absorbance; ϵ = molar absorptivity (characteristic of absorption); b = thickness; c = concentration.

For relative bands, the thickness (b) of the analyzed sample will be the same in the sample spectrum, and when dividing one band absorbance by the other, b cancels out.

$$\frac{A_1}{A_2} = \frac{\epsilon_1 bc_1}{\epsilon_2 bc_2} \quad (2)$$

According to Hórák & Vítek^[17], for a small set of data, the median ($\hat{\mu}$) is used instead of the average to calculate the relative deviation or relative error of a sample measurement.

$$\hat{\sigma} = K_R \times R \quad (3)$$

Where $\hat{\sigma}$ is the standard deviation, R represents the difference between the highest and the lowest absorbance values and K_R equals 0.430 for 5 measures^[17].

$$\hat{\sigma}_{\hat{\mu}} = \frac{\hat{\sigma}}{\sqrt{n}} \quad (4)$$

$$RD(\%) = \frac{\hat{\sigma}_{\hat{\mu}}}{\hat{\mu}} \times 100 \quad (5)$$

Where $\hat{\sigma}_{\hat{\mu}}$ is the mean standard deviation, n represents the total number of measures, RD is the relative deviation and $\hat{\mu}$ is the median absorbance value. The methodology errors (%) are calculated considering the median of RD, as described by Dutra & Soares^[18].

2.4 FT-IR methodologies verification

To verify the effectiveness of the developed FT-IR methodologies, the samples “Test 1” and “Test 2” were analyzed by the same conditions of samples used to calibrate the system. So, the median value was applied to the equation of plotted calibration curve^[17].

3. Results and Discussions

3.1 FT-IR NIRA – quantification of sodium polyacrylate and bentonite

Quality control of composite materials must be carried out to ensure the content uniformity to perform their purposed use. For this reason, this study approaches an effective and accurate analytical methods such as infrared spectroscopy as a qualitative and quantitative analysis, besides of the fact of this methodology by NIRA analysis is nondestructive, fast and could bring timesaving and costeffective.

First of all, the analytical bands of the components presented in the samples are represented in Figure 4. Since the intensity of these analytical bands increases or decreases according to the component content, the following are assigned below^[19]:

- Sodium polyacrylate (P): 7015 cm^{-1} (third overtone of 1730 cm^{-1} band - stretching region of carbonyl group) and 5202 cm^{-1} (second overtone of the same carbonyl-stretching region);
- Bentonite (B): 7200 cm^{-1} (first overtone of the 3600 cm^{-1} band - stretching region of the hydroxyl group) and 4360 cm^{-1} (combination of fundamental MIR bands of bentonite around 3600 cm^{-1} and 1000 cm^{-1}).

Although four bands have been assigned as shown in Figure 4 to determine P and B, in this present methodology applied for quantitative analysis it was assigned the band at 7200 cm^{-1} and at 5202 cm^{-1} , for sodium polyacrylate and bentonite, respectively. Since these bands increase in

intensity value (measured by the height in the spectrum) as long as there is more concentration of the analyte, by estimating low standard error might occur in these regions used as reference for the quantification purpose.

The probable assignment of NIR absorptions is based on the information that the combination bands (sum of fundamental MIR bands) lie between 4000 and 5000 cm^{-1} , while the overtones (multiples of fundamental MIR bands) are from 5000 to 12000 cm^{-1} [19].

Therefore, samples were analyzed by FT-IR NIRA using these two assigned bands, and the relative intensity of absorption bands was evaluated by means of identification of analytical or relative bands for the quantification of sodium polyacrylate and bentonite, as detailed in the NIRA methodology 1 and 2.

3.1.1 NIRA Methodology 1: Calibration curve - intensity of absorbance at 7200 cm^{-1} analytical band versus bentonite content (%)

This methodology has been applied for quantitative analysis of bentonite compound in the composite material supported by intensity of analytical band absorbance measured by a suitable software. Table 1 shows the NIRA data obtained for the band at 7200 cm^{-1} , measured with the baseline 7268 cm^{-1} at 6474 cm^{-1} , and Figure 5 presents the

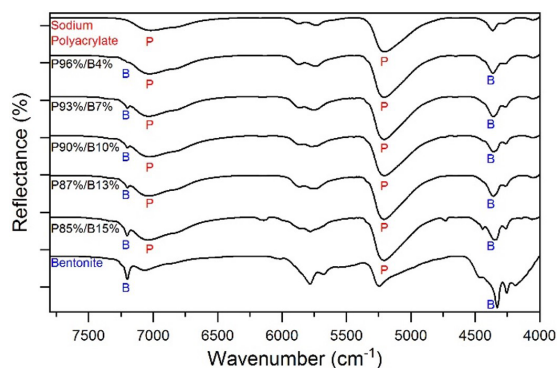


Figure 4. Comparison of FT-IR/NIRA spectra of sodium polyacrylate, bentonite and their composite combination.

calibration curve observed by this methodology and the methodology error is estimated at around 3.03%.

Since in the material composite samples, there are only sodium polyacrylate and bentonite, the concentration of sodium polyacrylate in test samples should be calculated by the difference of 100%.

It was observed that there is a Lambert Beer's law deviation of sample with 15% of bentonite, since in this concentration there was no increase of the absorbance value. This deviation may be associated with the lower intensities of NIR absorption bands. According to Smith^[16], in order to avoid this type of deviation the analytical band should have an intensity equivalent to 20-80% of transmittance. Nevertheless, when this intensity is not attainable due to the concentration range of the analytes, the relative bands could be applied to minimize the intensity measurement variation^[20,21]. In order to evaluate the values using the relative bands, a new NIRA methodology was carried out and discussed in the next item.

3.1.2 NIRA Methodology 2: Calibration curve - intensity of A_{7200}/A_{5202} relative band versus sodium polyacrylate/bentonite content (%)

Table 2 shows the data obtained for the bands at 7200 cm^{-1} and 5202 cm^{-1} , measured to constitute the relative band

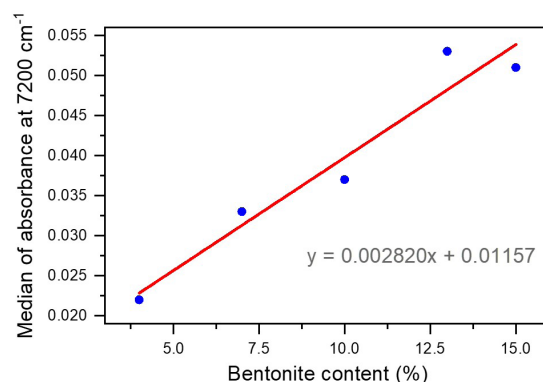


Figure 5. NIRA methodology 1 using A_{7200} - calibration curve for the samples with different bentonite contents.

Table 1. NIRA Methodology 1 (A_{7200}) for samples with different contents of P and B.

Sample	A_{7200} (B)	$\hat{\mu}$	$\hat{\sigma}$	RD (%)
96% P/4%B	0.018; 0.019; 0.023; 0.022; 0.022	0.022	0.001	4.54
93% P/7% B	0.033; 0.033; 0.034; 0.033; 0.034	0.033	0.001	3.03
90% P/10% B	0.043; 0.039; 0.037; 0.036; 0.034	0.037	0.002	5.40
87% P/13% B	0.054; 0.057; 0.053; 0.052; 0.051	0.053	0.001	1.89
85% P/15% B	0.051; 0.051; 0.053; 0.049; 0.050	0.051	0.001	1.51

Table 2. NIRA 2 methodology (A_{7200}/A_{5202}) for samples of different levels of sodium polyacrylate and bentonite.

Sample	A_{7200} (B)/ A_{5202} (P)	$\hat{\mu}$	$\hat{\sigma}$	RD (%)
96% P/4%B	0.085; 0.082; 0.103; 0.100; 0.100	0.100	0.004	4.00
93% P/7% B	0.191; 0.178; 0.188; 0.179; 0.186	0.186	0.002	1.08
90% P/10% B	0.212; 0.194; 0.196; 0.191; 0.185	0.194	0.005	2.58
87% P/13% B	0.276; 0.266; 0.276; 0.283; 0.264	0.276	0.004	1.45
85% P/15% B	0.313; 0.293; 0.312; 0.290; 0.301	0.301	0.004	1.33

A_{7200}/A_{5202} that includes the characteristic bands of bentonite and sodium polyacrylate, respectively. Figure 6 shows the curve plotted for this methodology. The baseline used for the 5202 cm^{-1} band was 5412 cm^{-1} to 4888 cm^{-1} ; for 7200 cm^{-1} absorption was in the same range as already mentioned for the calibration curve plotted only with this band. The methodology error is around 1.45%.

Table 3 shows a comparison of data obtained in the two methodologies, aiming at the evaluation of the results and the choice of the most appropriate one to determine the levels of sodium polyacrylate and bentonite contents.

The best methodology for determination of sodium polyacrylate and bentonite content is NIRA methodology 2. The calibration curve equation of methodology NIRA 2 showed a good linearity ($R=0.976$), without deviations of Lambert-Beer law and the result of $R^2=0.95$ means that 95% of the data can be explained by the methodology. Therefore, it is an indication that this methodology met the goal since the methodology error was calculated as 1.45% attending the acceptance criteria of $\leq 2\%$ ^[17].

Test samples were also analyzed to verify the effectiveness of the developed NIRA methodologies. NIRA methodology 1 was tested and the content results including the RD (%) for the proposed test samples are shown in Table 4.

Through the data in Table 4, it is possible to observe that NIRA methodology 1 adjusts better to intermediate values of the studied bentonite range, while for lower values there are greater errors (Table 1), in accordance with the deviation found of the Lambert-Beer law^[16]. For this reason, the results of "Test 2" were more according to the expected results and the RD% was also minor than the sample "Test 1".

One parameter that suggests that NIRA methodology 2 can meet the goal is the error of 1.45%, because it is

within the reference value of $\leq 2\%$ ^[17]. In addition, this value is also much lower than the expected error (8-10%) in the quantitative analysis of powders by FT-IR conventional methodology using transmission mode and pellet to incorporate the samples^[16].

So, NIRA methodology 2 was tested by means of the relative band A_{7200}/A_{5202} which includes the characteristic bands of bentonite/sodium polyacrylate. The results and the RD (%) of the proposed test samples are displayed in Table 5.

Through the equation of methodology 2 described in Table 3, where x = relative concentration of B/P and given that $[B] + [P] = 100\%$, the values of each component in the sample were determined. According to the data in Table 5, it is possible to observe that NIRA methodology 2 shows that values are close to the nominal, especially for lower bentonite content, with a relative error between 1.71-3.74%.

3.2 Qualitative analysis by FT-IR/MIR/UATR and SEM analysis of the new prototypes with epoxy resin-based

The samples were developed with 0.5% and 2.5% epoxy resin with the purpose of coating and were analyzed by UATR. The spectra obtained related to sodium polyacrylate and bentonite composite coated with 0.5% and 2.5% epoxy resin are shown in Figure 7. The analysis of the epoxy resin used as a coating in this work was performed by UATR, and the characteristic bands of epoxy resins are found at $\sim 1295 \text{ cm}^{-1}$ (ν C-O ether) and $\sim 914 \text{ cm}^{-1}$ (epoxide group vibration). For the cure agents, it is found that the absorption regions of the N-H (ν) stretching vibration at $\sim 3400 - 3200 \text{ cm}^{-1}$, and also in the region $\sim 1590 \text{ cm}^{-1}$, assigned to the NH_2 angular bending (δ)^[16]. These results contributed to the characterization of the coating of the polymer developed based on sodium polyacrylate and bentonite.

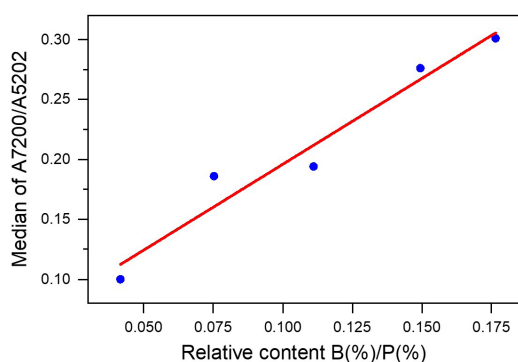


Figure 6. NIRA methodology 2 using relative bands (A_{7200}/A_{5202}) - calibration curve for the samples with relative contents of bentonite and sodium polyacrylate.

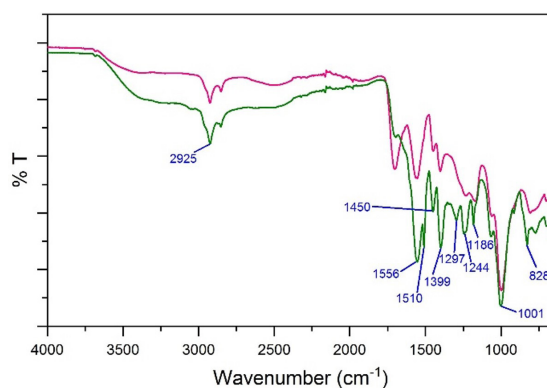


Figure 7. FT-IR/UATR spectra of composite samples treated with 0.5% (pink spectrum) and 2.5% epoxy resin (green spectrum).

Table 3. FT-IR data obtained for the two NIRA methodologies for sodium polyacrylate and bentonite system.

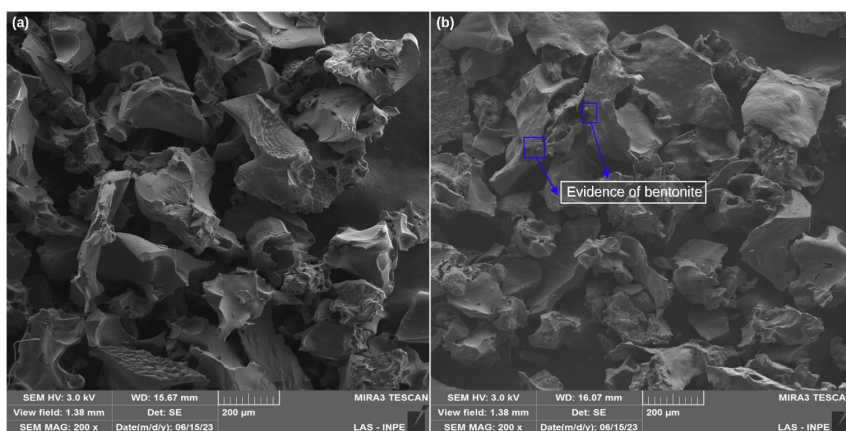
Methodology	Error (%)	Equation	R	R ²
1	3.03	$y = 0.0028x + 0.0116$	0.968	0.94
2	1.45	$y = 1.4333x + 0.0525$	0.976	0.95

Table 4. Results of the test samples according to the calibration curve of Methodology 1.

Sample	A_{7200}	$\hat{\mu}$	RD (%)	Result
Test 1	0.033; 0.030; 0.033; 0.034; 0.034	0.033	3.03	92.36% (P) 7.64% (B)
Test 2	0.051; 0.043; 0.047; 0.045; 0.045	0.045	2.22	88.07 (P) 11.93 (B)

Table 5. Results of the test samples according to the calibration curve of NIRA methodology 2.

Sample	A_{7200}/A_{5202}	$\hat{\mu}$	RD (%)	Result
Test 1	0.107; 0.095; 0.105; 0.111; 0.114	0.107	3.74	96.34% (P) 3.66% (B)
Test 2	0.185; 0.169; 0.175; 0.173; 0.175	0.175	1.71	92.17% (P) 7.83% (B)

**Figure 8.** SEM of samples without epoxy resin coating: (a) Sodium polyacrylate and (b) Sodium polyacrylate with bentonite.

Since the absorption in these regions increases, the content of the resin in the particles also increases. These spectral results by FT-IR of surface analysis demonstrated that the treatment with the epoxy resin is effective.

According to Andrade et al.^[22], epoxy adhesives are materials used in the interfaces to adhere metal/metal, carbon-carbon/aluminum and graphite/aluminum. Because of this interface could be exposed to high mechanical stress, the authors emphasize the importance of avoiding cracks in the materials used in aerospace applications, and the need to accommodate the tensions generated in the adhesion region. Therefore, different materials and instrumental techniques including FT-IR have been used for the characterization study of these epoxy systems, contributing with data to the state of the art of this line of research^[23].

Formulation of clay - polymer hydrogel based is cited in a recent study but the FT-IR analyses were conducted in MIR region by conventional transmission mode to identify the presence of functional groups existing in starting materials^[24]. Then, this actual paper about the development and characterization of sodium polyacrylate/bentonite hydrogel with epoxy resin coating, considering reflection (UATR) and reflectance (NIRA) modes that contribute with data to the state of the art of this line of research.

SEM analyses are crucial to evidence the coating of epoxy resin in sodium polyacrylate with and without bentonite. First off, to give a comprehensive overview of the structures captured without epoxy resin coating, images by SEM shown in Figure 8a (sodium polyacrylate without bentonite) and Figure 8b (sodium polyacrylate with 10% of bentonite) display particles which do not present different contrast formation mechanism in SEM images that evidences the absence of epoxy resin coating. The regions marked in blue are showing the presence of bentonite particles.

On the other hand, it is observed from SEM images, in Figure 9b and Figure 9c, that the particles with and without bentonite can be easily differentiated by the appearance of their surfaces. The composites have the superficial appearance of a cluster of bentonite particles and it can be observed that these particles are completely aggregated to the sodium polyacrylate polymer. On the other hand, sodium polyacrylate particles without bentonite have a smooth surface and more pronounced concave parts.

Figure 9 shows clearly that the coating by epoxy resin in the 2.5% sample (Figure 9a and Figure 9b) was superior to the 0.5% samples (Figure 9c and Figure 9d), suggesting that the process used to adhere the resin to the particles is

successfully performed and that the curing procedure is also consolidated on the surface of them.

The red arrows in Figure 9 are indicating the evidence of the epoxy resin coating in the particle, forming a film of a very thin aspect on the surface. Furthermore, the blue ones in the same figure are evidencing the presence of bentonite particles in the sodium polyacrylate.

Figure 10 presents the schematic of the physicochemical interaction between the sodium polyacrylate and bentonite composite with the epoxy resin coating. By the images observed by SEM, it is noted that there is an interface between the composite or sodium polyacrylate and the coating material, since there is the presence of two distinct phases (particle and coating). As the coating layer with epoxy

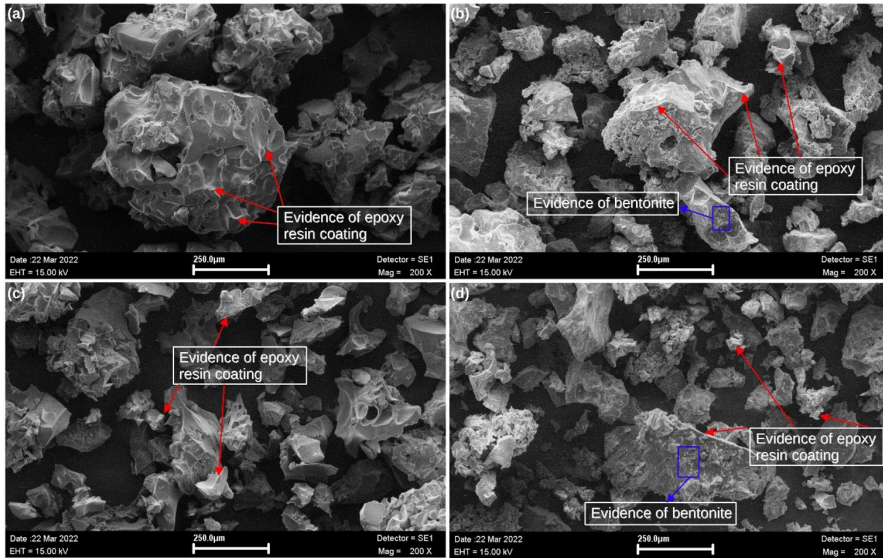


Figure 9. SEM of samples coated with 2.5% epoxy resin: (a) Sodium polyacrylate and (b) Sodium polyacrylate with bentonite. Samples coated with 0.5% epoxy resin: (c) Sodium polyacrylate and (d) Sodium polyacrylate with bentonite.

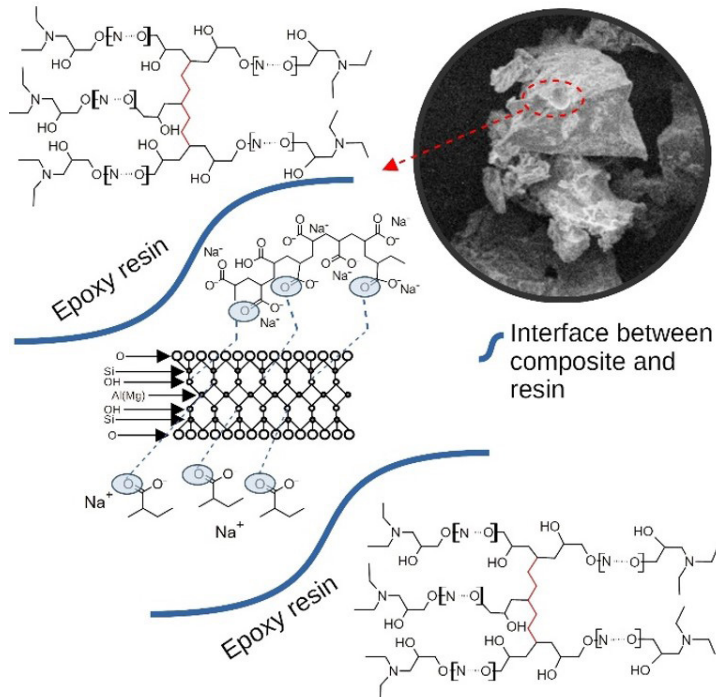


Figure 10. Schematic model of the physicochemical interaction between the sodium polyacrylate and bentonite and epoxy resin coating.

resin is very thin, it is possible to observe a perfect layer of interface stated by the red arrows. Also, a good adhesion of the resin material in the particles was observed as well, in the sodium polyacrylate polymer and composite material.

4. Conclusions

Since this paper aimed to develop epoxy resin coated hydrogel composite based on sodium polyacrylate/bentonite and to quantify the two last components by a rapid and precise FT-IR spectroscopy methodology, it is possible to conclude that with the use of a thermal initiator and heating, it was possible to develop a superabsorbent composite using acrylic acid, sodium hydroxide, bentonite and potassium persulfate, as starting materials.

Two methodologies were proposed in this paper with analytical or relative bands to quantify bentonite and sodium polyacrylate in the composite material. According to the study, the most robust methodology for the quantification was using the relative band A_{7200}/A_{5202} , referring respectively to bentonite and sodium polyacrylate, because the resulting calibration curve A_{7200}/A_{5202} versus the relative content of bentonite and sodium polyacrylate showed data of R, R², and methodology error very consistent and expected for this analytical technique. Thus, through the NIR reflectance technique, it is possible to suggest a quantification study of this hydrogel composite.

Regarding the practical applications of this study, it is possible to suggest the use of the developed hydrogel composite in the aerospace sector, especially in anti-corrosive applications due to the water absorption, with a fast and precise quantification methodology. This methodology can contribute to the state of the art of research as a model for quantification by NIRA of sodium polyacrylate and bentonite in different levels, once this FT-IR mode for this composite was not found in the literature.

The epoxy resin widely used in aerospace can be applied as a material coating of this composite. It is possible to conclude that the adhesion process of the epoxy resin material is consolidated on sodium polyacrylate particles with and without 10% bentonite.

5. Author's Contribution

- **Conceptualization** – Marcia Murakoshi Takematsu; Rita de Cássia Lazzarini Dutra.
- **Data curation** – NA.
- **Formal analysis** – NA.
- **Funding acquisition** – Rita de Cássia Lazzarini Dutra.
- **Investigation** – Marcia Murakoshi Takematsu; Amanda Faria Baruel.
- **Methodology** – Marcia Murakoshi Takematsu; Milton Faria Diniz; Rita de Cássia Lazzarini Dutra.
- **Project administration** – NA.
- **Resources** – Marcia Murakoshi Takematsu; Milton Faria Diniz; David Alexandro Graves.
- **Software** – NA.

- **Supervision** – Marcia Murakoshi Takematsu; Silvana Navarro Cassu; Amanda Faria Baruel; Rita de Cássia Lazzarini Dutra

- **Validation** – NA.

- **Visualization** – David Alexandro Graves, Marcia Murakoshi Takematsu.

- **Writing – original draft** – Marcia Murakoshi Takematsu; Rita de Cássia Lazzarini Dutra.

- **Writing – review & editing** – Marcia Murakoshi Takematsu; Silvana Navarro Cassu; Rita de Cássia Lazzarini Dutra.

6. Acknowledgements

The authors disclosed receipt of the following financial support for the research, authorship, and/or publication of this article. This work was supported, in part, by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001 and by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPQ). Finance Code 301626/2022-7. The authors would like to thank Thiago Sidooski and Joyce Baracho Azevedo for their technical support. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Received: Apr. 16, 2023

Revised: Jul. 01, 2023

Accepted: Jul. 11, 2023

Appendix A. Abbreviations.

A: Absorbance
B: Bentonite
BTA: Benzotriazole
CAE: Cycloaliphatic diepoxide
DETA: Diethylenetriamine
DGEBA: Diglycidyl ether of bisphenol A
FRSC: Fiber-reinforced soft composites
FT-IR: Fourier transform infrared spectroscopy
GO: Graphene oxide
MIR: Mid-infrared region
NaOH: Sodium hydroxide
NIR: Near-infrared region
NIRA: Near-infrared reflectance analysis
P: Sodium polyacrylate
PAAm: Polyacrylamide
RD: Relative deviation
SEM: Scanning electron microscopy
UATR: Universal attenuated total reflection
UHMWPE: Ultra-high molar mass polyethylene