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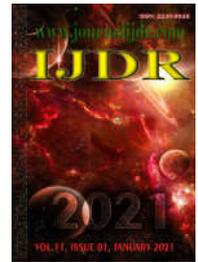
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RESEARCH ARTICLE

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STUDY OF THE INTERACTIONS OF THE NANOCOMPOSITE FORMED BY POLY (VINYL ALCOHOL), CLAY AND ZINC OXIDE NANOPARTICLES

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ABSTRACT

Polyvinyl alcohol (PVA) is a biodegradable and biocompatible polymer; and due to these characteristics, it is being widely applied in health systems. Zinc oxide (ZnO) nanoparticles have several properties, including antimicrobial activity. Bentonite is a sodium-type clay that has water-absorbing properties, allowing the opening of its coverslips and the entry of other molecules between them. This article studied the interactions of nanocomposites formed by PVA, bentonite and ZnO nanoparticles, generating nanostructured systems. These systems were produced by solution mixing method at different concentrations. The characterization was made by Thermogravimetric Analysis (TGA), X-ray Diffraction (XRD) and Time-Domain Nuclear Magnetic Resonance (TD-NMR). The results showed that nanocomposites containing both 5 wt% PVA and 0.5 wt% ZnO of the polymer, and bentonite at concentrations of 3% and 5% by mass of the polymer were randomly organized, being highly amorphous compared to other systems. The clays in these two systems were predominantly exfoliated. These data indicate the synergistic effect between nanoparticles, and a highly random system, containing drug, would retard its diffusion to the outside environment, contributing to a more controlled and lasting release of drugs, enabling their application in pharmacological systems.

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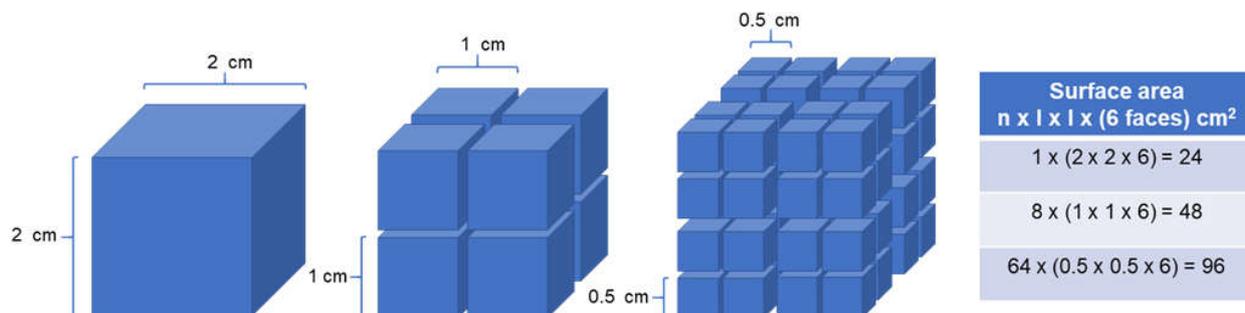
INTRODUÇÃO

Nanotechnology appears to obtain materials that present better physical, chemical, and other properties, with a large reduction in the amount of filler used, compared to additives on a micrometric scale (in the range of 40%). Consequently, there is a lighter material and with a possible simplification of its production process (Potts *et al.*, 2011). When observing the same type of application, nanoscale materials may exhibit improved performance compared to bulk materials, which have larger dimensions than nanoscale materials. The great advantage of particles on a nanoscale, compared to particles of much larger sizes, is the effect of the surface. Nanoparticles have both a surface area and many particles per mass of material (Figure 1). Because of size reduction, nanoparticles have an extremely high surface reactivity, making them tend to easily agglomerate (Buzea; Pacheco; Robbie, 2007). Nanocomposites are a type of nanostructured system, characterized as multiphase systems containing at least one phase that has one or more dimensions in scale ranging from 1 nm to 100 nm. These nanomaterials are dispersed in a matrix. When the matrix is formed by the polymer, this nanostructured system is called a polymeric nanocomposite and the dispersed inorganic nanomaterial is a nanofiller (Vardanyan *et al.*, 2015; Anadão, 2017).

Both have different properties and structures, but when combined, they can offer improved properties compared to conventional composites, such as strength, stiffness, thermal stability, low weight, and other characteristics (Thakur; Kessler, 2015). Furthermore, these properties are improved by using very low amount of nanofiller, generally less than 5% by weight of the polymer (Farhoodi, 2015). It is important to have a good dispersion, distribution and affinity of the nanofiller with the matrix, so that it doesn't agglomerate in the polymer, which would generate stress concentration points, which can lead to premature fracture, thus decreasing the properties of the produced material (Chen *et al.*, 2013; Loste *et al.*, 2019). It is expected that the combination of nanofiller in the same polymeric matrix offers improved and distinct properties that could not be obtained by each separately (Ma *et al.*, 2010). Using different characterization techniques together, it is possible to obtain information about the interactions of the system and, consequently, understand the behavior for future applications. Poly(vinyl alcohol) (PVA) is a polymer obtained through the hydrolysis of poly(vinyl acetate) (PVAc), using potassium or sodium hydroxide in a methanolic medium (Figure 2) (Sakurada, 1985). The more modified acetate groups, the greater the degree of hydrolysis of PVA and the greater the polar character of PVA. In the case of low hydrolysis degrees, PVA dissolves in nonpolar solvents, since the number of

existing acetate groups is greater, and this attributes a nonpolar character to the polymer (Alves et al., 2011). PVAI is a biodegradable polymer (Tsujiyama; Nitta; Maoka, 2011; Marusincová et al., 2013; Bian et al., 2019) and biocompatible (Batista et al., 2012). This polymer also has no oral toxicity, impaired motor activity, or any other adverse effect (Kelly et al., 2003; Nien et al., 2009). PVAI has been described in the literature for a long time and has notable applications in the biomedical, biotechnological and pharmaceutical areas, such as tissue engineering, biomass conversion, protein and cell immobilization (Orienti et al., 2001; Totani; Teramura; Iwata, 2008; Alves et al., 2011; Terence et al., 2011).

Bentonite is a clay that consists mainly of montmorillonite and belongs to the group of smectite clays. The crystalline structure of the clay is formed by two sheets of tetrahedral silica and one of octahedral alumina (Figure 3), forming a layer. Aluminum, within the octahedron, can be replaced by magnesium or iron. In this case, it is necessary to add metals such as sodium, potassium, or calcium to maintain charge balance. More difficultly, there may be silicon, or aluminum within the tetrahedral structure (Zakaria et al., 2009; Adeyemo; Adeoye; Bello, 2017). With the mixing of the clay with the polymer, there are 3 types of formations for the clay: tactoid- is the structure in which the clay lamellae remain together, without



Data: n- number of cubes, l- size of the cube side.

Figure 1. Illustration of the increase in the surface area of a cube with the reduction of its dimensions

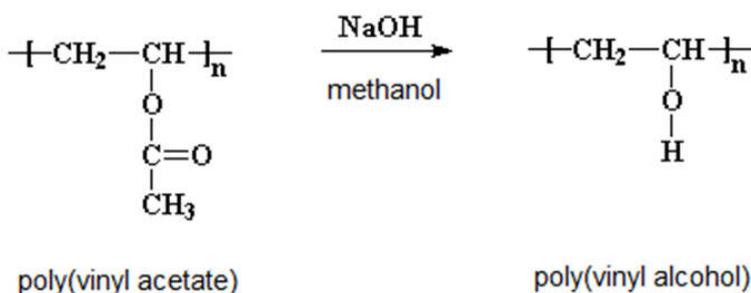


Figure 2. PVAc hydrolysis reaction

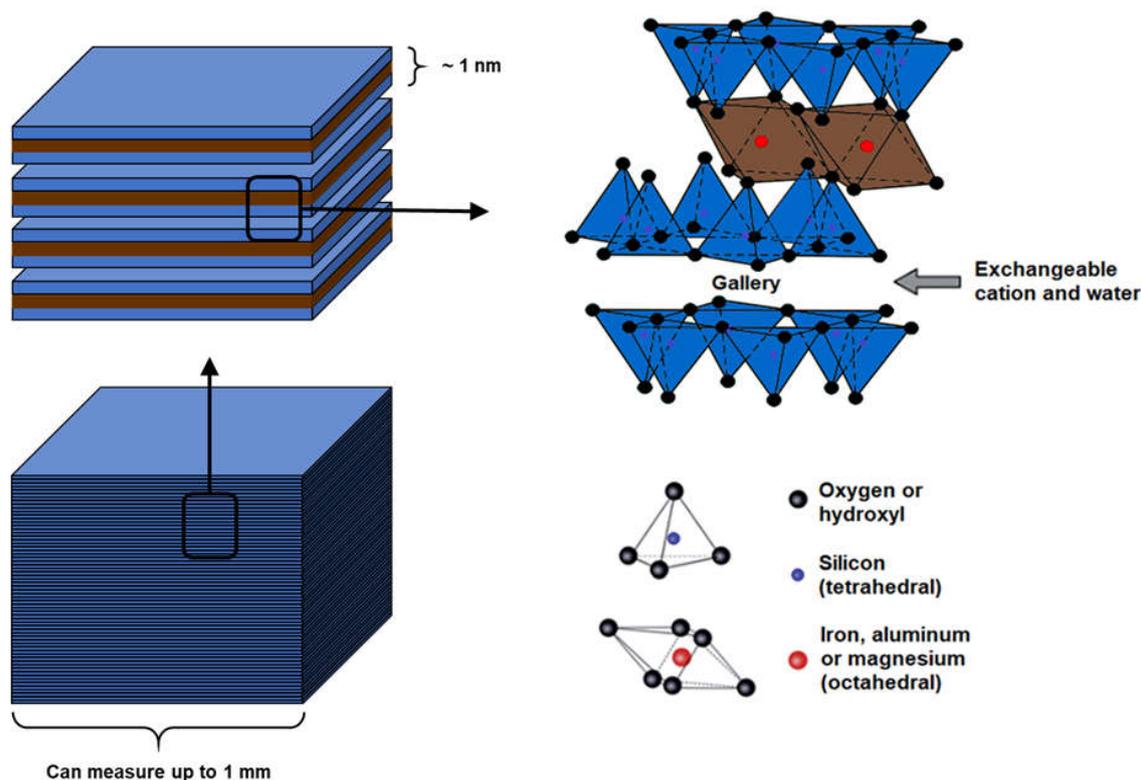


Figure 3. Scheme of montmorillonite and its crystalline structure

separation by the action of the polymer; intercalated- where there is an intermediate expansion of the lamellae, with the entry of the polymer between them, alternating the materials; and exfoliated- due to the high affinity between the polymer and the clay, its lamellae expand in such a way that they lose the ordering that was in its other 2 forms (Arora; Padua, 2010). Clays are well known for their barrier properties. This property is very interesting from a pharmaceutical viewpoint, since it would contribute to a more controlled and lasting release of drugs (Depan; Kumar; Singh, 2009; Kevadiya *et al.*, 2012).

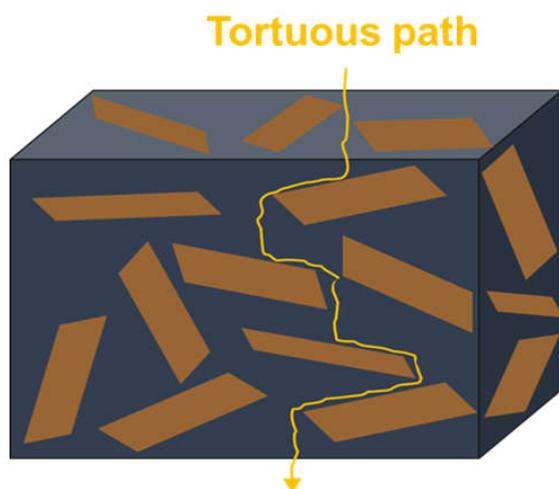


Figure 4. Scheme of the tortuous path generated by the barrier property of clays

It is classified by the U.S. Food and Drug Administration (FDA) as "generally recognized as safe" (GRAS) as a direct food additive (Code of Federal Regulations) (21 CFR 184.1155, 1996). It is considered non-toxic, being approved by the FDA (Code of Federal Regulations, 1996). In addition, because it is used as a food fortifier, it is also classified by the FDA as GRAS (Whittaker, 1998). ZnO has several applications in various areas of Science. It can be used as a catalyst in photodegradation (Lee *et al.*, 2016) for the removing dyes (Xie *et al.*, 2011; MAI *et al.*, 2008; Danwittayakul; Jaisai; Dutta, 2015). In the electronic area, it is used to create transistors (Heo *et al.*, 2004). ZnO nanoparticles exhibit bactericidal properties (Brayner *et al.*, 2006; JALAL *et al.*, 2010, Emami-Karvani; Chehrazi, 2011). Khalid *et al.* (2017) developed nanocomposites containing BC and ZnO, which has antibacterial properties, in addition to promoting improved properties for the material. The structure of the nanocomposites, the healing potential of burns and the antimicrobial activity were analyzed. The nanocomposites contained ZnO at a concentration of 1% by mass and were produced by the solution casting. The ZnO nanoparticles were distributed homogeneously by the BC matrix and are strongly linked to it. Antimicrobial activity was evaluated in bacteria that can appear in wounds. The system showed 90%, 87.4%, 94.3% and 90.9% of activity against *Escherichia coli* (*E. coli*), *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Citrobacter freundii*, respectively. The nanocomposite showed tissue regeneration activity greater than that of pure BC. The authors suggest that this system can be used as a new healing material for burns. As presented by Feng *et al.* (2009), who prepared formulations containing poly (lactic acid) (PLA), derived from vitamin E and nanoparticulate bentonite for the oral release of Docetaxel, an anti-cancer drug. The results showed that the nanoparticle formulation was more effective in killing cancer cells than the system currently used, in addition to 1 oral dose being able to perform sustained chemotherapy

for 3 weeks, compared to only 22h for the intravenous administration of the current system. Pathania *et al.* (2016) developed nanocomposites consisting of chitosan, polyacrylamide, and zinc nanoparticles for the controlled release of the drug ofloxacin, which has an antimicrobial effect for a variety of systemic infections. It was observed that the formulation, in an acidic environment, allowed a greater release of the drug, in comparison with environments with higher pH. In addition, the nanocomposite inhibited the growth of the bacteria under study *E. coli*, through the external connection with the bacteria membrane. Nanocomposites were also studied by Yamamoto *et al.* (2007) to evaluate the effects of insulin treatment, through inhalation of nanospheres powder formed by poly (D,L-lactic acid-co-glycolic acid) and mannitol, containing insulin. This system showed that there was a significant reduction in blood glucose levels. In addition, the pharmacological effect of the powder was prolonged, compared to the insulin solution administered via intravenous and inhalation. These studies, in addition to many others, indicate the potential use of nanostructured systems for use as drug carriers. This article aims to study the interactions of nanocomposites formed by PVAI and by bentonite clay nanomaterials and zinc oxide nanoparticles, for the generation of nanostructured systems with the function of carrying drugs.

MATERIALS AND METHODS

Materials: The materials used for this project were: PVAI 86.5% hydrolyzed, obtained from Sigma-Aldrich; sodium bentonite, received from Bentonite União; zinc oxide with an average size of 50 nm, obtained from Sigma-Aldrich.

Preparation of Nanocomposite Films: The nanocomposites were obtained by the method of solution casting, as illustrated in Figure 5. The concentration of PVAI is a function of water, and those of bentonite and ZnO, a function of the polymer mass. The 5% PVAI by mass was dissolved in water and heated to 90 °C with stirring for 24 hours. Bentonite at concentrations of 1%, 3% and 5% by mass was dispersed in water and heated to 50 °C with stirring for 3 hours. Then, the bentonite was poured into the PVAI under stirring at 70 °C for 1 hour. ZnO at concentrations of 0.2%, 0.5% and 0.8% by mass was dispersed in water using TURRAX. Then, the ZnO was poured into the PVAI/bentonite dispersion and heated to 70 °C under stirring for 1 hour. Finally, the dispersion was poured into a Petri dish and placed in an oven, at a temperature of 50 °C, for 3 days. The film, already without the solvent, was separated for further analysis.

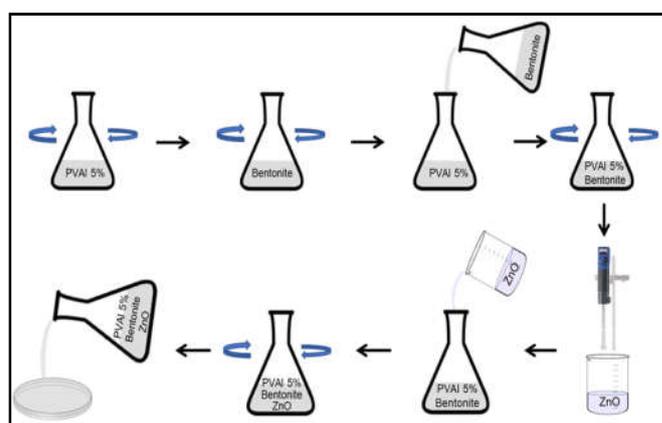


Figure 5. Scheme of the methodology for the synthesis of nanocomposites

Each sample was named according to the concentrations of its components, as shown in Table 1.

| Sample | PVAI (m/m%) | Bentonite (m/m%) | ZnO (m/m%) |
|-------------------|----------------|---------------------|---------------|
| PVAI5 | 100.00 | 0.00 | 0.00 |
| BEN | 0.00 | 100.00 | 0.00 |
| ZnO | 0.00 | 0.00 | 100.00 |
| PVAI5.BEN1 | 99.01 | 0.99 | 0.00 |
| PVAI5.BEN3 | 97.09 | 2.91 | 0.00 |
| PVAI5.BEN5 | 95.24 | 4.76 | 0.00 |
| PVAI5.ZnO0.2 | 99.80 | 0.00 | 0.20 |
| PVAI5.ZnO0.5 | 99.50 | 0.00 | 0.50 |
| PVAI5.ZnO0.8 | 99.21 | 0.00 | 0.79 |
| PVAI5.BEN1.ZnO0.2 | 98.81 | 0.99 | 0.20 |
| PVAI5.BEN1.ZnO0.5 | 98.52 | 0.99 | 0.49 |
| PVAI5.BEN1.ZnO0.8 | 98.23 | 0.98 | 0.79 |
| PVAI5.BEN3.ZnO0.2 | 96.90 | 2.91 | 0.19 |
| PVAI5.BEN3.ZnO0.5 | 96.62 | 2.90 | 0.48 |
| PVAI5.BEN3.ZnO0.8 | 96.34 | 2.89 | 0.77 |
| PVAI5.BEN5.ZnO0.2 | 95.06 | 4.75 | 0.19 |
| PVAI5.BEN5.ZnO0.5 | 94.79 | 4.74 | 0.47 |
| PVAI5.BEN5.ZnO0.8 | 94.52 | 4.73 | 0.76 |

Film Characterization

Thermogravimetric Analysis: To evaluate the thermal stability of the samples, thermogravimetric analyzes were performed based on the following parameters: N₂ atmosphere; temperature range from 30 to 700 °C; heating rate of 10 °C/min. The error is ± 2 °C.

X-Ray Diffraction (XRD): X-ray diffraction was used to obtain characteristics related to the organization of nanocomposites, and also variations in the diffraction peaks were made following the parameters: Angle 2θ between 2° and 60°; scan rate of 0.5° / min; wavelength λ = 0.154 nm; X-ray generation source: Copper.

Time-Domain Nuclear Magnetic Resonance (TD-NMR): TD-NMR analyzes were performed by determining the longitudinal relaxation time of the hydrogen nucleus (T₁H). The samples were placed in the probe in an 18mm tube. The conditions used are mentioned below: pulse used: 90°; pulse sequence used: inversion-recovery; temperature: (30 ± 2) °C; 1H core observation frequency: 23 MHz; range: 0.01 to 10,000 ms; list of points: 100 - 5,000,000 μs.

RESULTS AND DISCUSSION

Thermogravimetric Analysis: The TG analysis was performed with the objective of evaluating the thermal stability of the nanocomposites by determining the degradation temperature of the polymer and the nanocomposite systems. The thermal degradation profile for pure PVAI, bentonite and ZnO samples is shown in Figure 6. The degradation profiles obtained correspond to those presented in the literature for PVAL (Islam; Rahamana; Yeum, 2015), bentonite (Elkhalifah *et al.*, 2012; García-López *et al.*, 2005) and ZnO (Tang *et al.*, 2006). The first mass loss of PVAI and bentonite, at temperatures close to 50°C, occurs through the evaporation of the adsorbed water (Elkhalifah *et al.*, 2012). The second mass loss of PVAI involves the leaving of hydroxyl and acetate groups. The third stage of loss probably indicates the degradation of polyene-molecules that contain one or more sequences of double and single carbon-carbon bonds, producing carbon and shorter chain hydrocarbons (Lewandowska, 2009; Qiu; Netravali, 2012). Both clay and ZnO have high thermal stability, since more than 80% of their masses did not degrade until the analysis temperature (700 °C). The TG analysis of the nanostructured systems, containing different levels of bentonite, is shown in Figure 7. It is observed that the increase in the amount of bentonite contributed to a decrease in the thermal stability of the system. The concentration of 1% showed a lower rate of mass loss compared to 3% and 5%. Evaluating the thermogram in Figure 8 that shows the nanocomposites with the incorporation of ZnO nanoparticles, the increase in the nanofiller contributed to a reduction

in thermal stability, suggesting that ZnO acted catalytically in the degradation of PVAI. Evaluating the nanocomposite systems containing the two nanoparticles, the inclusion of ZnO nanoparticles in the system that contains 1% bentonite showed different thermal decompositions (Figure 9).

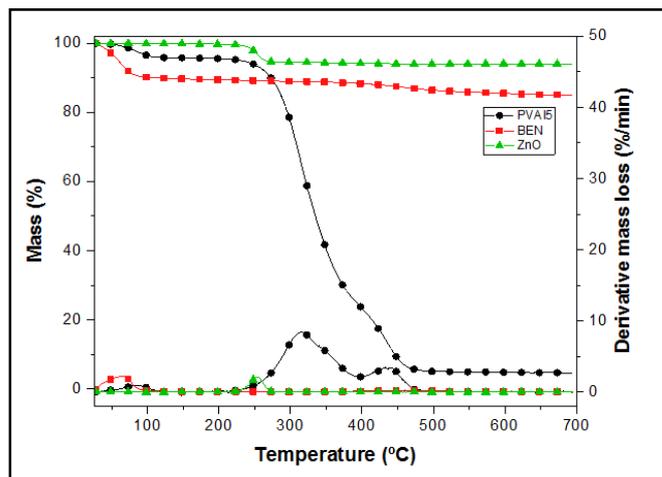


Figure 6. TGA of pure PVAI, bentonite and ZnO samples

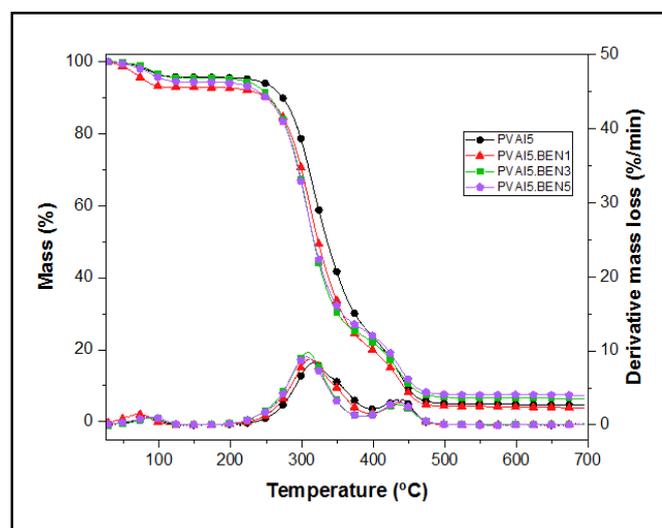


Figure 7. TGA of samples PVAI5, PVAI5.BEN1, PVAI5.BEN3 and PVAI5.BEN5

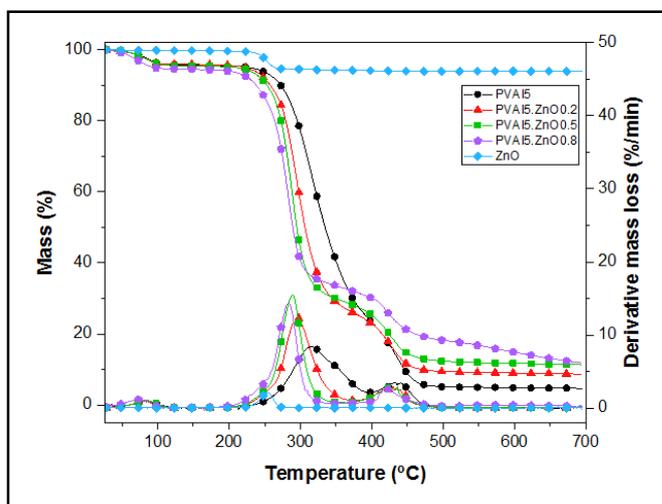


Figure 8. TGA of samples PVAI5.ZnO0.2, PVAI5.ZnO0.5 and PVAI5.ZnO0.8

The first stage was due to the loss of humidity around 100 °C and the second, due to the loss of hydroxyl and acetate groups from PVAI. The third stage of degradation occurred around 450 °C due to the

degradation of polyene. The observed residue is due to the formation of carbon and the residues of the nanofillers. Different decomposition profiles were presented for systems containing 3% clay and varying the ZnO concentration (Figure 10). With the increase in the amount of ZnO nanofiller, the thermal degradation events of the nanocomposite increase. The influence of 0.5% and 0.8% ZnO were the same, showing that these compositions showed similar behaviors, due to a better dispersion of the nanofiller. The TG analyses of the nanocomposites containing 5% clay and changing only the ZnO content are shown in Figure 11. For these samples, the addition of ZnO presented a degradation behavior like that of the nanocomposite containing 1% bentonite.

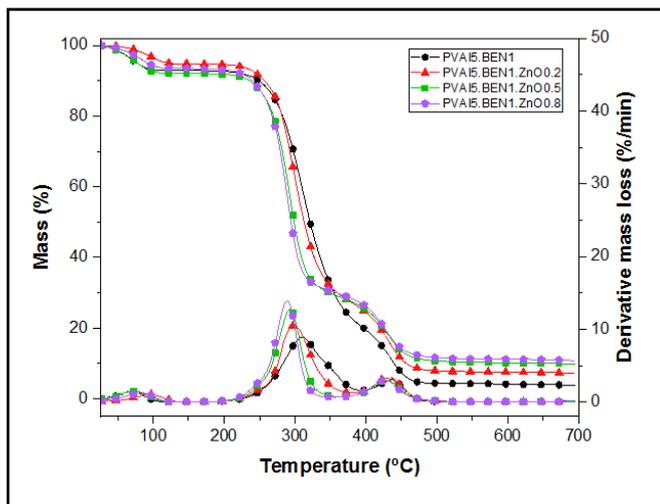


Figure 9. TGA of samples PVA15.BEN1, PVA15.BEN1.ZnO0.2, PVA15.BEN1.ZnO0.5 and PVA15.BEN1.ZnO0.8

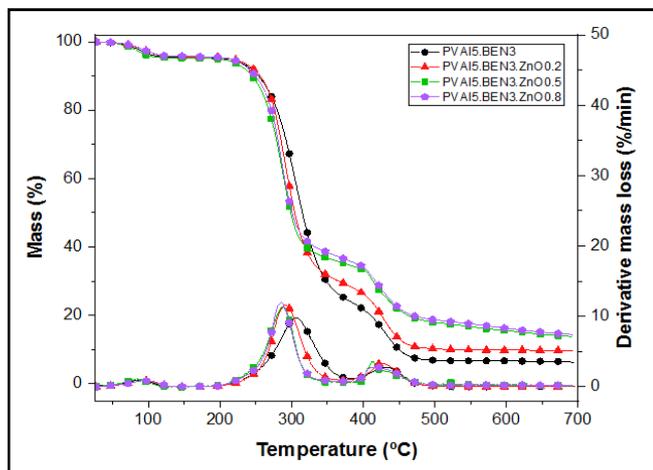


Figure 10. TGA of samples PVA15.BEN3, PVA15.BEN3.ZnO0.2, PVA15.BEN3.ZnO0.5 and PVA15.BEN3.ZnO0.8

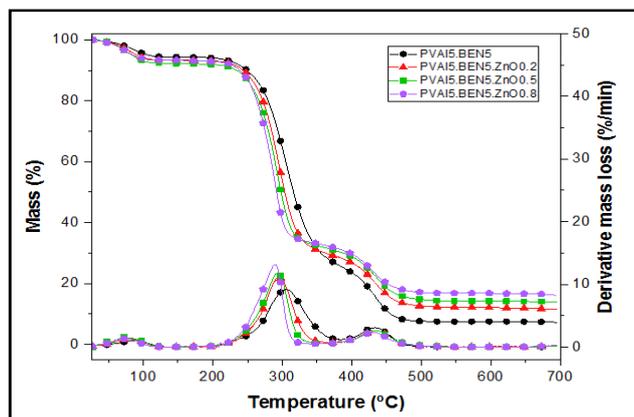


Figure 11. TGA of samples PVA15.BEN5, PVA15.BEN5.ZnO0.2, PVA15.BEN5.ZnO0.5 and PVA15.BEN5.ZnO0.8

X-Ray Diffraction: Figure 12 shows the XRD curves for pure PVAI, bentonite and ZnO. The diffractograms observed were like those presented in the literature for PVAI (Sapalidis *et al.*, 2012; ISLAM; RAHAMANA; YEUM, 2015), bentonite (García-López *et al.*, 2005) and ZnO (Tang *et al.*, 2006). For the PVAI spectrum, there is a diffraction peak at $2\theta = 19.35^\circ$, indicating that it is an organized polymer (Lim, 2015). PVAI has a strong interaction between its chains, due to intermolecular hydrogen bonds (Chandrakala *et al.*, 2013). ZnO is a very crystalline material, as can be seen through its several fine and high intensity peaks. The bentonite, in its tactoid form, has some peaks, among them, the peak at $2\theta = 5.95^\circ$ which corresponds to the plane (001), important for the subsequent analyzes.

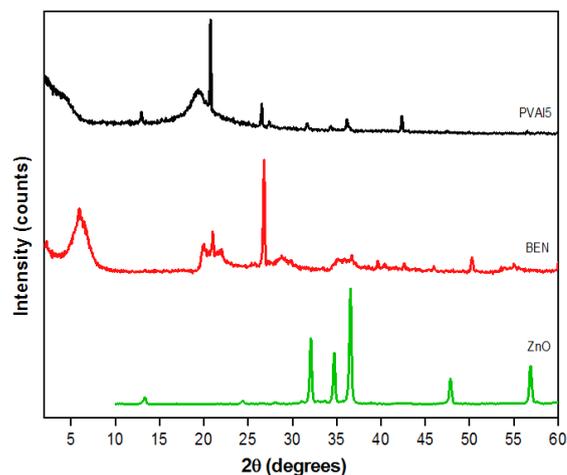


Figure 12. XRD patterns of pure PVAI, bentonite and ZnO

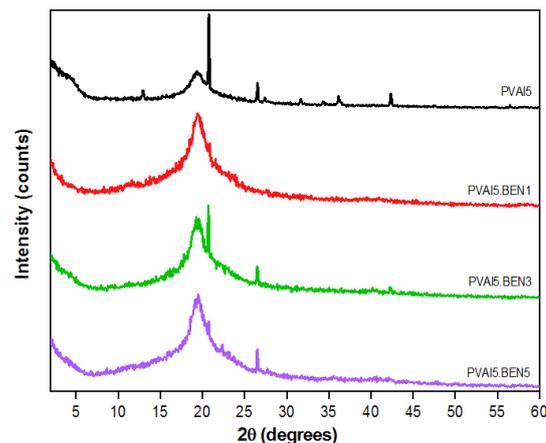


Figure 13. XRD patterns of PVA15, PVA15.BEN1, PVA15.BEN3 and PVA15.BEN5

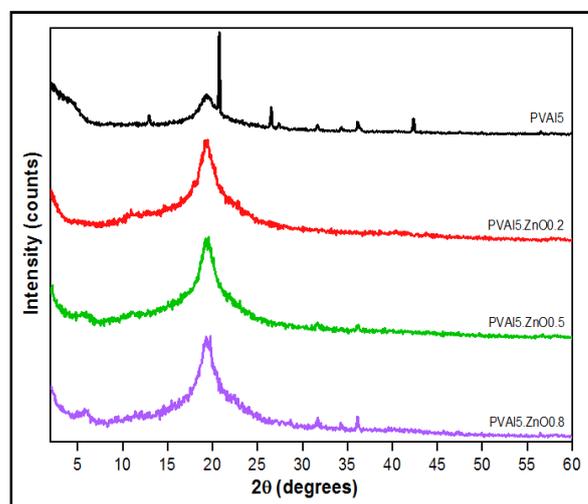


Figure 14. XRD patterns of PVA15, PVA15.ZnO0.2, PVA15.ZnO0.5 and PVA15.ZnO0.8

Figure 13 illustrates the XRD curves for pure PVAI and mixed with bentonite in different concentrations. For 2θ between 19.2° and 19.5° , the increase in the bentonite content contributes to a higher peak PVAI intensity value, indicating that the material formed has a different structural organization than PVAI. It is important to note that no peak is observed for samples containing clay in the range of 2θ less than 5.95° , indicating that they were well dispersed in the polymeric matrix, being able to be in both forms, intercalated and exfoliated (Chang *et al.*, 2003). The hydroxyl functional groups of PVAI interact strongly with the negative charges present in the bentonite, providing a good interaction between the filler and the matrix and, therefore, causing an increase in its basal spacing, facilitating the generation of intercalated and exfoliated materials (Mondal *et al.*, 2013). Figure 14 shows only the ZnO added to the PVAI. It is possible to observe that there was an increase in intensity with the addition of ZnO, in the range of 2θ between 19.3° and 19.8° , confirming that, in the same case of clay, ZnO also interferes in the structural organization of the formed system, due to the new and strong interactions between the nanoparticle and the matrix. For this same interval, the higher the ZnO concentration, the lower the intensity value. In addition, for 2θ greater than 25° , the crystalline peaks that appeared in the pure ZnO nanoparticles disappeared in the PVAI5.ZnO0.2 spectrum. In the case of the PVAI5.ZnO0.5 sample, most of the peaks also disappeared and those detected showed a very small intensity value. This is due to the good dispersion of these nanoparticles at the molecular level (Chandrakala *et al.*, 2013). In the PVAI5.ZnO0.8 spectrum, the peaks reappear, indicating that there may have been ZnO agglomeration for higher concentrations of it in the nanocomposite. The inclusion of ZnO nanoparticles in systems that already contain 1% clays is shown in Figure 15.

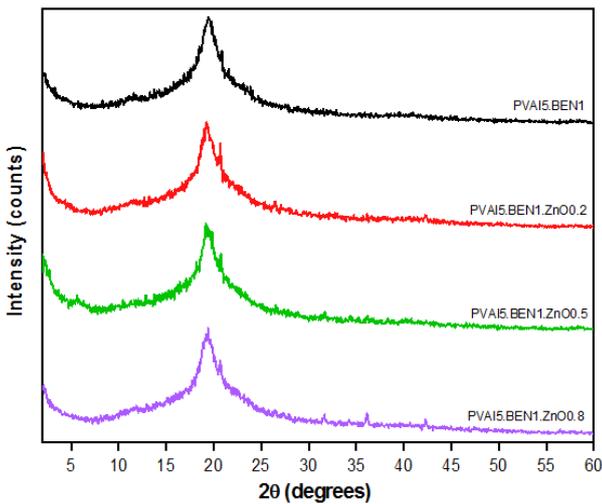


Figure 15. XRD patterns of PVAI5.BEN1, PVAI5.BEN1.ZnO0.2, PVAI5.BEN1.ZnO0.5 and PVAI5.BEN1.ZnO0.8

The increase in the ZnO nanoparticle raises the value of the peak intensity located at 2θ in the range of 19.1° to 19.4° . The opposite effect occurs for the 0.5% ZnO nanoparticle, indicating that ZnO also forms strong interactions with the polymeric matrix, thus influencing its structural organization. The absence of a peak for 2θ below 5.95° of the samples PVAI5.BEN1.ZnO0.2 and PVAI5.BEN1.ZnO0.8 suggests that the clay exfoliation may have occurred, that is, the polymeric chains and ZnO managed to permeate through the galleries, increasing the interlamellar spaces and providing the opening, separation and consequent disorder of the clay sheets (Fu; Qutubuddin, 2000; Arora; Padua, 2010; Sapalidis *et al.*, 2012). In Figure 16, there is a drastic reduction in the degree of organization of PVAI5.BEN3.ZnO0.5 nanocomposite. The decrease in the peak of PVAI may indicate that there was the formation of a new phase, caused by a better dispersion and interaction of the nanoparticles with the PVAI matrix, causing a change in these molecular structures (El-Tantawy *et al.*, 2004). In addition, the absence of peaks, in values of 2θ below 5.95° , in the sample PVAI5.BEN3.ZnO0.5 indicates that clay exfoliation may have occurred. No peaks are observed for values

of 2θ below 5.95° , in the nanocomposites PVAI5.BEN3.ZnO0.2 and PVAI5.BEN3.ZnO0.8, characterizing the existence of intercalated and possibly exfoliated clay (Zhu *et al.*, 2007). With a very large difference from the others, the spectrum of the nanocomposite PVAI5.BEN5.ZnO0.5 indicates that the polymer has become predominantly amorphous, with a very low intensity peak at $2\theta = 18.7^\circ$ (Figure 17).

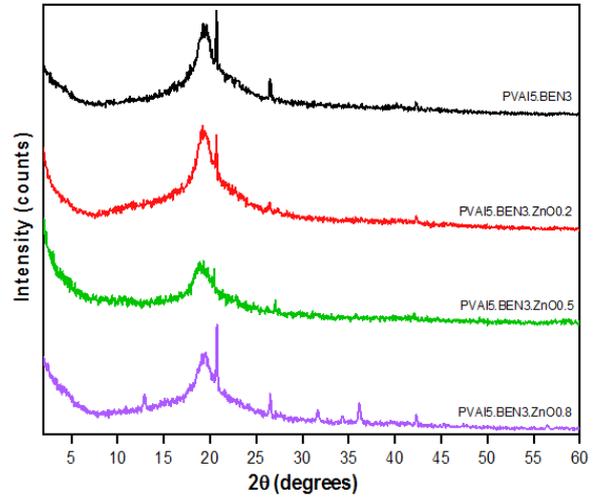


Figure 16. XRD patterns of PVAI5.BEN3, PVAI5.BEN3.ZnO0.2, PVAI5.BEN3.ZnO0.5 and PVAI5.BEN3.ZnO0.8

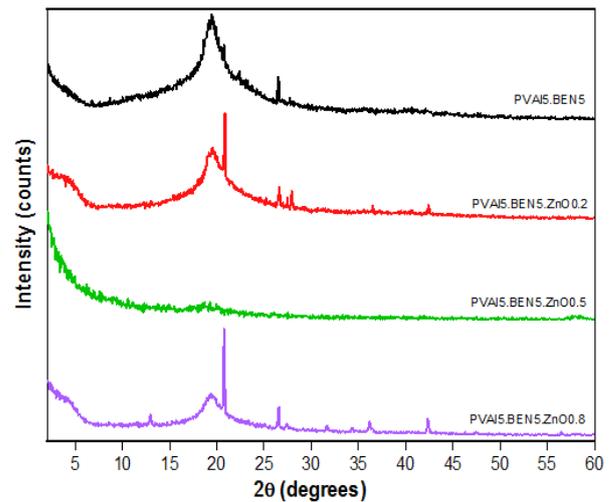


Figure 17. XRD patterns of PVAI5.BEN5, PVAI5.BEN5.ZnO0.2, PVAI5.BEN5.ZnO0.5 and PVAI5.BEN5.ZnO0.8

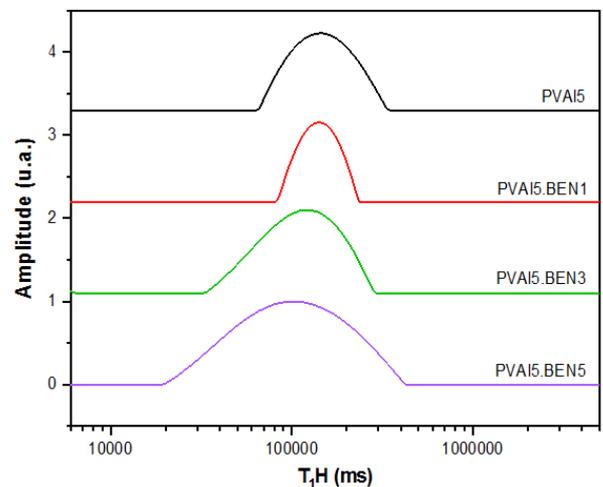


Figure 18. Domain curves of nanocomposites PVAI5, PVAI5.BEN1, PVAI5.BEN3 and PVAI5.BEN5

This suggests that this concentration of ZnO provided such a strong interaction between bentonite and PVAI that they dispersed very well, to the point where the PVAI chains and the clay leaves disorganized. Both the sample PVAI5.BEN5.ZnO0.2 and PVAI5.BEN5.ZnO0.8 showed a smooth peak at angles of 2θ less than 5.95° , also suggesting the presence of the intercalated clay. It was observed that, for both PVAI5.BEN3.ZnO0.5 and PVAI5.BEN5.ZnO0.5 nanocomposites containing 0.5% ZnO, highly amorphous nanostructured systems were generated, indicating the existence of a synergistic effect that contributed to a better interaction and consequent dispersion of the components.

Time-domain nuclear magnetic resonance: From the Time-Domain Nuclear Magnetic Resonance (TD-NMR) technique, information about the molecular mobility of the desired sample can be obtained, that is, whether the sample is rigid or flexible. One of the possible data obtained is that of longitudinal relaxation, by determining the value of the spin-rede relaxation time of the hydrogen nucleus (T_{1H}). Generally, lower values for T_{1H} are related to the high molecular mobility domain (BARBOSA, 2010). Table 2 shows the T_{1H} values for the starting materials and the nanocomposites.

Table 2. T_{1H} of hydrogen for pure reagents and nanocomposites.

| Sample | T_{1H} (ms) |
|-------------------|---------------|
| PVAI5 | 144 |
| PVAI5.BEN1 | 131 |
| PVAI5.BEN3 | 96 |
| PVAI5.BEN5 | 89 |
| PVAI5.ZnO0.2 | 141 |
| PVAI5.ZnO0.5 | 141 |
| PVAI5.ZnO0.8 | 142 |
| PVAI5.BEN1.ZnO0.2 | 142 |
| PVAI5.BEN1.ZnO0.5 | 125 |
| PVAI5.BEN1.ZnO0.8 | 116 |
| PVAI5.BEN3.ZnO0.2 | 106 |
| PVAI5.BEN3.ZnO0.5 | 89 |
| PVAI5.BEN3.ZnO0.8 | 101 |
| PVAI5.BEN5.ZnO0.2 | 75 |
| PVAI5.BEN5.ZnO0.5 | 85 |
| PVAI5.BEN5.ZnO0.8 | 81 |

T_{1H} value can be used to verify the presence of exfoliated and/or intercalated clays. If the T_{1H} of the analyzed nanocomposite increases in relation to the pure polymer, an intercalated material tends to be formed predominantly. However, if there is a reduction, a material obtained tends to be predominantly in the exfoliated state (ALMEIDA *et al.*, 2012). The systems containing the clay and both nanoparticles showed a reduction in T_{1H} compared to PVAI, showing that these nanoparticles affected the molecular dynamics of this polymer. Through the data presented in Table 2, it can be seen that, with the insertion of bentonite in the PVAI5.BEN_x systems, there was a decrease in T_{1H} compared to PVAI, showing that there was a predominance of the exfoliation process. This is due to the clay has paramagnetic metals in its structure, which, when close to the hydrogen atoms in the sample, cause a decrease in the value of T_{1H} because they are relaxation agents. If the clays were agglomerated or intercalated, there would be no interference by these metals on the hydrogens. Consequently, there would be no reduction in T_{1H} , and may even increase. In the incorporation of ZnO to PVAI, it is observed that the non-variation of T_{1H} of PVAI5.ZnO_x systems indicates that the polymeric matrix interacts differently with ZnO.

Analyzing the nanocomposites PVAI5.BEN1.ZnO_x and comparing them with PVAI5.BEN1, there was an increase in T_{1H} for the concentration of 0.2% ZnO, indicating the influence and predominance of the intercalated clay. In 0.5% and 0.8% there were reductions in T_{1H} , which are associated with the exfoliation process, this effect being greater for the concentration of 0.8%. The PVAI5.BEN3.ZnO_x nanocomposites showed that there was a more pronounced reduction in T_{1H} than in the PVAI5.BEN1.ZnO_x system. When linking PVAI5.BEN3.ZnO_x with PVAI5.BEN3, concentrations of 0.2% and 0.8% provided an increase in T_{1H} , suggesting that they induce the predominance of clay in the intercalated state. It is possible

to observe that the relaxation times of the PVAI5.BEN5.ZnO_x system were the smallest. In comparison with the nanocomposite PVAI5.BEN5, all ZnO contents contributed to a greater exfoliation process of the clays. This indicates that an increase in the concentration of bentonite is necessary to provide a better dispersion of its sheets and PVAI chains, causing an increase in the degree of exfoliation, in addition to an increase in the amount of ZnO to contribute even more to this dispersion, generating the synergistic effect. The clay exfoliation process occurred mainly in nanocomposites containing 3% and 5% bentonite, due to the synergistic effect of both nanoparticles.

When analyzing the systems with the two nanoparticles, but keeping the ZnO content fixed and changing only that of the bentonite, for the samples PVAI5.BEN_x.ZnO0.2, the increase in the concentration of the clay caused the reduction of T_{1H} . However, the nanocomposite PVAI5.BEN1.ZnO0.2 showed a higher T_{1H} , suggesting the predominance of clay in the intercalated state. Analyzing the PVAI5.BEN_x.ZnO0.5 system, the addition of the clay provided a decrease in T_{1H} , being very pronounced for concentrations of 3% and 5%, showing that these proportions of bentonite and 0.5% ZnO have a synergistic effect in order to provide a high dispersion of the system. The PVAI5.BEN_x.ZnO0.8 samples showed the same trend. The increase in the clay content reduced T_{1H} in all of these samples, with a greater effect for the nanocomposite containing 5% bentonite, suggesting that this concentration is good to enable a good interaction with PVAI and ZnO. From this, it can be concluded that bentonite contributed to a better dispersion of the system than ZnO nanoparticles. The nanocomposite systems were also evaluated using the relaxation domain curves (Figures 18 to 22). These Figures show the nanocomposite domain curves. The wider peak tends to greater the degree of disorder in the system. Thinner peaks indicate the presence of a more organized system. In Figure 18, the addition of 1% clay showed a new organization and the narrowing of its peak of the relaxation curve, in relation to pure PVAI, showed that the system became more organized. At concentrations of 3% and 5%, there was a widening of the peak, indicating disorders in the organization, typical of heterogeneous systems that contain intercalation and exfoliation, but more predominantly exfoliation.

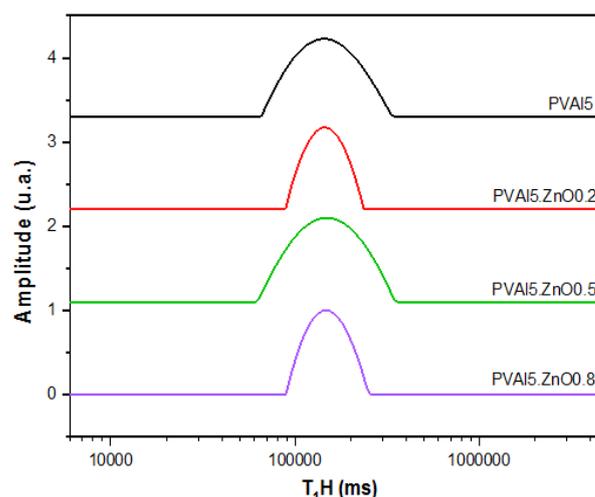


Figure 19. Domain curves of nanocomposites PVAI5, PVAI5.ZnO0.2, PVAI5.ZnO0.5 and PVAI5.ZnO0.8

Figure 19, which shows the effect of the ZnO nanoparticle, when added alone, reveals that the base of the nanocomposite containing 0.5% ZnO is wider, with less organization and suggesting multiple interactions between ZnO and polymer chains. For the proportions of 0.2% and 0.8%, the behavior was like PVAI, showing that these proportions of ZnO did not significantly affect molecular mobility. The curves in Figure 20 show that nanocomposites containing two nanoparticles have an extension indicating a heterogeneous system, favored by the insertion of ZnO. The curves in Figure 21 indicate that the nanocomposites with levels of 0.2% and 0.8% of ZnO showed an

enlargement of the base, different from 0.5%, which presented a better organization.

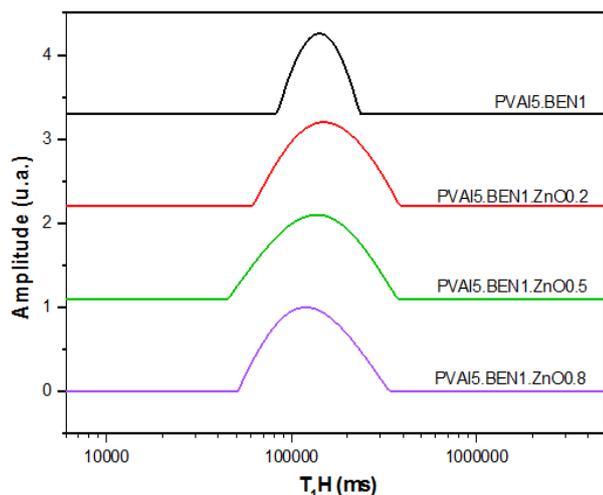


Figure 20. Domain curves of nanocomposites PVAI5, PVAI5.BEN1, PVAI5.BEN1.ZnO0.2, PVAI5.BEN1.ZnO0.5 and PVAI5.BEN1.ZnO0.8

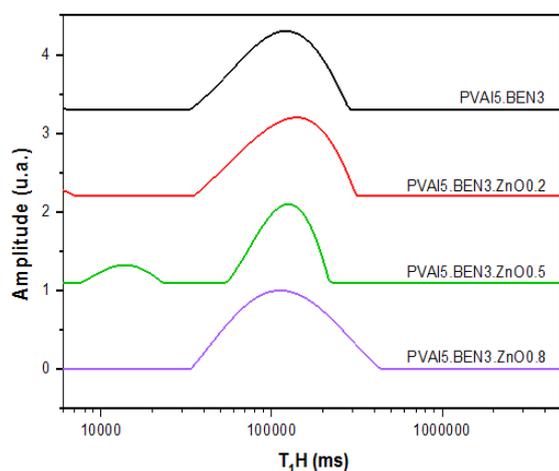


Figure 21. Domain curves of nanocomposites PVAI5.BEN3, PVAI5.BEN3.ZnO0.2, PVAI5.BEN3.ZnO0.5 and PVAI5.BEN3.ZnO0.8

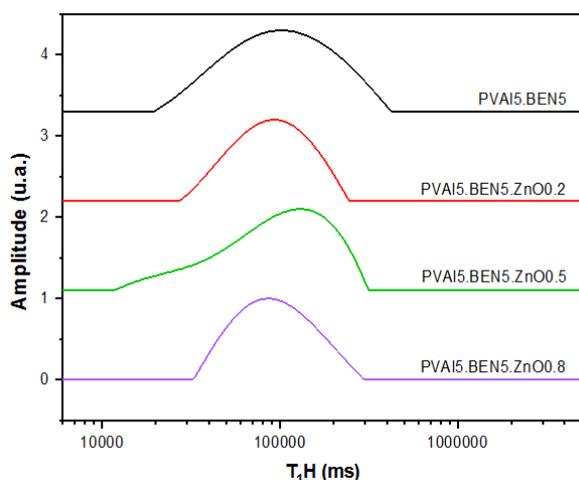


Figure 22: Domain curves of nanocomposites PVAI5.BEN5, PVAI5.BEN5.ZnO0.2, PVAI5.BEN5.ZnO0.5 and PVAI5.BEN5.ZnO0.8

This data corroborates with that presented by XRD, which showed a predominance of clay in the exfoliated state. The smallest peaks shown in the curves for the PVAI5.BEN3.ZnO0.2 and PVAI5.BEN3.ZnO0.5 nanocomposites refer to the presence of water in the system. Evaluating the relaxation curves of Figure 22, it is

observed that the formed systems suffered ZnO action, generating disorganized hybrid systems.

CONCLUSIONS

The nanocomposite films containing PVAI, bentonite and ZnO, produced in solution, were successfully obtained. It was observed that the bentonite nanomaterials were found in intercalated and / or exfoliated form, varying according to the concentration of the sample components. TG analyzes showed that the addition of bentonite nanomaterials and ZnO nanoparticles altered the degradation profile of the nanocomposites, reducing the stability of these systems. The XRD data showed the possibility of the existence of exfoliated forms in some systems, which could be verified through the results of TD-NMR. The nanocomposites PVAI5.BEN3.ZnO0.5 and PVAI5.BEN5.ZnO0.5 proved to be highly random, in comparison with the others, indicating the synergistic effect between these two nanoparticles. This property presented by the two nanocomposites allows its applicability in drug delivery systems, since a highly random system, which already contains the drug, would delay the diffusion of these drugs to the outside environment, contributing to a more controlled and lasting release of drugs.

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