

## Comparative analysis of electrospun PNIPAAm blends with some biodegradable polymers

Liege Aguiar Pascoalino<sup>1</sup>, Breno Augusto Tabosa Thome da Silva<sup>2</sup>,  
Ricardo Luiz de Souza<sup>1</sup>, Priscila Schroeder Curti<sup>1</sup>

<sup>1</sup>Chemistry Academic Department, Federal Technological University of Parana, Campus Londrina, Av. dos Pioneiros, 3131, CEP: 86036-370, Jardim Morumbi, Londrina, Parana, Brazil

<sup>2</sup>Post-graduate Program in Materials Science and Engineering, Federal Technological University of Parana, Campus Londrina, Av. dos Pioneiros, 3131, CEP: 86036-370, Jardim Morumbi, Londrina, Parana, Brazil  
e-mail: priscilacurti@utfpr.edu.br

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### ABSTRACT

In this work, electrospun fibers of poly(butylene adipate-co-terephthalate)/poly(N-isopropylacrylamide), PBAT/PNIPAAm, and ecovio<sup>®</sup>/PNIPAAm blends were obtained. These blends presented a thermoresponsive behavior including a sudden response to temperature variation between 32 and 35 °C. The addition of PNIPAAm to PBAT and ecovio<sup>®</sup> solutions significantly improved the electrospinnability of both solutions as blends, allowing them to form rounded fibers without defects and with diameters varying between 1000 and 1700 nm. The analysis of attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) spectra for PBAT/PNIPAAm and ecovio<sup>®</sup>/PNIPAAm electrospun fibers revealed that the electrospinning process does not lead to the formation of strong intermolecular interactions, such as hydrogen bonds, between the constituents of the studied blends' electrospun fibers. Significant drop water contact angle variation as a function of temperature was observed for both PBAT/PNIPAAm and ecovio<sup>®</sup>/PNIPAAm electrospun fibers; both presented PNIPAAm's hydrophilic-hydrophobic transition in the range between 32 and 35 °C. Comparing PBAT/PNIPAAm and ecovio<sup>®</sup>/PNIPAAm electrospun fibers, the former was revealed to be more temperature-sensitive than the latter, regarding changes in wettability as the former presented larger gaps in drop water contact angle values compared to the latter. With these results, these blends in the form of electrospun fibers may have a potential application in the field of cell adhesion/detachment.

**Keywords:** PBAT, ecovio<sup>®</sup>, PNIPAAm, blends, fibers.

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### 1. INTRODUCTION

The electrospinning technique has been increasingly exploited, especially in the last two decades, in order to produce continuous, uniform polymer fibers with a high area/volume ratio and diameters at the micro- and nanometric scales [1]. This technique presents a relatively simple and inexpensive yet highly versatile experimental apparatus. With the proper adjustment of experimental parameters, it is possible to produce fibers with specific morphologies and properties. Several types of polymers, both natural [2-4] and synthetic [5-8], have been subjected to electrospinning using different experimental conditions in order to obtain fibrous materials with a high area/volume ratio. The resulting fibers present specific properties for application in many areas, such as tissue engineering [9], biomedicine [10, 11], drug delivery [4, 12], and wound dressing [8, 13, 14], among others.

Recently, synthetic and biodegradable aliphatic polyesters have been studied using the electrospinning technique [15-18], which is probably due to the good control of their degradation processes. Numerous papers report electrospinning studies using poly(butylene adipate co-terephthalate) (PBAT) [5, 9, 19-25], a synthetic and compostable biodegradable polyester produced by BASF. The balance between aliphatic and aromatic chemical groups present in the repeating unit of this polymer provides interesting properties, such as flexibility, elongation at break, and low crystallinity [9, 22].

Ecovio<sup>®</sup> is the trade name of a polymer blend also produced by BASF. It consists of two biodegradable polymers: PBAT and poly(lactic acid) (PLA), where the latter is a linear aliphatic polyester. The presence of PLA in ecovio<sup>®</sup> enhances its mechanical resistance while the presence of PBAT boosts the

elastic modulus of the blend as a whole [26]. Literature searches reveal papers that report the intent of producing ecovio<sup>®</sup> composites in order to improve their mechanical properties [26-29]. Until this moment, there is also a work which presents studies on the electrospinning of ecovio<sup>®</sup> [30].

In some polymers, alteration of a property such as color, conformation, solubility, etc., may be a response to being subjected to certain external stimuli, which may include, among others, temperature [8, 31], light [32, 33], electric or magnetic fields [17, 34], and pH [31, 35]. Such polymers are called smart polymers and they can be applied in many areas, for example, in filtration [36, 37], cell growth/detachment [38, 39], and sensors [33, 40], as well as those already mentioned above (drug delivery, tissue engineering scaffolds, wound dressing, and biomedicine). Electrospinning as a method of processing for obtaining smart polymers (particles, films, membranes, and others) has attracted a lot of attention. This is because smart polymers, when processed into a fiber form, can respond much faster to an applied external stimulus due to having a greater surface area available to interact and respond to the external stimulus.

Poly(N-isopropylacrylamide), PNIPAAm, is a smart and biocompatible synthetic polymer that presents a hydrophilic-hydrophobic thermoresponsive phase transition around 32 °C, known as its lower critical solution temperature (LCST) [41]. Below the LCST, PNIPAAm is soluble in an aqueous medium as a result of the presence of intermolecular hydrogen bonding interactions between water molecules and the C=O and N-H hydrophilic groups of PNIPAAm's amide side chains. Above the LCST, PNIPAAm's C=O and N-H amide groups undergo conformational contraction, in which intramolecular interactions between these groups become more favorable, leaving the hydrophobic N-isopropyl groups more exposed, turning this polymer insoluble in an aqueous medium [8, 41, 42]. This hydrophilic-hydrophobic transition is reversible. Since PNIPAAm's LCST occurs close to the human body temperature, this polymer has been extensively studied for controlled release, cell growth/detachment, and biomedicine [8, 43-45], among other areas, because it presents good cellular adhesion at temperatures above its LCST; similarly, this adhesion gets weaker spontaneously below its LCST. In the recent years, many electrospinning studies have been performed on PNIPAAm, either in pure solution or associated with other polymers [8, 42, 44-48].

Thus, considering the interesting properties presented by PBAT, ecovio<sup>®</sup> and PNIPAAm, this report presents a study carried out on the electrospinning of PBAT/PNIPAAm and ecovio<sup>®</sup>/PNIPAAm solutions, in different mass ratios. Evaluation of both their morphology and structural properties was carried out by scanning electron microscopy (SEM) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), respectively. In addition, a wettability evaluation of the surfaces of both PBAT/PNIPAAm and ecovio<sup>®</sup>/PNIPAAm blends was performed by drop water contact angle (DWCA) as a function of temperature. This technique would allow the verification of the mass ratio at which the PNIPAAm would turn the fiber thermosensitive, considering the potential application of these electrospun fibers for the cell adhesion/detachment field.

## 2. MATERIALS AND METHODS

### 2.1 Materials

Pellets of PBAT (Ecoflex<sup>®</sup> F BX 7011, average molecular weight of 40 kg·mol<sup>-1</sup>) and ecovio<sup>®</sup> (F-Blend C2224, which consists of 55% of Ecoflex and 45% of PLA average molecular weight of 40 kg·mol<sup>-1</sup>) were kindly supplied by BASF. The solvents used to prepare polymeric solutions were: chloroform (CHCl<sub>3</sub>) (Alfathec) and N,N-dimethylformamide (DMF) (F. Maia). All reagents were used as received. The PNIPAAm used in this study was synthesized via radical polymerization in aqueous solution using Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as initiator, as described in previous work [25]. The dilute solution viscosimetry technique was carried out to estimate the PNIPAAm's average molecular weight ( $\bar{M}_V$ ) in aqueous solution at 25 °C using the Mark-Houwink equation,  $[\eta] = K\bar{M}_V^\alpha$ . The values for the  $\alpha$  and K constants used were 0.97 and 2.26 x 10<sup>-4</sup> cm<sup>3</sup>·g<sup>-1</sup>, respectively. The ( $\bar{M}_V$ ) value estimated using this technique for PNIPAAm was 8.7 x 10<sup>5</sup> g·mol<sup>-1</sup>.

### 2.2 Preparation and Electrospinning of PBAT/PNIPAAm and ecovio<sup>®</sup>/PNIPAAm Blends' Solutions

Solutions of PBAT/PNIPAAm and ecovio<sup>®</sup>/PNIPAAm with different mass ratios (m/m) were prepared using a solvent mixture consisting of CHCl<sub>3</sub>/DMF at the volume ratio (V/V) of 85/15 [49]. Studies on the optimization of experimental parameters for electrospinning have previously been performed [25, 50]. All polymeric solutions were prepared at the concentration of 10% (m/V). The electrospinning experiments were performed at a temperature and relative humidity of 22 °C and 55%, respectively, using a high voltage source (maximum of 30 kV), a syringe attached to an infusion pump (KD Scientific – 100) and a grounded collector

consisting of a static circular metal plate [25]. The experimental parameters for electrospinning solutions of PBAT/PNIPAAm and ecovio<sup>®</sup>/PNIPAAm blends are presented in Table 1.

**Table 1:** Electrospinning experimental parameters, average diameter and standard deviation for samples of PBAT/PNIPAAm and ecovio<sup>®</sup>/PNIPAAm blends' electrospun fibers.

Sample	Voltage [kV]	Flow rate [mL h <sup>-1</sup> ]	Distance [cm]	Average diameter [nm]	Standard deviation [nm]
PBAT/PNIPAAm 100/0	25	1.3	15	320.4	± 78.9
PBAT/PNIPAAm 90/10	25	1.3	15	214.8	± 43.4
PBAT/PNIPAAm 70/30	25	1.3	15	1001.7	± 121.2
PBAT/PNIPAAm 50/50	25	1.3	15	1394.1	± 277.5
PBAT/PNIPAAm 0/100	25	1.3	15	1309.1	± 176.1
ecovio <sup>®</sup> /PNIPAAm 100/0	15	1.0	25	–	–
ecovio <sup>®</sup> /PNIPAAm 85/15	15	1.0	25	276.6	± 97.6
ecovio <sup>®</sup> /PNIPAAm 70/30	15	1.0	25	1691.7	± 328.9
ecovio <sup>®</sup> /PNIPAAm 50/50	15	1.0	25	1429.8	± 314.0
ecovio <sup>®</sup> /PNIPAAm 0/100	15	1.0	25	1379.3	± 203.9

### 2.3 Characterization of PBAT/PNIPAAm and ecovio<sup>®</sup>/PNIPAAm Electrospun Fibers

The morphology characterization of the PBAT/PNIPAAm and ecovio<sup>®</sup>/PNIPAAm electrospun fibers was accomplished by SEM using an FEI microscope (Quanta 200 model). Prior to analysis, all fibers were covered with a thin layer of gold. The average diameter of the electrospun fibers, estimated directly from the SEM images, was evaluated using Sizermeter 1.1 software. All images were analyzed by measuring at least 20 fibers in triplicate.

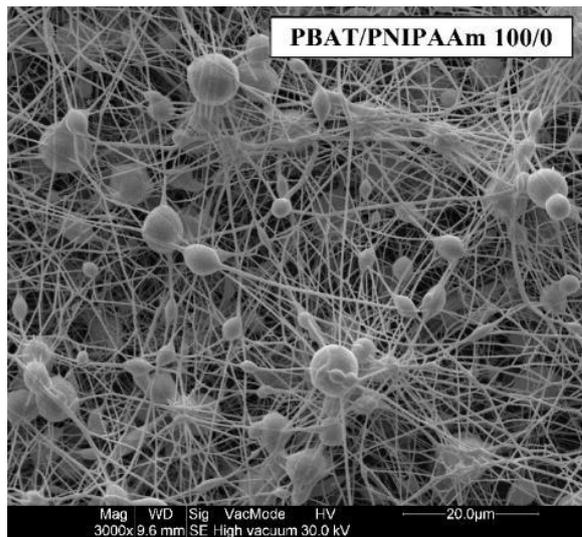
Structural analysis of the PBAT/PNIPAAm and ecovio<sup>®</sup>/PNIPAAm electrospun fibers was carried out by ATR-FTIR using a Perkin-Elmer Spectrum Two spectrometer with a Universal ATR accessory (UATR). The ATR-FTIR spectra were obtained in transmittance mode in the wave number range of 450-4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>.

The surface wettability of the PBAT/PNIPAAm and ecovio<sup>®</sup>/PNIPAAm electrospun fibers was evaluated by drop water contact angle (DWCA) measurements by depositing a deionized drop of water onto the surface of the electrospun fibers. The DWCA measurements were analyzed using ImageJ software. At 5 °C intervals over the temperature range of 20 °C to 45 °C, estimations of DWCA measurements were taken six times at different points on the surfaces of the electrospun fibers.

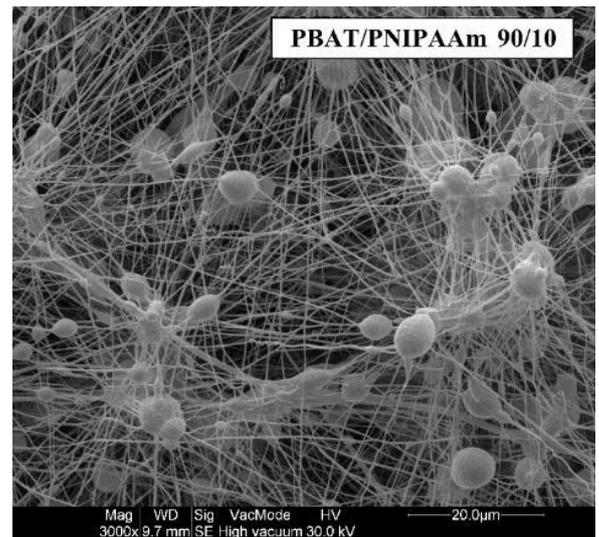
## 3. RESULTS AND DISCUSSION

### 3.1 Scanning Electron Microscopy (SEM)

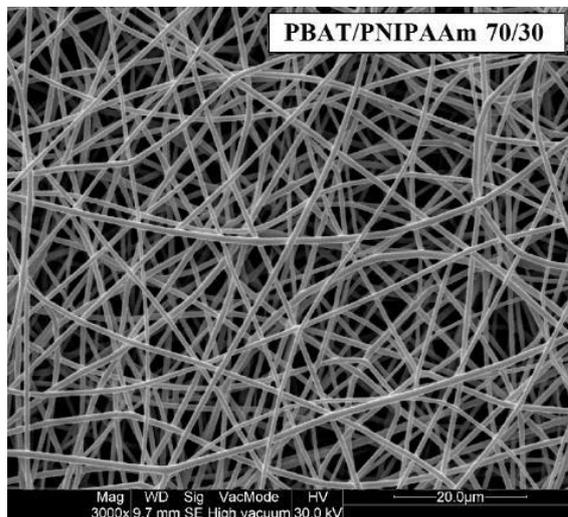
An optimized set of experimental parameters for electrospinning PBAT/PNIPAAm and ecovio<sup>®</sup>/PNIPAAm fibers has previously been developed [25, 50]. Figure 1 and 2 shows SEM images for PBAT/PNIPAAm and ecovio<sup>®</sup>/PNIPAAm electrospun fibers, respectively.



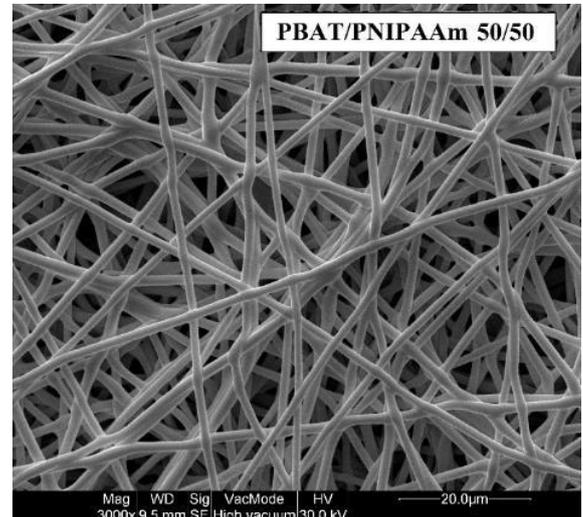
(a)



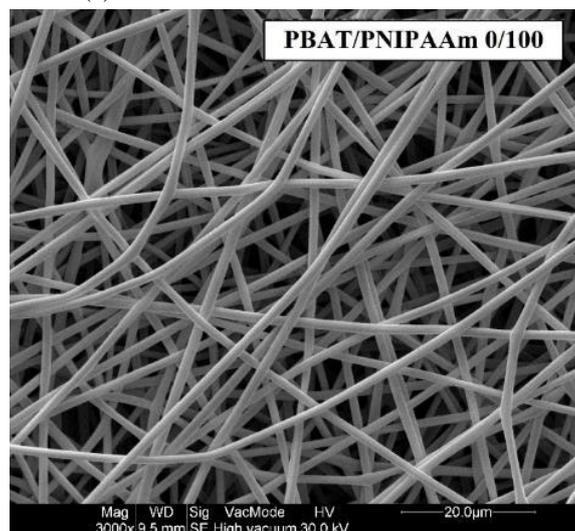
(b)



(c)



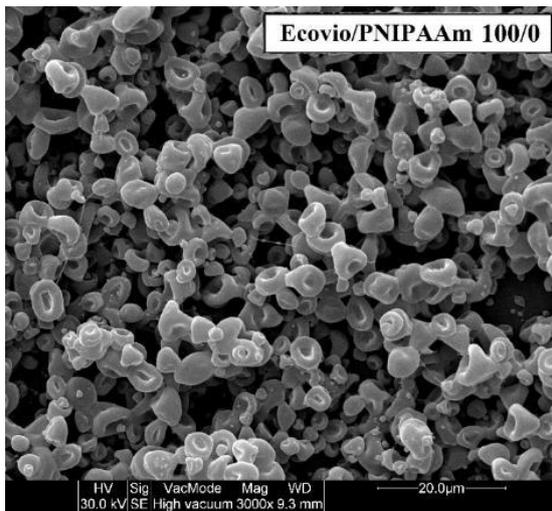
(d)



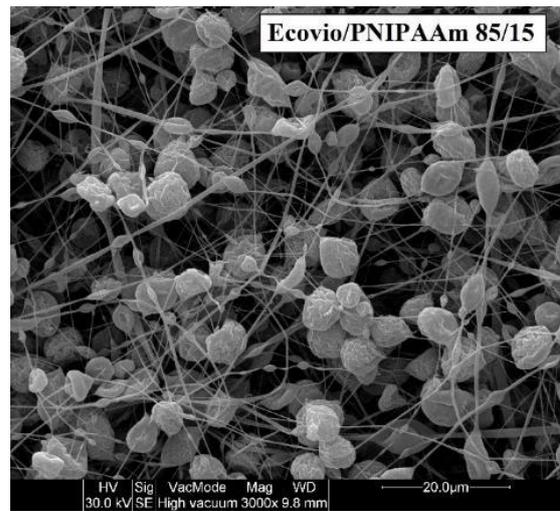
(e)

**Figure 1:** SEM micrographs for PBAT/PNIPAAm electrospun fibers with mass ratio of: (a) 100/0, (b) 90/10,

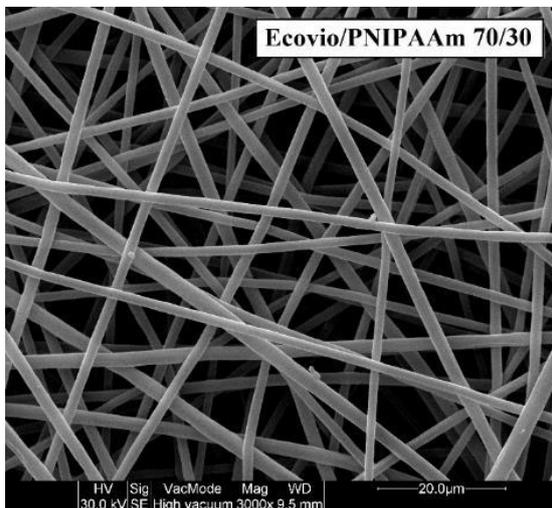
(c) 70/30, (d) 50/50 and (e) 0/100.



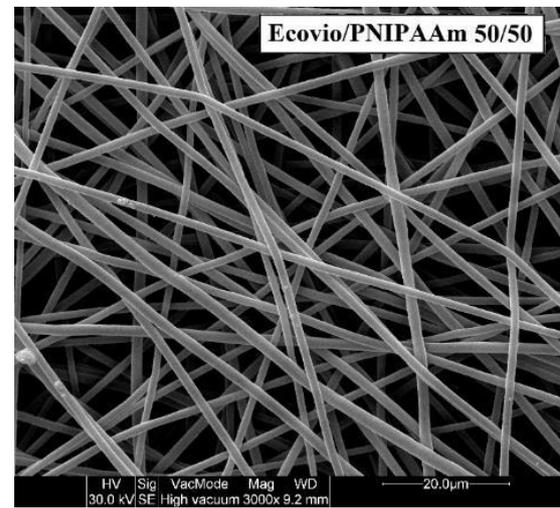
(a)



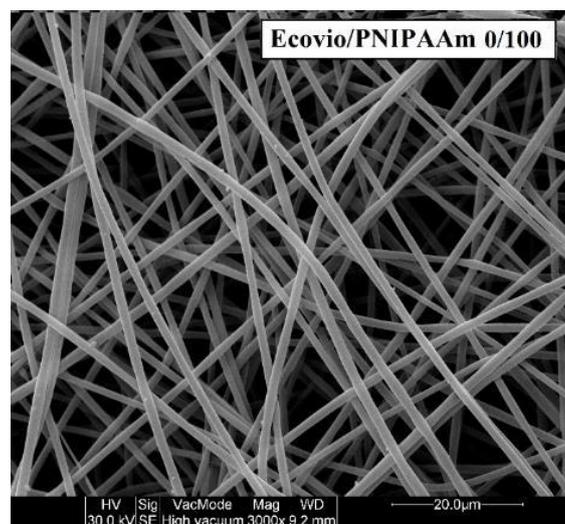
(b)



(c)



(d)



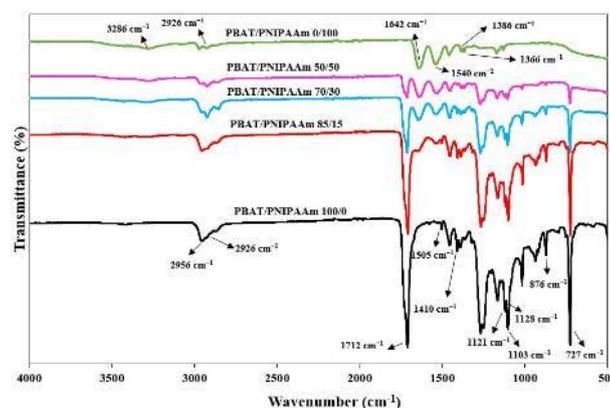
(e)

**Figure 2:** SEM micrographs for ecovio@PNIPAAm electrospun fibers with mass ratio of: (a) 100/0, (b) 85/15, (c) 70/30, (d) 50/50 and (e) 0/100.

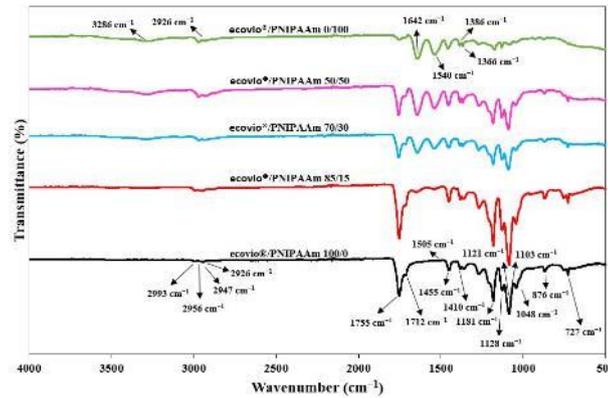
It was possible to observe that pure solutions of both PBAT and ecovio<sup>®</sup> presented low electrospinnability. In addition, the electrospinning of a pure PBAT solution at a concentration of 10% resulted in fibers with an average diameter in the region of 300 nm (Table 1), but with the presence of many beads; on the other hand, the electrospinning of a pure ecovio<sup>®</sup> solution at a concentration of 10% resulted in no fibers formation. An interesting result was observed when both PBAT and ecovio<sup>®</sup> solutions were mixed with PNIPAAm at a mass ratio of 30%. From this mass ratio of PNIPAAm, the morphology of the blends formed with PBAT (Figure 1c and 1d) and ecovio<sup>®</sup> (Figure 2c and 2d) significantly improved, so that the electrospun fibers became rounded and lacked beads. In this case, the main effect associated with the improvement in fiber morphology and the increase in average diameter is the fact that PNIPAAm presents a higher molar mass value than both PBAT and ecovio<sup>®</sup>, which, in turn, increases the solution viscosity and consequently improves the electrospinning process due to the greater entanglement between the polymer chains in solution. The increase in average diameter for the electrospun fibers containing PNIPAAm at a minimum mass ratio of 30% in the blend was enough so that these fibers could reach the micrometric range, as can be seen in Table 1. For the PBAT/PNIPAAm blends, the average diameter of the electrospun fibers reached the range between 1000 and 1400 nm; likewise, the average diameter of the electrospun fibers from ecovio<sup>®</sup>/PNIPAAm blends reached the range between 1400 and 1700 nm. Thereby, electrospun fibers from both the PBAT/PNIPAAm and ecovio<sup>®</sup>/PNIPAAm blends presented an average diameter closer to that of the pure PNIPAAm electrospun fibers (around 1300 to 1380 nm).

### 3.2 Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR)

Figure 3 and 4 presents the ATR-FTIR spectra for electrospun fibers from PBAT/PNIPAAm and ecovio<sup>®</sup>/PNIPAAm blends with different mass ratios, respectively. The main absorption bands in the PBAT's ATR-FTIR spectrum (Figure 3) were: 2956 cm<sup>-1</sup>, related to the stretching of CH<sub>2</sub> groups; 2926 cm<sup>-1</sup>, related to the symmetric stretching of CH groups; 1712 cm<sup>-1</sup>, related to the C=O of ester groups; 1505 cm<sup>-1</sup> and 876 cm<sup>-1</sup>, related to the stretching and bending of =CH of phenyl groups, respectively; 1410 cm<sup>-1</sup>, related to the bending of CH<sub>2</sub>; 1128 cm<sup>-1</sup>, related to the stretching of C–O of ester groups; 1103/1121 cm<sup>-1</sup>, related to the stretching of C–O–C of ester groups; 727 cm<sup>-1</sup>, related to the bending of C–H of phenyl groups. Nevertheless, the main FTIR bands that could be used to identify PBAT were at 1712 cm<sup>-1</sup>, 1103 cm<sup>-1</sup> and 727 cm<sup>-1</sup> [21]. It was possible to observe the absorption bands related to PLA in the ATR-FTIR spectra for the electrospun fibers of pure ecovio<sup>®</sup> (Figure 4): 2993 cm<sup>-1</sup> and 2947 cm<sup>-1</sup>, which were related to the asymmetric and symmetric stretching of CH<sub>3</sub> groups, respectively; 1755 cm<sup>-1</sup>, a characteristic band for the stretching of C=O groups; 1455 cm<sup>-1</sup>, related to the bending of CH<sub>3</sub> groups; 1181/1048 cm<sup>-1</sup>, related to the stretching of C–O–C groups [51]. These were in addition to the characteristic absorption bands of PBAT. The following bands could be observed in the ATR-FTIR spectrum of PNIPAAm (Figure 3 and 4): an absorption band at 3286 cm<sup>-1</sup>, related to the stretching of N–H groups; 2926 cm<sup>-1</sup>, due to the symmetric stretching of C–H groups; two relatively broad bands at 1642 cm<sup>-1</sup> and 1540 cm<sup>-1</sup>, characteristic of the stretching of C=O groups and N–H deformation of amide groups, respectively, and two small absorption bands at 1386 cm<sup>-1</sup> and 1366 cm<sup>-1</sup>, which were related to the stretching of the CH<sub>3</sub> of PNIPAAm's isopropyl groups [52]. Therefore, from the ATR-FTIR spectra obtained in this study, it was possible to observe the presence of the characteristic bands for PBAT (Figure 3) [21], ecovio<sup>®</sup> (Figure 4) [51], and PNIPAAm (Figure 3 and 4) [52].



**Figure 3:** ATR-FTIR spectra for PBAT/PNIPAAm electrospun fibers with different mass ratios.

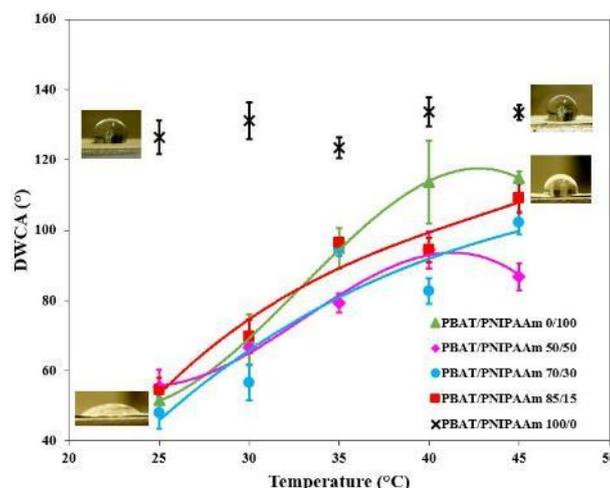


**Figure 4.** ATR-FTIR spectra for ecovio<sup>®</sup>/PNIPAAm electrospun fibers with different mass ratios.

Analysis of all presented spectra revealed that no shift occurred to any of the absorption bands of the polymers that were employed for electrospinning. Thus, this result indicated that there was no formation of strong intermolecular interactions, like hydrogen bonds, between the oxygen from PBAT's and ecovio<sup>®</sup>'s carbonyl groups and the hydrogen from PNIPAAm's amide groups in the PBAT/PNIPAAm and ecovio<sup>®</sup>/PNIPAAm blends' electrospun fibers. In this case, the fact that there are no strong intermolecular interactions, such as hydrogen bonding, between the nitrogen of PNIPAAm's amide group and the carbonyl groups present in both PBAT and ecovio<sup>®</sup> is a great advantage for the electrospun fibers of their blends. The reason is that PNIPAAm's amide groups are free to shrink or expand as the temperature of the medium gets above or below its LCST, respectively.

### 3.3. Drop Water Contact Angle (DWCA) Measurements

The wettability of a solid surface can be determined by measuring the contact angle formed between a drop of a liquid and the solid surface. Consequently, wettability depends on the relationship between the adhesive forces of a solid-liquid system and the cohesive forces of the liquid. Figure 5 shows the results of DWCA measurements of PBAT/PNIPAAm electrospun fibers with different mass ratios as a function of temperature. It was observed that in the temperature range studied, the contact angle values measured for the pure PBAT electrospun fibers were in the region of 130°, revealing PBAT's hydrophobic behavior.



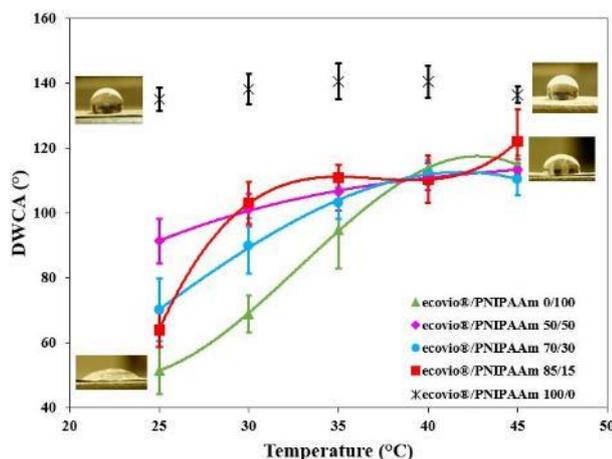
**Figure 5:** DWCA measurements as a function of temperature for PBAT/PNIPAAm electrospun fibers with different mass ratios.

For the PBAT/PNIPAAm electrospun fibers, all mass ratios analyzed revealed an abrupt change in contact angle as the temperature increased, mainly in the temperatures between 32 and 35 °C. When the temperature varied around PNIPAAm's LCST, a change in contact angle values of around 50° to 60° was

observed. There was also a fast and efficient response to temperature variation. Similar results could be found in the literature [8, 44-46], which indicated that the electrospinning processing significantly raised the surface area/volume ratio of the processed material, allowing the fibril mesh to respond rapidly to temperature variation. Therefore, the gap in contact angle values determined for these electrospun fibers was much larger, when compared to the gap in contact angle values for PNIPAAm existing in materials that were processed by other techniques [53-57]. When PNIPAAm is subjected to processing techniques that form film, its chains become very close to each other (compacted); as a result, the mobility of the amide side groups is hampered, making the hydrophilic-hydrophobic transition slower in the range of the LCST. Thus, in this case, the gap variations in DWCA measurements are small. On the other hand, when PNIPAAm is processed by techniques that form fibers, like electrospinning, the fibers that are formed present a very high surface area/volume ratio when compared to the film. Thus, in the fibers form, the amide groups of PNIPAAm's chains present more freedom and mobility; consequently, the hydrophilic-hydrophobic transition occurs much faster in the LCST range for the fibers when compared to the film, leading to a faster and higher gap values in DWCA measurements.

These results, in general, present potential applications for PBAT/PNIPAAm blends' electrospun fibers. Still, it could be inferred that the addition of PNIPAAm to PBAT at a mass ratio of 15% or above had not changed the LCST value for the electrospun fibers as there was no kind of modification to PNIPAAm during processing. These results were corroborated by the analysis of the SEM images and ATR-FTIR spectra.

Figure 6 shows the results of DWCA measurements as a function of temperature for ecovio®/PNIPAAm electrospun fibers with different mass ratios.



**Figure 6.** DWCA measurements as a function of temperature for ecovio®/PNIPAAm electrospun fibers with different mass ratios.

The contact angle measurements for the pure ecovio® electrospun fibers did not change significantly with temperature variation between 25 and 45 °C, remaining around 140°. This result indicated that the presence of PLA in the repeating unit of ecovio® made its electrospun fibers more hydrophobic because the structure of PLA has a more hydrophobic effect compared to that of PBAT. After the addition of PNIPAAm in different mass ratios, it was observed that the electrospun fibers from ecovio®/PNIPAAm blends (Figure 6) presented a significant decrease in contact angle values at temperatures below PNIPAAm's LCST. At 25 °C, the contact angle values decreased to around 60°, which indicated that the fibrous surfaces were wetted and presented hydrophilic behavior. As the temperature increased, especially in the range of PNIPAAm's LCST, contact angle values increased. Above 32–35 °C, the contact angle values were around 110–120° due to the conformational change of PNIPAAm's chain that turned the ecovio®/PNIPAAm electrospun fibers fully hydrophobic. This abrupt variation in contact angle values for the ecovio®/PNIPAAm electrospun fibers with the studied mass ratios was not so evident in PBAT/PNIPAAm electrospun fibers measured in the same temperature range (Figure 5). However, it is worth reaffirming that electrospun fibers using both PBAT and ecovio® in blends with PNIPAAm exhibited a rapid response to temperature variation. Nonetheless, it could be stated that ecovio®/PNIPAAm blends' electrospun fibers were slightly more hydrophobic than those of PBAT/PNIPAAm blends due to the presence of PLA in the former, which is more hydrophobic in character.

#### 4. CONCLUSIONS

In this study, it was possible to obtain PBAT/PNIPAAm and ecovio<sup>®</sup>/PNIPAAm electrospun fibers that presented thermoresponsive behavior and a sudden response to temperature in PNIPAAm's LCST range. As the mass ratio of PNIPAAm in the solutions increased, the morphology of the electrospun fibers became rounded and lacked beads; moreover, they presented average diameters in the micrometric range. From the analysis of ATR-FTIR spectra, it could be verified that the electrospinning process did not lead to the formation of strong intermolecular interactions, like hydrogen bonds, between chains of either PBAT and PNIPAAm or ecovio<sup>®</sup> and PNIPAAm. Furthermore, a significant variation in contact angle as a function of temperature was observed for the ecovio<sup>®</sup>/PNIPAAm electrospun fibers; however, the variation was stronger for the PBAT/PNIPAAm electrospun fibers. These exhibited PNIPAAm's hydrophilic-hydrophobic transition in the range between 32 and 35 °C with a sudden response to temperature variation observed when using the PNIPAAm mass ratio of 15% or above. Along these lines, the studied electrospun fibers may have a potential application in the cell adhesion/detachment field.

#### 5. ACKNOWLEDGMENTS

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#### 6. BIBLIOGRAPHY

- [1] CORRADINI, C., CURTI, P.S., GONZALEZ, R.S., *et al.* "Preparation of Polymeric Mats Through Electrospinning for Technological Uses", In: Longo, E., La Porta, F.A. (eds), *Recent Advances in Complex Functional Materials: From Design to Application*, chapter 4, Cham, Switzerland, Springer; 2017. DOI: [https://doi.org/10.1007/978-3-319-53898-3\\_4](https://doi.org/10.1007/978-3-319-53898-3_4)
- [2] ERDOGAN, I., DEMIR, M., BAYRAKTAR, O., "Olive Leaf Extract as a Crosslinking Agent for the Preparation of Electrospun Zein Fibers", DOI: <https://doi.org/10.1002/app.41338> *Journal of Applied Polymer Science*, 2015; v. 132, n. 4, pp. 41338 (9p), January 2015.
- [3] LIN, W.-H., YU, J., CHEN, G., *et al.* "Fabrication of multi-biofunctional gelatin-based electrospun fibrous scaffolds for enhancement of osteogenesis of mesenchymal stem cells", DOI: <https://doi.org/10.1016/j.colsurfb.2015.11.017> *Colloids and Surface B: Biointerfaces*, v. 138, pp. 26-31, February 2016.
- [4] LIU, G., GU, Z., HONG, Y., *et al.*, "Electrospun starch nanofibers: Recent advances, challenges, and strategies for potential pharmaceutical applications", DOI: <https://doi.org/10.1016/j.jconrel.2017.03.016> *Journal of Controlled Release*, v.252, n. 28, pp. 95-107, April 2017.
- [5] NETO, W. A. R., PEREIRA, I. H. L., AYRES, E., *et al.*, "Influence of the microstructure and mechanical strength of nanofibers of biodegradable polymers with hydroxyapatite in stem cells growth. Electrospinning, characterization and cell viability", <https://doi.org/10.1016/j.polymdegradstab.2012.03.048> *Polymer Degradation and Stability*, v. 97, n. 10, pp. 2037-2051, October 2012. DOI:
- [6] STEYAERT, I., VANCOILLIE, G., HOOGENBOOM R., *et al.*, "Dye immobilization in halochromic nanofibers through blend electrospinning of a dye-containing copolymer and polyamide-6", DOI: <https://doi.org/10.1039/C5PY00060B> *Polymer Chemistry*, v.6, pp. 2685-2694, February 2015.
- [7] WEI, Z., LIU, Y., HU, H., *et al.*, "Biodegradable poly(butylene succinate-co-terephthalate) nanofibrous membranes functionalized with cyclodextrin polymer for effective methylene blue adsorption", DOI: <https://doi.org/10.1039/C6RA22941G> *RSC Advances*, v. 6, pp. 108240-108246, October 2016.
- [8] LI, H., WILLIAMS, G. R., WU, J., *et al.*, "Poly(N-isopropylacrylamide)/poly(L-lactic acid-co-ε-caprolactone) fibers loaded with ciprofloxacin as wound dressing materials", DOI: <https://doi.org/10.1016/j.msec.2017.04.058> *Materials Science & Engineering C-Materials for Biological Applications*, v.79, pp. 245-254, October 2017.
- [9] NETO, W. A. R., PAULA, A. C. C., MARTINS, T. M. M., *et al.*, "Poly (butylene adipate-co-terephthalate)/hydroxyapatite composite structures for bone tissue recovery", DOI: <https://doi.org/10.1016/j.polymdegradstab.2015.06.009> *Polymer Degradation and Stability*, v. 120, pp. 61-69, October 2015.
- [10] KAI, D., LIOW, S. S., LOH, X. J., "Biodegradable polymers for electrospinning: Towards biomedical applications", DOI: <https://doi.org/10.1016/j.msec.2014.04.051> *Materials Science and Engineering: C*, v. 45, pp. 659-670, December 2014.
- [11] WADE, R. J., BURDICK, J. A., "Advances in nanofibrous scaffolds for biomedical applications: From electrospinning to self-assembly", DOI: <https://doi.org/10.1016/j.nantod.2014.10.002> *NanoToday*, v. 9, n. 6, pp. 722-742, Decem-

ber 2014.

- [12] HAMORI, M., NAGANO, K., KAKIMOTO, S., *et al.*, “Preparation and pharmaceutical evaluation of acetaminophen nano-fiber tablets: Application of a solvent-based electrospinning method for tableting”, DOI: <https://doi.org/10.1016/j.biopha.2015.12.023>. *Biomedicine & Pharmacotherapy*, v. 78, pp. 14-22, March 2016.
- [13] KIM, S., PARK, S.-G., KANG, S.-W., *et al.*, “Nanofiber-Based Hydrocolloid from Colloid Electrospinning Toward Next Generation Wound Dressing”, DOI: <https://doi.org/10.1002/mame.201600002>. *Macromolecular Materials and Engineering*, v. 301, n. 7, pp. 818-826, July 2016.
- [14] UNNITHAN, A. R., NEJAD, A. G., SASIKALA, A. R. K., *et al.*, “Electrospun zwitterionic nanofibers with in situ decelerated epithelialization property for non-adherent and easy removable wound dressing application”, DOI: <https://doi.org/10.1016/j.cej.2015.11.086>. *Chemical Engineering Journal*, v. 287, pp. 640-648, March 2016.
- [15] TRINCA, R. B., ABRAHAM, G. A., FELISBERTI, M. I., “Electrospun nanofibrous scaffolds of segmented polyurethanes based on PEG, PLLA and PTMC blocks: Physico-chemical properties and morphology”, DOI: <https://doi.org/10.1016/j.msec.2015.07.018>. *Materials Science & Engineering C-Materials for Biological Applications*, v. 56, pp. 511-517, November 2015.
- [16] NUNE, M., KRISHNAN, U. M., SETHURAMAN, S., “PLGA nanofibers blended with designer self-assembling peptides for peripheral neural regeneration”, DOI: <https://doi.org/10.1016/j.msec.2016.01.057>. *Materials Science & Engineering. C, Materials for Biological Applications*, v. 62, pp. 329-337, May 2016.
- [17] SASIKALA, A. R. K., UNNITHAN, A. R., YUN, Y.-H., *et al.*, “An implantable smart magnetic nanofiber device for endoscopic hyperthermia treatment and tumor-triggered controlled drug release”, DOI: <https://doi.org/10.1016/j.actbio.2015.12.015>. *Acta Biomaterialia*, v. 31, pp. 122-133, February 2016.
- [18] KARAHALILOĞLU Z., “Cell-compatible PHB/silk fibroin composite nanofiber mat for tissue engineering applications”, *Turkish Journal of Biology*, v. 41, n. 3, pp. 503-513, 2017.
- [19] WANG, A., GAN, Y., YU, H., *et al.*, “Improvement of the cytocompatibility of electrospun poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyvalerate] mats by Ecoflex”, DOI: <https://doi.org/10.1002/jbm.a.34034>. *Journal of Biomedical Materials Research: Part A*, v. 100A, n. 6, pp. 1505-1511, June 2012.
- [20] DÍEZ-PASCUAL, A. M., DÍEZ-VICENTE, A. L., “Antimicrobial and sustainable food packaging based on poly(butylene adipate-co-terephthalate) and electrospun chitosan nanofibers”, DOI: <https://doi.org/10.1039/C5RA14359D>. *RSC Advances*, v. 5, n. 113, pp. 93095- 93107, October 2015.
- [21] CASTRO, J. G., RODRIGUES, B. V. M., RICCI, R., *et al.*, “Designing a novel nanocomposite for bone tissue engineering using electrospun conductive PBAT/polypyrrole as a scaffold to direct nanohydroxyapatite electrodeposition”, DOI: <https://doi.org/10.1039/C6RA00889E>. *RSC Advances*, v. 6, pp. 32615- 32623, March 2016.
- [22] RODRIGUES, B. V. M., SILVA, A. S., MELO, G. F. S., *et al.*, “Influence of low contents of superhydrophilic MWCNT on the properties and cell viability of electrospun poly (butylene adipate-co-terephthalate) fibers”, DOI: <https://doi.org/10.1016/j.msec.2015.10.075>. *Materials Science and Engineering: C*, v. 59, pp. 782-791, February 2016.
- [23] SANTANA-MELO, G. F., RODRIGUES, B. V. M., SILVA, E., *et al.*, “Electrospun ultrathin PBAT/nHAp fibers influenced the in vitro and in vivo osteogenesis and improved the mechanical properties of neofomed bone”, DOI: <https://doi.org/10.1016/j.colsurfb.2017.04.053>. *Colloids and Surfaces B: Biointerfaces*, v. 155, pp. 544-552, July 2017.
- [24] ZEHETMEYER, G., MEIRA, S. M. M., SCHEIBEL, J. M., *et al.*, “Biodegradable and antimicrobial films based on poly(butylene adipate-co-terephthalate) electrospun fibers”, DOI: <https://doi.org/10.1007/s00289-016-1896-8>. *Polymer Bulletin*, v. 74, pp. 3243- 3268, August 2017.
- [25] SILVA, B. A. T. T., PASCOALINO, L. A., SOUZA, R. L., *et al.*, “Characterization of novel thermoresponsive poly(butylene adipate-co-terephthalate)/poly(N-isopropylacrylamide) electrospun fibers”, DOI: <https://doi.org/10.1007/s00289-019-02783-2>. *Polymer Bulletin*, v. 77, pp. 1157-1176, March 2020.
- [26] FREITAS, A. L. P. L., TONINI FILHO, L. R., CALVÃO, P. S., *et al.*, “Effect of montmorillonite and chain extender on rheological, morphological and biodegradation behavior of PLA/PBAT blends”, DOI: <https://doi.org/10.1016/j.polymertesting.2017.06.030>. *Polymer Testing*, v. 62, pp. 189-195, September 2017.
- [27] HARNNECKER, F., ROSA, D. S., LENZ, D. M., “Biodegradable Polyester-Based Blend Reinforced with Curauá Fiber: Thermal, Mechanical and Biodegradation Behaviour”, DOI: <https://doi.org/10.1007/s10924-011-0382-5>. *Journal of Polymers and the Environment*, v. 20, pp. 237-244, March 2012.
- [28] GEORGIPOULOS, P., KONTOU, E., NIAOUNAKIS, M., “Thermomechanical Properties and Rheological Behavior of Biodegradable Composites”, DOI: <https://doi.org/10.1002/pc.22761>. *Polymer Composites*, v.35, n. 6, pp. 1140-1149, June 2014.
- [29] GEORGIPOULOS, P., KONTOU, E., “The effect of wood-fiber type on the thermomechanical performance of a biodegradable polymer matrix”, DOI: <https://doi.org/10.1002/app.42185>. *Journal of Applied Polymer Science*, v. 132, n. 27, pp. 42185 (10p), July 2015.
- [30] SCHNEIDER, R., MERCANTE, L. A., ANDRE, R.S ., *et al.*, “Biocompatible electrospun nanofibers containing cloxacillin: Antibacterial activity and effect of pH on the release profile”, DOI: <https://doi.org/10.1016/j.reactfunctpolym.2018.09.001>. *Reactive and Functional Polymers*, v. 132, pp. 26-35, November

2018.

- [31] WANG, Y. M., ZHENG, S. X., CHANG, H. I., *et al.*, “Microwave-assisted synthesis of thermo- and pH-responsive antitumor drug carrier through reversible addition–fragmentation chain transfer polymerization”, DOI: <https://doi.org/10.3144/expresspolymlett.2017.29>. *eXPRESS Polymer Letters*, v. 11, n. 4, pp. 293-307, April 2017.
- [32] PANJA, S., DEY, G., BHARTI, R., *et al.*, “Metal Ion Ornamented Ultrafast Light-Sensitive Nanogel for Potential in Vivo Cancer Therapy”, DOI: <https://doi.org/10.1021/acs.chemmater.6b03440>. *Chemical of Materials*, v. 28, n. 23, pp. 8598-8610, November 2016.
- [33] PARK, M., LEE, K. S., SHIM, J., *et al.*, “Environment friendly, transparent nanofiber textiles consolidated with high efficiency PLEDs for wearable electronics”, DOI: <https://doi.org/10.1016/j.orgel.2016.05.030>. *Organic Electronics*, v. 36, pp. 89-96, September 2016.
- [34] IANNOTTI, V., AUSANIO, G., LANOTTE, L., *et al.*, “Magneto-piezoresistivity in iron particle-filled silicone: An alternative outlook for reading magnetic field intensity and direction”, DOI: <https://doi.org/10.3144/expresspolymlett.2016.7>. *eXPRESS Polymer Letters*, v. 10, n. 1, pp. 65-71, 2016.
- [35] LIU, W. T., YANG, Y., SHEN, P. H., *et al.*, “Facile and simple preparation of pH-sensitive chitosan-mesoporous silica nanoparticles for future breast cancer treatment”, DOI: <https://doi.org/10.3144/expresspolymlett.2015.96>. *eXPRESS Polymer Letters*, v. 9, n. 12, pp. 1068-1075, July 2015.
- [36] ELBAHRI, M., HOMAEIGOHAR, S., ABDELAZIZ, R., *et al.*, “Smart Metal–Polymer Bionanocomposites as Omnidirectional Plasmonic Black Absorber Formed by Nano fluid Filtration”, DOI: <https://doi.org/10.1002/adfm.201200768>. *Advanced Functional Materials*, v. 22, n. 22, pp. 4771-4777, November 2012.
- [37] LI, Q., BI, Q.-Y., LIN, H.-H., *et al.*, “A novel ultrafiltration (UF) membrane with controllable selectivity for protein separation”, DOI: <https://doi.org/10.1016/j.memsci.2012.09.010>. *Journal of Membrane Science*, v. 427, pp. 155-167, January 2013.
- [38] BRUN-GRAEPI, A. K. S., RICHARD, C., BESSODES, M., *et al.*, “Thermoresponsive surfaces for cell culture and enzyme-free cell detachment”, DOI: <https://doi.org/10.1016/j.progpolymsci.2010.07.007>. *Progress in Polymer Science*, v. 35, n. 11, pp. 1311-1324, November 2010.
- [39] RUSEN, L., DINCA, V., MITU, B., *et al.*, “Temperature responsive functional polymeric thin films obtained by matrix assisted pulsed laser evaporation for cells attachment–detachment study”, DOI: <https://doi.org/10.1016/j.apsusc.2013.09.122>. *Applied Surface Science*, v. 302, pp. 134-140, May 2014.
- [40] WANG, J.-T., CHIU, Y.-C., SUN, H.-S., *et al.*, “Synthesis of multifunctional poly(1-pyrenemethylmethacrylate)-b-poly(N-isopropylacrylamide)-bpoly(N-methylolacrylamide)s and their electrospun nanofibers for metal ion sensory applications”, DOI: <https://doi.org/10.1039/C4PY01773K>. *Polymer Chemistry*, v. 6, pp. 2327-2336, January 2015.
- [41] SCHILD, H. G., “(N-isopropylacrylamide): experiment, theory and application”, DOI: [https://doi.org/10.1016/0079-6700\(92\)90023-R](https://doi.org/10.1016/0079-6700(92)90023-R). *Progress in Polymer Science*, v. 17, n. 2, pp. 163-249, 1992.
- [42] GU S.-Y., WANG, Z.-M., LI, J.-B., *et al.*, “Switchable Wettability of Thermo-Responsive Biocompatible Nanofibrous Films Created by Electrospinning”, DOI: <https://doi.org/10.1002/mame.200900215>. *Macromolecular Materials and Engineering*, v. 295, n.1, pp. 32-36, January 2010.
- [43] LIZUNDIA, E., MEAURIO, E., LAZA, J. M., *et al.*, “Study of the chain microstructure effects on the resulting thermal properties of poly(L-lactide)/poly(N-isopropylacrylamide) biomedical materials”, DOI: <https://doi.org/10.1016/j.msec.2015.01.097>. *Materials Science and Engineering: C*, v. 50, pp. 97-106, May 2015.
- [44] LIN, X., TANG, T., LYU, H., *et al.*, “Poly(N-isopropylacrylamide)/polyurethane core–sheath nanofibres by coaxial electrospinning for drug controlled release”, DOI: <https://doi.org/10.1049/mnl.2015.0503>. *Micro & Nano Letters*, v. 11, n.5, pp. 260-263, 2016.
- [45] MAEDA, T., KIM, Y.-J., AOYAGI, T., *et al.*, “The Design of Temperature-Responsive Nanofiber Meshes for Cell Storage Applications”, DOI: <https://doi.org/10.1049/mnl.2015.0503>. *Fibers*, v. 5, n. 1, pp. 13(10p), March 2017.
- [46] LIN, X., TANG, D., GU, S., *et al.*, “Electrospun poly(N-isopropylacrylamide)/poly(caprolactone)-based polyurethane nanofibers as drug carriers and temperature-controlled release”, DOI: <https://doi.org/10.1039/C3NJ00275F>. *New Journal of Chemistry*, v. 37, pp. 2433-2439, April 2013.
- [47] YUAN, H., BI, L., LIANG, K., *et al.*, “Regulating drug release from pH-and temperature-responsive electrospun CTS-g-PNIPAAm/poly(ethylene oxide) hydrogel nanofibers”, DOI: <https://doi.org/10.1088/1748-6041/9/5/055001>. *Biomedical Materials*, v. 9, n. 5, pp. 055001(10p), August 2014.
- [48] LI, J.-J., ZHU, L.-T., LUO, Z.-H., “Electrospun fibrous membrane with enhanced switchable oil/water wettability for oily water separation”, DOI: <https://doi.org/10.1016/j.cej.2015.11.057>. *Chemical Engineering Journal*, v. 287, pp. 474-481, March 2016.
- [49] GOES, A. M., CARVALHO, S., ORÉFICE, R. L., *et al.*, “Viabilidade celular de nanofibras de polímeros biodegradáveis e seus nanocompósitos com argila montmorilonita”, DOI: <https://doi.org/10.1590/S0104-14282012005000012>. *Polímeros*, v. 22, n. 1, pp. 34-40, February 2012.
- [50] CURTI, P. S., SOUZA, R. L., “Caracterização morfológica de fibras de Ecovio®/PNIPAAm obtidas por meio da técnica de eletrofição”, In: 22º Congresso Brasileiro de Engenharia e Ciência dos Materiais, pp. 8326-8336, Natal, Nov.

2016.

- [51] WANG, L.-F., RHIM, J.-W., HONG, S.-I., “Preparation of poly(lactide)/poly(butylene adipate-co-terephthalate) blend films using a solvent casting method and their food packaging application”, DOI: <https://doi.org/10.1016/j.lwt.2015.12.062>. *LWT - Food Science and Technology*, v. 68, pp. 454-461, May 2016.
- [52] ZHANG, J., PEPPAS, N. A., “Molecular interactions in Poly(methacrylic acid/Poly(N-isopropyl acrylamide) Interpenetrating Polymer Networks)”, DOI: <https://doi.org/10.1002/app.1942>. *Journal of Applied Polymer Science*, v. 82, n. 5, pp. 1077-1082, October 2001.
- [53] MAURICIO, M. R., CARVALHO, G. M., RADOVANOVIC, E., *et al.*, “Analysis of poly(N-isopropylacrylamide) grafted onto the surface of PET films by SI-ATRP technique”, DOI: <https://doi.org/10.1016/j.msec.2008.10.017>. *Materials Science and Engineering: C*, v. 29, n. 2, pp. 594-598, March 2009.
- [54] TAI, X., MA, J. H., DU, Z., *et al.*, “The facile preparation for temperature sensitive silica/PNIPAAm composite microspheres”, DOI: <https://doi.org/10.1016/j.apsusc.2012.12.153>. *Applied Surface Science*, v. 268, pp. 489-495, March 2013.
- [55] TAI, X., MA, J. H., DU, Z., *et al.*, “A simple method for synthesis of thermal responsive silica nanoparticle/PNIPAAm hybrids”, DOI: <https://doi.org/10.1016/j.powtec.2012.08.026>. *Powder Technology*, v. 233, pp. 47-51, January 2013.
- [56] CHEN, T., FANG, Q., ZHONG, Q., *et al.*, “Synthesis and Thermosensitive Behavior of Polyacrylamide Copolymers and Their Applications in Smart Textiles”, DOI: <https://doi.org/10.3390/polym7050909>. *Polymers*, v. 7, n. 5, pp. 909-920, May 2015.
- [57] GOLSHAELI, P., GÜVEN, O., “Chemical modification of PET surface and subsequent graft copolymerization with poly(N-isopropylacrylamide)”, . DOI: <https://doi.org/10.1016/j.reactfunctpolym.2017.06.015>. *Reactive & Functional Polymers*, v. 118, pp. 26-34, September 2017.

#### ORCID

Liege Aguiar Pascoalino

Breno Augusto Tabosa Thome da Silva

Ricardo Luiz de Souza

Priscila Schroeder Curti

<https://orcid.org/0000-0001-9855-6450>

<https://orcid.org/0000-0002-5574-917X>

<https://orcid.org/0000-0003-0658-0694>

<https://orcid.org/0000-0002-0525-3109>