Hybrid Nanocomposite from γ-Fe_2O_3 Nanoparticles Functionalized in the Amazon Oil Polymers matrix

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Abstract

tIn recent years, there was a crescent increase in studies involving hybrid magnetic nanocomposites from renewable resources, because of its importance in the synthesis of new organic biomaterials. Herein, we report a synthesis of Magnetic Nanocomposites (MNCs) from superparamagnetic nanoparticles based on iron oxide of maghemite (γ-Fe_2O_3) coated by a polymeric matrix. In this study, we used γ-Fe_2O_3 which are prepared using co-precipitation method, where salts with ions Fe^{+2} and Fe^{+3} are dissolved in distilled water and stirred until they reach about 60 ° C. Shortly after the mixture is add a solution of NH_4OH. After this step, the magnetite solute (Fe_3O_4) is left in oxidizing solution, thus forming nanoparticles of γ-Fe_2O_3. For activation of the functional groups and extraction of the polymer we used polycondensation method, wherein the oil extracted from Carapa Guianensis Aubl. is diluted in ethylene glycol ($C_2H_6O_2$). After that, the mixture undergoes processes: hydrothermal and isobaric-isothermal. Then, purification was performed polymer, thus obtaining a polymer of natural oil. The nanoparticles was coated for the polymeric matrix using dispersion method and freeze drying, thereby forming a hybrid MNCs ready for characterization. For the samples characterization was utilized X-ray diffraction (XRD) and spectroscopy: UV-Vis, Fourier Transform Infrared (FTIR), EDX and PAS. The results indicate that magnetic-polymeric nanocomposites structure formed was type core/shell, wherein the core was formed γ-Fe_2O_3 nanoparticles, coated by the polymer matrix, which presents some characteristics of the natural oil used in their synthesis.

Keywords: Hybrid Nanostructures; Nanocomposites; Organic Polymers;

1. Introduction

There was an expansion in Nanosciences researches, in the last century, due mainly its interdisciplinary nature. Advances in Nanoscience leads development of Nanotechnology its products have a wide variety of applications such as microelectronics, environment and medicine [1-4]. Among this research can highlight the development of hybrid nanostructures of polymer type that can provide new physical-chemical properties of the material [5]. It is also included the development of nanocomposites hybrids with magnetic properties polymeric matrix. For the synthesis of magnetic nanocomposites is common to use magnetic nanoparticles based on iron oxides (SPIONs). These nanoparticles exhibit a good attraction due to its characteristic superparamagnetic, as well as low toxicity, biocompatibility and stability in organic

media [6,7]. Another group of compounds that has promising properties and possible applications are polymers based on vegetable oils. The synthesis of this type of polymer is described in the literature as a great alternative, due to both its origin and its renewable unexploited properties [8].

In this work was synthesized magnetic nanocomposites (MNCs) from superparamagnetic nanoparticles based on iron oxide (SPIONs) coated by a polymeric matrix. The matrix used is extracted from natural oil of almond Carapa guianensis Aubl. Popularly known in the Amazon Region as Andiroba, the oil is formed by triglycerides rich in unsaturated fatty acids being traditionally used in medicine and in cosmetics [9]. For material characterization are employed optical techniques, aiming at the analysis of the crystal structure of the NPs, the molecular structure of Carapa guianensis almond oil, the molecular structure of the polymer extracted and the encapsulation of nanoparticles in the polymer matrix [10].

2. Experimental

2.1 Materials

The analytical grade reagents were commercially available and used without further purification protocols. Iron (III) chloride hexahydrate ($FeCl_3 \bullet 6H_2O$) and iron (II) chloride tetrahydrate ($FeCl_2 \bullet 4H_2O$) were purchased from Aldrich. Ammonium hydroxide (NH_4OH), ethylene glycol ($C_2H_6O_2$) and potassium hydroxide (KOH) were purchased from Sigma. Then, the Carapa guianensis oil was extracted from seeds, found in the Amazon Rainforest, through artisanal processes.

2.2 Synthesis of nanocomposite

In this study, we used maghemite nanoparticles (γ-Fe_2O_3) which are prepared using co-precipitation method, where salts with ions Fe^{+2} and Fe^{+3} are dissolved in distilled water and stirred until they reach about 60 ° C. Shortly after the mixture is add a solution of ammonium hydroxide (NH_4OH), thereby forming a precipitate of dark color. Then, the solution is heated to 70 °C and left for about 30 minutes under constant agitation. After this step, the magnetite solute (Fe_3O_4) is washed for several days with distilled water until the pH reaches between patterns 8 and 9. Finally, SPIONs are left in oxidizing solution, thus forming nanoparticles of γ-Fe_2O_3 [11]. For activation of the functional groups and extraction of the polymer we used polycondensation method [12,13], wherein the oil extracted from *C. guianensis* is diluted in ethylene glycol ($C_2H_6O_2$). After that, the mixture undergoes processes: hydrothermal and isobaric-isothermal. Then, purification was performed polymer, thus obtaining a polymer of natural oil. The SPIONs was coated for the PLCG using dispersion method and freeze drying, thereby forming a hybrid MNCs ready for characterization.

3. Characterization of Nanocomposites

For the samples characterization was utilized X-ray diffraction (XRD) technique, used for evaluation the crystallinity and the average size of the crystalline domains of SPIONs and spectroscopy: UV-Vis, Fourier Transform Infrared (FTIR), EDX and PAS, for analyze the molecular structure of the polymer matrix and the MNCs and checks of encapsulation of SPIONs for the polymeric matrix.

The XRD patterns showed characteristics peaks of crystalline structure of y-Fe_3O_4 nanoparticles (Fig. 1).

The reflection peaks relative to 220, 311, 400, showed similar results regarding from cubic spinel structured of Iron Oxide composite (JCPDS file No. 19-0629). Using the Debye-Scherrer equation, with it is possible to calculate the average diameter of the crystalline domains in this work have an average value of 6.9 ± 0,1 nm.

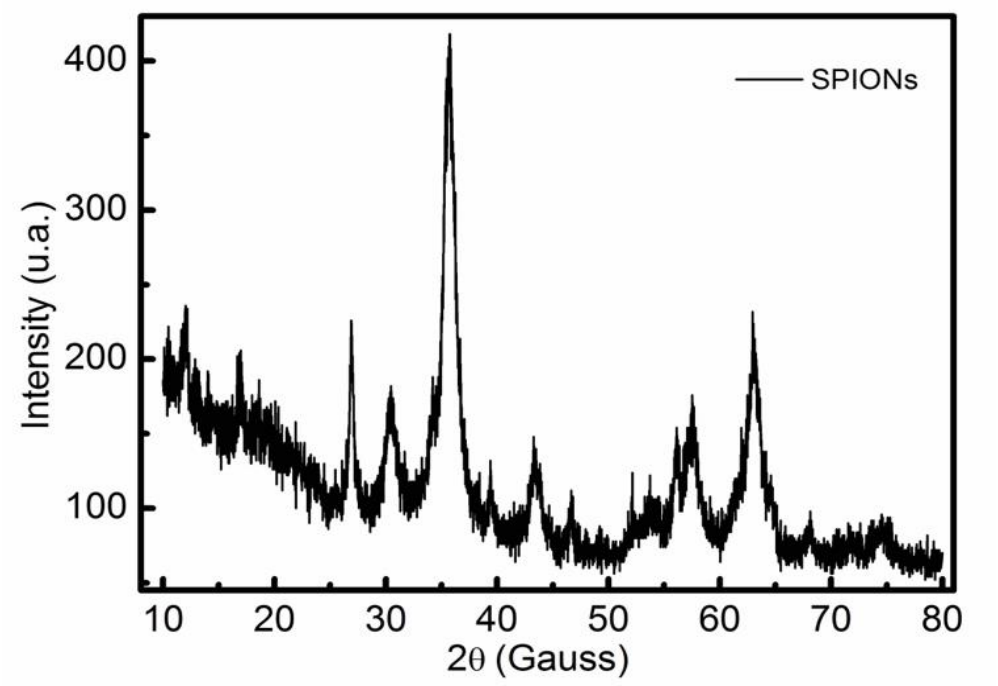

Figure 1: X-ray diffraction patterns (XRD) of SPIONs.

TEM was carried out using a JEOL 100 CXII. The figure 02 show the agglomeration of the nanoparticles, the data were treated generating a histogram thus estimating the polydispersity and the mean diameter. For nanoparticles the diameter remained at 6.4 nm with a polydispersity of 0.23 nm with an acurrancy of 0.1 nm. The estimated mean particle diameter measured from the TEM images is found to be consistent with the XRD results. The images of the MNC at a magnification of 80.000x it was possible to visualize a large agglomerate with branches of about 200 nm in length, by increasing the magnification to 300,000x it is observed that within these branches are the *y*-Fe_3O_4 nanoparticles.

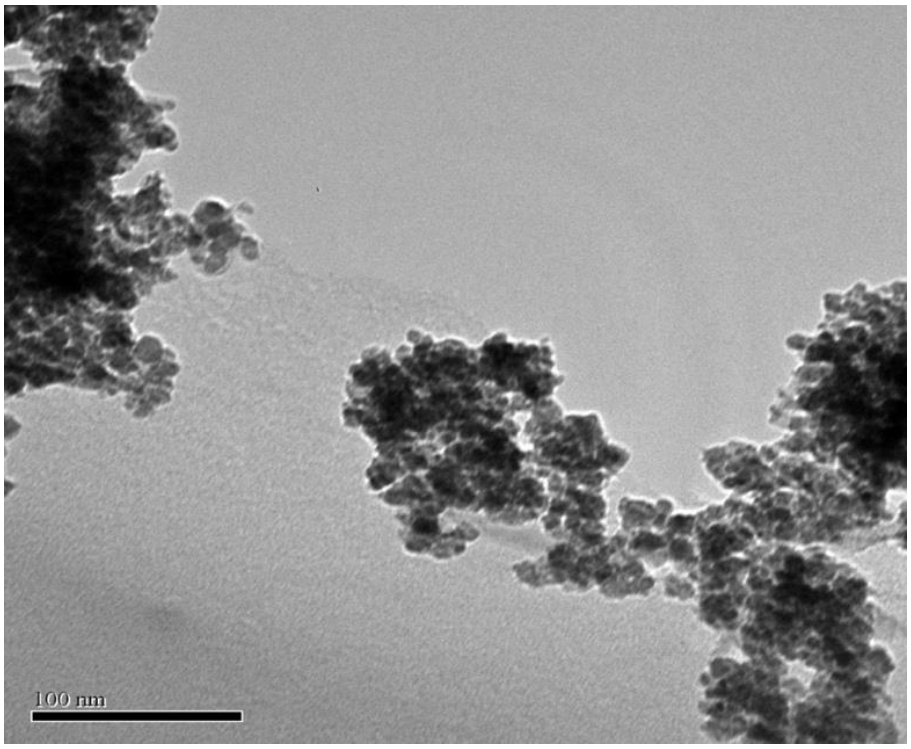

Figure 2 - Transmission electron microscopy of γ-Fe2O3 synthesized nanoparticles.

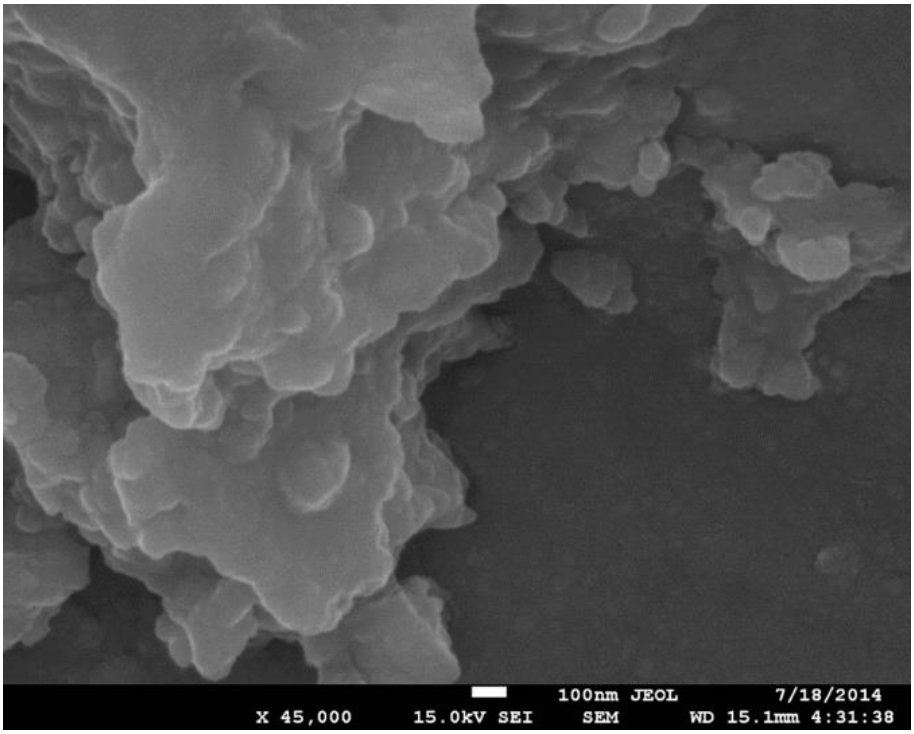

Figura 3 – Scanning electron microscopy of magnetic polymer nanocomposite, the base of the oil extracted from the seed of Carapa guianensis, with an increase of 45,000 x.

Having seen the image obtained by Scanning Electron Microscopy with a magnification of 45,000 x the NMC (Figure 3) it was possible to observe the surface observing a large structure, probably the surface of the polymer layer that surrounds the maguemita nanoparticles.

In Figure 4a, we have the FTIR comparison between the natural oil of C. Guianensis (OCG) and polymeric

matrix extracted (PLCG). At both was observed peaks at 2918 cm-1 and 2851 cm-1 that are characteristic vibrations of symmetric and asymmetric stretching of C-H bonds. In the OCG was observed interactions in 1754 cm-1 have the C=O bonds, in 1212 cm-1 and 1167 cm-1 have bonds esters CO and in 1095 cm-1 have the OCC bonds. For the PLCG the FTIR showed peaks at 881 cm-1 and 1035 cm-1 that are characteristic bands of asymmetric vibrations of the CO bond of ethyl esters, in 3309 cm-1 have characteristics of OH band with the suppression of C=O peak. The spectrum of the Andiroba natural oil has characteristic peaks of oils rich fatty acids, the appearance of connections CO in the organic polymer indicate the breakdown of the OH bonds that form the fatty oil caused by the attack using alcohol $C_2H_6O_2$, thereby forming a group of polyesters [14 - 16].

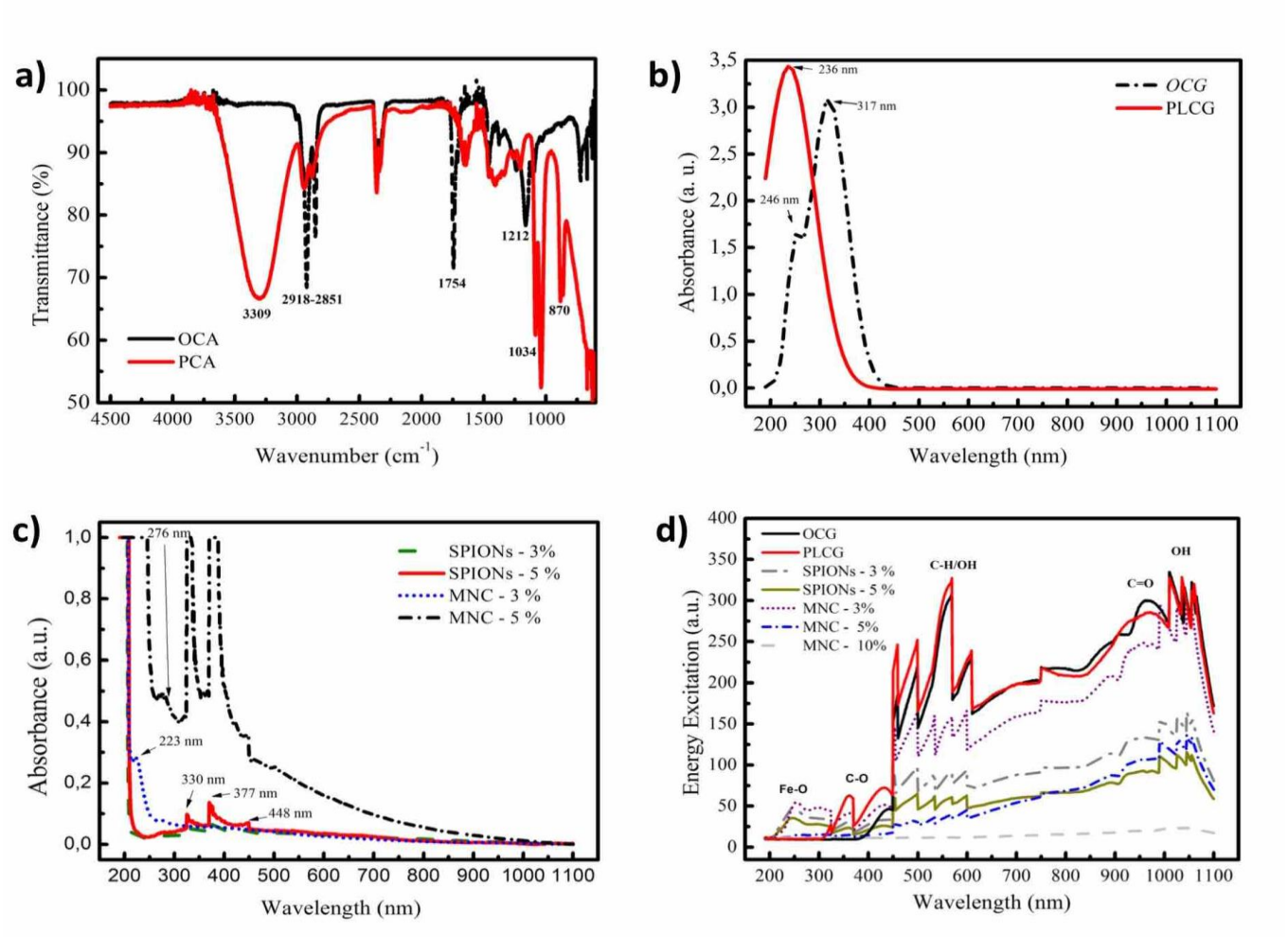

Figure 4: Spectrum FTIR and UV-Vis of samples: a) FTIR analysis of OCG and the PLCG. b) Absorbance spectrum (UV-VIS) of OCG and PLCG. c) Absorbance spectrum (UV-VIS) of SPIONs diluted (3% and 5%) and MNCs diluted (3%, 5%). d) Energy Spectrum (UV-VIS) of OCG, PLCG, SPIONs (3% and 5%) and MNC (3%, 5% and 10%).

The Figure 4b shows absorption peaks at 317 and 246 nm to the OCG and 236 nm for PLCG, we observe a displacement to the blue absorption and a prolongation of the line, suggesting polymerizing organic chains diterpene and sesquiterpene contributing to the formation of the polymer. Figure 4c shows spectra of SPIONs (3% and 5%) and MNC (3%, 5% and 10%). The spectra of SPIONs 5% and 3% have the same

characteristics only by difference the intensities of the signals of the structures. The data suggest electronics transitions in the O2 on the surface of nanoparticles in three regions 2.78, 3.35 and 3.85 (eV). Already the MNC 3 %, 5 % and 10% had responses in 3.28, 3.77 and 5.63 (eV), the response in 3% suggests two structures of type OH and Fe-O on the surface of SPIONs, in 5% the response occurs in three structures of type OH, C=O and Fe-O on the surface of nanoparticles. Consequently, to 10% the signal was saturated throughout the ultraviolet region and visible indicating coating of the SPIONs by polymer and formation of MNC.

Energy distributions in relation to wavelength were observed with specific structures as seen in Figure 4d. The SPIONs showed interactions associate the bonds OH and FeOH (253-324 nm, 450-600 nm and 1000-1068 nm). The OCG and PLCG presented peaks between 330-600 nm, 923-1000 nm and 1000-1068 nm. These interactions were associated the functional groups OH, C=O and CH. Compared the OCG with PLCG was possible to observe a change in spectrum behavior at approximately 965 nm which is related to the C=O bond, the decrease in the peak of excitement can be associate with removal of carbonyls links during polymerization. The MNC diluted to 3% and had much energy peaks PLCG, as the SPIONs, which suggests interaction of molecular structures Fe-O, C=O, CO and OH.

The PAS spectrum (Figure 3a) showed only interactions in the C-band (250-340 nm), this band is related to the absorption of the light that strikes the core of this nanomaterial and its encapsulation. The SPIONs strongly interacted at 265 nm, since the organic polymer obtained strong interaction peaks at 265, 291 and 306 nm, the spectrum peaks obtained MNC interaction was related to both polymer matrix and with the SPIONs, however, showed peaks with more intensity [17]. The EDX spectrum (Figure 3b) showed the chemical composition of OCG, PLCG and MNC. In the OCG was observed concentrations on Ru, Au, Cu. In the PLCG was observed the same concentrations in the OCG and the appearance of a small peak related to the K which was used in the synthesis. The MNC shows the chemical composition of PLCG, it was almost suppressed by a peak related interacting with iron, which can indicate a high concentration of SPIONs in its structure.

4. Considerations

This study reports on the successful preparation of the polymeric matrix from almond oil Andiroba (C. guianensis) and complexation nanocomposite maghemite nanoparticles (average diameter 6.9 nm). The procedures employed confirmed through the UV-Vis measurements, FTIR and EDX formation of the polymeric matrix. PAS measures indicate an encapsulation SPIONs by PLCG matrix. In summary, results from this study showed that the hybrid nanocomposite from PLCG showed good stability and biocompatible characteristics.

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Science and Technology of Rondônia – Brasil.

6. References

[1] Arca-Lafuente, S., Martínez-Román, P., Mate-Cano, I., Madrid, R., Briz, V. Journal of Infection, 2020, 80, 1, 8-15.
Link: https://doi.org/10.1016/j.jinf.2019.09.010

[2] Tu, Z., Zhang, B., Yang, G., Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2013, 436: 854 Link? https://doi.org/10.1016/j.colsurfa.2013.08.019

[3] Bkaria, R., Ltaief, A., Chehata, N., Chaaben, N., Saidi, F., Bouazizi, A., Vacuum, 2014, 104: 33 Link? https://doi.org/10.1016/j.vacuum.2013.12.018

[4] Yue-jian, C., Juan, T., Fei, X., Jia-bi, Z., Ning, G., Yi-hua, Z., Ye, D., Liang, G. Drug development and industrial pharmacy, 2010, 36, 10: 1235 Link: https://doi.org/10.3109/03639041003710151

[5] Pyun, J. Polymer Reviews, 2007, 47, 2: 231 Link: https://doi.org/10.1080/15583720701271294

[6] Mamani, J. B., Costa-filho, A. J., Cornejo, D. R., Vieira, E. D., Gamarra, L. F. Materials Characterization, 2013, 81:
28 Link: https://doi.org/10.1016/j.matchar.2013.04.001

[7] WU, W., HE, Q., JIANG, C., et al., Nanoscale research letters, 3(11), (2008), 397–415. Link: https://doi.org/10.1007/s11671-008-9174-9

[8] Tsujimoto, T., Uyama, H., Kobayashi, S., Polymer Degradation and Stability, 2010, 95: 1399. Link: https://doi.org/10.1016/j.polymdegradstab.2010.01.016

[9] Santos, J. G., Silveira, L. B., Fegueredo, P. H., Araújo, B. F., Peternele, W. S., Rodriguez, A. F., Vilela, E. C., Garg, V. K., Oliveira, A. C., Azevedo, R. B., Morais, P. C. Nanosci. Nanotechnol., 2012, 12: 4757 Link: https://doi.org/10.1166/jnn.2012.4917

[10] Esteves, A. C. C., Barros-Timmons, A., Trindade, T., Química Nova, 2004, 27: 798 Link: static.sites.sbq.org.br/quimicanova.sbq.org.br/pdf/Vol27No5_798_19-RV03285.pdf

[11] Chin, A. B., Yaacob I. I., Journal of Materials Processing Technology, 2007, 191: 235 link: http://dx.doi.org/10.1016/j.jmatprotec.2007.03.011

[12] Sharma, V., Kundu, P.P., Progress in Polymer Science, 2008, 33: 1199 Link: https://doi.org/10.1016/j.progpolymsci.2008.07.004

[12] Abbasi, A., Nasef, M. M., Yahya, W. Z. N., Sustainable Chemistry and Pharmacy, 2019, 13: 1. Link: https://doi.org/10.1016/j.scp.2019.100158

[13] G.-X. Chen, H.-S. Kim, E.-S. Kim, et al., European Polymer Journal, 2006, 42, 468. Link: https://doi.org/10.1016/j.eurpolymj.2005.07.022

[14] Roumanet, P., Lafleche, F., Jarroux, N., Raoul, Y., Claude, S., Guégan, P., European Polymer Journal, 2013, 49, 4: 813 Link: https://doi.org/10.1016/j.eurpolymj.2012.08.002

[15] Fakirov. S. Progress in Polymer Science, 2019, 89, 1. Link: https://doi.org/10.1016/j.progpolymsci.2018.09.003

[16] Gunatilake, S. K. International Journal for Innovation Education and Research, 2016, 4, 44-54. Link: https://doi.org/10.31686/ijier.vol4.iss4.531

[17] Rodriguez, A F R; Coaquira, J. A. H., Morales, M. A., Faria, F. S. E. D. V., Cunha, R. M., Santos, J. G., Silveira, L. B., Candela, D. R. S., Baggio- Saitovitch, E. M., Rabelo, D., Azevedo, R. B., Morais, P. C. Spectrochimica acta. Part A, Molecular and Biomolecular spectroscopy, 2013, 100: 101 Link: https://doi.org/10.1016/j.saa.2012.02.081