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AIP Conf. Proc. 2065, 030022 (2019)

<https://doi.org/10.1063/1.5088280>



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P-aminobenzoate intercalation into Layered Nickel hydroxide salt using a hydrothermal methodology: Synthesis, characterization, and evaluation as potential ultraviolet radiation absorber properties of polyethylene

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Abstract. This paper aims to synthesize nanocomposites based in nitrate hydroxide salts intercalated with organic ultraviolet (UV) absorbent molecule to use in lining of cables based in polyethylene that could be apply in the electrical center. The synthesis procedure was performed using urea hydrolysis of Ni (II) nitrate melts at 160 °C and its modification carryout in an oven at 70 and 120 °C in a simple process. The modified structure and thermal stability of the hydroxide salt with formula Ni(PABA)_{0,16}(OH)_{1,84} called NiHAB were characterized by XRD, FTIR, TGA, DRUV-Vis. Its studies suggest that NiHAB may have potential application as a UV absorber, because it improves this property when mixing with polyethylene, when the UV spectra shows a big band that covered the region between 400-200 nm.

Keywords: Hydroxides salt, Nitrate hydroxide, ultraviolet absorber, p-aminobenzoic acid, urea.

INTRODUCTION

The polyethylene is the most useful polymer in the daily days, and is the most popular plastic in the world. This compound is using in packaging, in the manufacture of pipes and lining of cables in the electrical sector (Coutinho, Mello, & Maria, 2003) (Munaro, Souza, & Akcelrud, 2003). Different processes play an important role in polymer degradation, leading to chain scission and chain linking in polymers, causing deterioration of mechanical properties and leading to formation useless materials (Yousi & Haddad, 2013). An example is the photo oxidative processes that are induced by ultraviolet (UV) and visible light absorption that results in breaking of the polymer.

In recent years, layered double hydroxides (LDH), also known as hydrotalcite-like compounds are probably the most investigated filler for nanocomposites (Crepaldi & Barros Valim, 1998) (Basu, Das, Werner Stockelhuber, Wagenknecht, & Heinrich, 2014).

The structure of LDH is similar to the mineral brucite (Mg(OH)₂), whose layers consists of slightly distorted octahedron containing an Mg²⁺ cation in the center and hydroxyl anions in the vertices. More recently, scientists have proposed layered hydroxide salt (LHS) as fillers for polymer nanocomposites. In LHS, with an analogous structure to LDH that consist in brucite-like host layers with positive charge, oxoanions or water molecules substitute part of the hydroxyl anions in the Brucite-like structure. The importance of this layered compound is bases on their ability to retain chemical species with electrical charges compatible to those of the layers. The LHS present the general formula (M^{x+}(OH)_{2-x}(A^{m-})_{x/m}.nH₂O), where M^{x+} is a divalent metallic cation and A is an intercalated counterion with charge n- (Guadalupe Carbaljal, Gundapa, & Wypych, 2007)(Zimmermann, Jaerger, Faria Zawadzki, & Wypych, 2013).

The intercalated anions have great impact in the properties of the composite but unfortunately, limited examples have been published in relationship with this kind of materials. Due to this fact and considering the UV radiation absorption properties of p-aminobenzoic acid, besides the potential of hydroxide salts to retain anions, the objective of the present work aimed to use this class of compounds to produce a new class of multifunctional materials improving the UV absorption of polymer material.

EXPERIMENTAL SECTION

MATERIALS

The nickel hydroxide nitrate was obtained via urea hydrolysis following some indications described elsewhere (Rajamthi & Vishnu Lamath, 2001) but with some modifications. In short, nickel nitrate (61.9 mmols) were mixed with 2 g of urea (33.3mmols) and 2 mL of distilled water in a mortar and allocated into the muffle at 160 °C for 35 minutes. Thereafter, the green solid was removed from the muffle and cooled to room temperature, filtered and washed several times with deionized water and ethanol. The product was dried overnight under vacuum at 50 °C. Ten milliliters of an aqueous solution of NaOH (1 molL⁻¹) was added to 9.3 mmol of PABA to neutralized the acid. A solution containing 9,4 mmols of AB was introduced to a Teflon reactor together with 2.4 mmols of NiHN. The reactor was closed and heated at 70 °C for 17 h and at 120 °C for 35 minutes. The mixture was cooled to room temperature, was washed three times with milliQ water and dried in a vacuum oven at 50 °C, resulting in a green solid clearer than its predecessor (NiHAB).

The composite preparation was fed into a HAAKE MiniLab II micro compounder. The specimens were prepared by melting the polyethylene/ filler mixture at 190 °C and 100 rpm.

CHARACTERIZATION

X-ray powder diffraction (XRD) patterns were recorded using a Shimadzu XRD- 6000 equipment with CuK α (1.5418 Å) radiation, and dwell time of 2°/min, 30 mA and 40kV. The samples were placed and oriented by hand on aluminum sample holders. The polymeric films were evaluated putting the material in an aluminum sample holder with a cavity in the middle and to avoid peaks displacements, a small amount of silicon powder was used as an internal standard.

Fourier transform infrared spectroscopy (FTIR) spectra were acquired on a Bio-Rad FTS 3500GX and Bomem Michelson MB 100 instruments, operating in a transmission mode with 32 scans with a nominal resolution of 2 cm⁻¹. The samples were mixed with spectroscopic grade KBr in pellets pressed at 10 tons.

Thermogravimetry analyses (TGA and DSC) were carried out using 0.065 ml alumina crucibles with a Netzsch (STA 449 F3 series EP model).

Diffuse reflectance ultraviolet-visible (DRUV-VIS) spectra were acquired at room temperature, between 200-800 nm with a Hewlett Packard-8452A-Diode Array spectrophotometer.

RESULTS

The X-ray diffraction pattern of NiHN (Figure 1a), is characterized by an intense and sharp reflection at 6.87 Å, followed by less intense peaks which can be indexed according to a hexagonal cells, as reported in the literature (Biswick, Jones, Pacula, & Serwicka, 2006).

The nitrate incorporation could take place due a substitution of a fraction of the hydroxyl ions by nitrate ions, leading to a hydroxyl-deficient compound, and the nitrate is grafted to the metal ion, resulting in a comparatively smaller basal spacing (Rajamthi & Vishnu Lamath, 2001). After the nitrate exchange by AB, a new compound was observed (Figure 1b) with basal distance of 8.39 Å, showing that the organic UV absorbent was successfully intercalated.

In the p-aminobenzoic acid FTIR spectrum (Figure 2a) showed an asymmetric and symmetric bands of C-O bonds of the carboxylate groups at 1533 and 1409 cm⁻¹ respectively. The delta between this bands (close to 130 cm⁻¹) is useful to determinate the coordination of the organic anion with the metal in the matrix layer using as a reference the sodium salt of the respective acid. The bands at 3329 and 3230 cm⁻¹ were attributed to primary amine N-H bonds (Li, Tang, Zhou, & Wang, 2016). (Nakamoto, 1968).

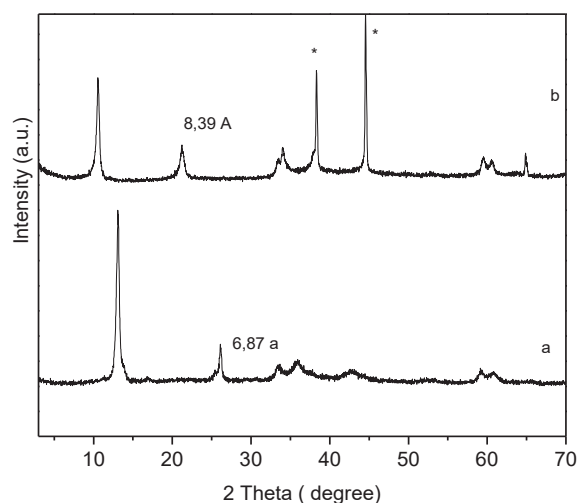


Figure 1. X-ray diffraction patterns of NiHN (a) and NiHAB (b). *Aluminum sample holder.

The FTIR spectrum of NiHN (Figure 2b) displayed a strong absorption peak at 1355 cm^{-1} referent to the nitrate anion, and ν_2 fundamental absorption of N-O at 994 cm^{-1} (Biswick, Jones, Pacula, & Serwicka, 2006). To NiHAB, different bands indicating the intercalation of p-aminobenzoate (Figure 2c). Bands at 3429 e 3354 cm^{-1} were attributed to asymmetry and symmetric vibration of N-H, C-O bands of the carboxylate group at 1519 and 1398 cm^{-1} . The band at 1061 cm^{-1} due to ring breathing vibration of benzene ring also attesting the anion exchange (Biswick, Jones, Pacula, & Serwicka, 2006), and bands of aromatic N-C bonds at 1175 cm^{-1} (Trindade Cursino, Ferreira da Costa Gardolinski, & Wypych, 2010).

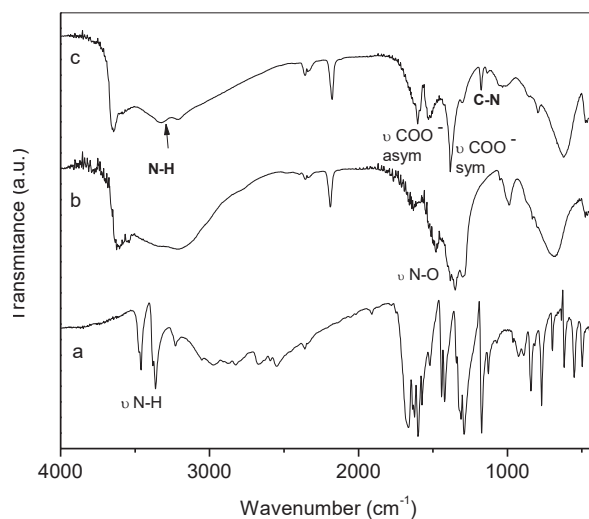


Figure 2. FTIR spectra of p-aminobenzoic acid (a), NiHN (b) and NiHAB (c).

In the DRUV-Vis spectra, the absorption of p-aminobenzoic acid was observed in the region around 215 and 337 nm (Figure 3a), the sodium p-aminobenzoate (Figure 3b) present absorption band at 229 and 294 owing the presence of chromophore groups with unshared electron pairs in carboxyl and amino groups, and due the of the instaurations present in the benzene ring. For NiHN, the UV-spectra showed maximum absorption in the UVC region at 232 and 272 nm , in UVA region at 386 nm and two peaks centered at 427 and 665 nm in the visible region (Figure 3c).

The DRUV-Vis spectra of the compound NiHAB (Figure 3d) shows that this salts have a broader absorption region after the intercalation of the organic molecule between the UVC and UVA region, leading to increase of

the protection range and enabling its potential use as modifier UV protector. This modified hydroxide salt exhibits absorption maxima at 224, 278, 297 and 390 nm due transition a $\pi - \pi^*$ and $\eta - \pi^*$, and an absorption maxima at 677 nm in the visible region.

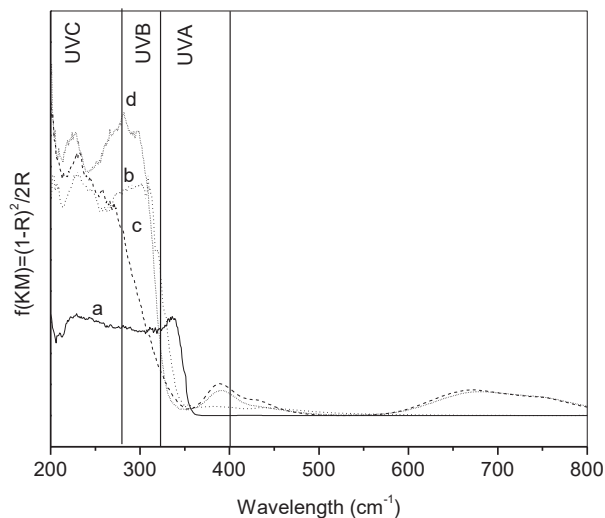


Figure 3. DRUV-Vis spectra of p-aminobenzoic acid (a), sodium p-amino benzoate (b), CoHN (c) and CoHAB (d).

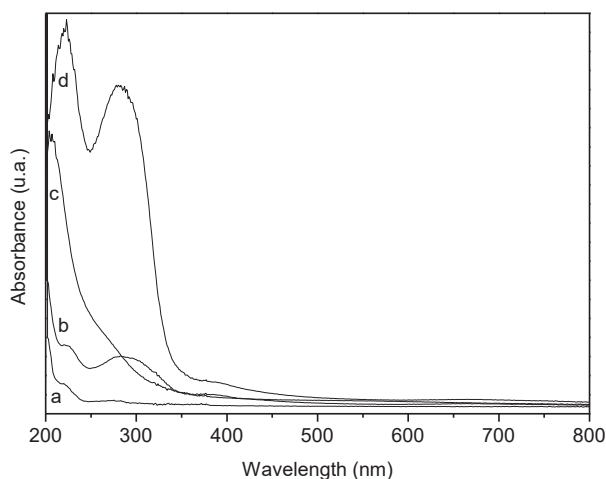


Figure 4. Polyethylene (a), polyethylene/AB (b), polyethylene/NiHN (c) and polyethylene/NiHAB (d)

Polyethylene composite present maximum at 274 nm and being able to absorb in the region between 400-250 nm. Results showed that polyethylene improves its absorption properties due to use of PABA, NiHN and NiHAB as fillers (Figure 4). Polyethylene/PABA present maximums absorption at 285 nm indicating the effect of the UV molecule absorber. The composite made with polyethylene and NiHN was analyzed according to the UV abortion region, showing an abortion between 200 and 400 nm. In the case of the composite polyethylene//NiHAB, the material showed a maximum absorption centered at 220 and 281 nm, covering a higher region than the others analyzed composite.

CONCLUSIONS

The hydrothermal method showed to be a simple procedure to produce the hydroxide salt of nickel and for the replacement of nitrate ions from nickel hydroxide nitrate by of p-aminobenzoate in a quick way.

The intercalation of this anion was first verified using a X-ray diffraction, when the basal spacing increases from 6.87 to 8.39 Å. The presence of p-aminobenzoate anions in NiHAB was also confirmed by FTIR. The NiHAB showed be a good compound where are mixing organic/ inorganic compounds, because it showed higher UV absorption in a comparison to the isolated species (PABA and a CoHN). This composite absorbed radiation between UVC and UVA region with an absorption maximum at 224, 278, 297 and 390 nm and at visible region with a absorption maximum at 677 nm. The composite made with polyethylene and NiHAB indicated to have better

absorption properties than the pure polymer, showing the high potential to improve this property when mixture polymeric compound with hydroxysal. This is a great industrial alternative, once the hydroxysal synthesis is relatively simple

ACKNOWLEDGMENTS

The authors thank CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior), CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico), Leibniz-Institut für Polymerforschung, FINEP (Financiadora de estudos e projetos) for financial support. N.A.G. and S.A.M thanks CNPq for the PhD and post-doctorate scholarships, respectively.

REFERENCES

1. Biswick, T., Jones, W., Pacula, A. & Serwicka E. Synthesis, characterisation and anion exchange properties of copper, magnesium, zinc and nickel hydroxy nitrates. *Journal of Solid State Chemistry*, 179, 49-55 (2006).
2. Coutinho, F., Mello, I., & Maria, L. Polietileno: principais tipos, propriedades e aplicações. *Polimeros: Ciência e tecnologia*, 3, 1-13 (2003).
2. Crepaldi, E. L., & Barros Valim, J. Hidroxidos duplos lamelares: Síntese, estrutura, propriedades e aplicações. *Química Nova*, 3(21) (1998).
3. Guadalupe Carbaljal, G., Gundapa, S., & Wypych, F. Layered hydroxide salts: Synthesis, properties and potential applications. *Solid state Ionics*(178), 1143-1162 (2007).
4. Li, Y., Tang, L.-p., Zhou, W., & Wang, X.-R. Fabrication of intercalated p-aminobenzoic acid into ZnTi layered double hydroxide and its application as UV absorbent. *Chinese Chemical Letters* (2016).
5. Munaro, M., Souza, G., & Akcelrud, L. Estudo da degradação do polietileno usado em revestimento de cabos elétricos. *Belo Horizonte: 7CBPol*. 2003, pp. 65-67.
6. Nakamoto, K (2009). *Infrared and raman spectra of inorganic and coordination compounds part A*. New York: J. Wiley.
7. Rajamthi, M., & Vishnu Lamath, P. (2001). Urea hydrolysis (II) nitrate melts: Synthesis of novel hydroxides and hydroxynitrates. *International Journal of inorganic materials*, 2, 901-906 (1968).
8. Trindade Cursino, A., Ferreira da Costa Gardolinski, J., & Wypych, F. Intercalation of anionic organic ultravioletec ray absorbers into layered zinc hydroxide nitrate. *Journal of Colloid and Interface science*(347), 49-55 (2010).
9. Yousi, E., & Haddad, R. Phodegradação and photosbtabilization of polyxmer: especially polystyrene. *Springer plus*, 2(398) (2013).
10. Zimmermann, A., Jaeger, S., Faria Zawadzki, S., & Wypych, F. Synthetic zinc layered hydroxide salts intercalated with anionic azo dyes as fillers into high-density polyethyelene composites: first insights. *J. Polym Res*(20), 224 (2013).