

## LAYERED MATERIALS AS COLOURED FILLERS FOR POLYMERIC MULTIFUNCTIONAL MATERIALS

Rafael Marangoni <sup>1</sup>, Alexandre Mikowski <sup>2</sup> and Fernando Wypych <sup>3</sup>

Zn<sub>2</sub>Al layered double hydroxides (LDHs) were intercalated with anionic dyes, namely, Orange G (OG), Orange II (OII), Methyl Orange (MO), by zinc and aluminium nitrates simultaneously precipitated with an alkaline aqueous solution, in the presence of excess anionic dyes. After washing procedure to remove the excess of the dye sodium salts, the intercalation compound were dried and characterized by several instrumental techniques. Homogeneous composite films were obtained by casting, after dispersing the LDH intercalated dyes (pigments) into commercial poly (vinyl alcohol) (PVA) aqueous solution and evaporation of water in a vacuum oven. The obtained composite films were transparent, coloured, and capable of absorbing UV radiation. Improved mechanical and thermal properties were also observed compared to the non-filled PVA films or filled with the sodium dye salts. These results demonstrate the onset of a new range of potential applications for LDHs in the preparation of polymer nanocomposite multifunctional materials.

Key words: layered double hydroxides, nanocomposites, PVA

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<sup>1</sup> PhD - Departamento de Química. <sup>2</sup> Prof. - Departamento de Física. <sup>3</sup> Prof. - Departamento de Química. Universidade Federal do Paraná, UFPR, CP 19081, 81531-980, Curitiba – Paraná – Brazil

## 1 – INTRODUCTION

Layered Double Hydroxides (LDHs) are compounds whose individual layers are of Brucite-like ( $Mg(OH)_2$ ) structure. In Brucite, the layers are electrically neutral with magnesium cations located in the center of a regular octahedron with 6 hydroxyl groups in the vertices. The isomorphous substitution of magnesium by a trivalent cation like aluminium introduces a positive charge in the LDH layers. These layers are then stabilized by the presence of hydrated anions in the interlayer space. LDHs are represented by the formula  $[M^{+2}_{1-x}M^{+3}_x(OH)_2]A^{m-}_{x/m} \cdot nH_2O$ , where  $M^{2+}$  and  $M^{3+}$  are divalent and trivalent cations with similar cationic radii,  $A^{m-}$  represents an anion with charge  $m-$  and “ $x$ ” has a value normally between 0.25 and 0.33. The anions category to be exchanged is wide, going from organic, inorganic, polymers, inorganic complexes with different oxidation states and also some biological anions.

Synthetic LDHs intercalated with anionic dyes are known for almost one decade [1-6]. More recently, these materials were used as coloured filler material for polymer with some advantages over the traditional fillers based on mineral clays [7-11]. The main advantage is the aggregation of more than one property to the polymer, these materials being called “multifunctional” materials.

As our research group is for many years involved with studies of intercalation compounds and chemical modification of layered materials and fibers surfaces, the aim of this study is to show that anionic dyes intercalated between the layers of a LDH can be dispersed into a polymer and new coloured composite materials can be obtained with multifunctional properties. As the filler and the polymer should have similar chemical properties to maximize the interactions we have chosen commercial PVA as matrix and hydrophilic LDH as filler.

## 2 - MATERIALS AND METHODS

Orange dyes, Orange G ( $C_{16}H_{10}N_2Na_2O_7S_2$ , Nuclear – OG), Orange II ( $C_{16}H_{11}N_2NaO_4S$ , Merck – OII), methyl orange ( $C_{14}H_{14}N_3NaO_3S$ , Vetec – MO), were used in this study.  $Al(NO_3)_3 \cdot 9H_2O$  (Vetec, 99,5%),  $Zn(NO_3)_2 \cdot 6H_2O$  (Vetec, 99,5%), NaOH (Vetec, 98%) were used to prepare the intercalation compounds as previously reported [10,11]. The structure of the dyes can be seen in figure 1. The proportion of the chemicals used during the intercalation compounds synthesis can be seen in table 1, where the Zn/Al molar ratio (positive charge density of the layers) was chosen to be 2 ( $Zn_2Al$ ).

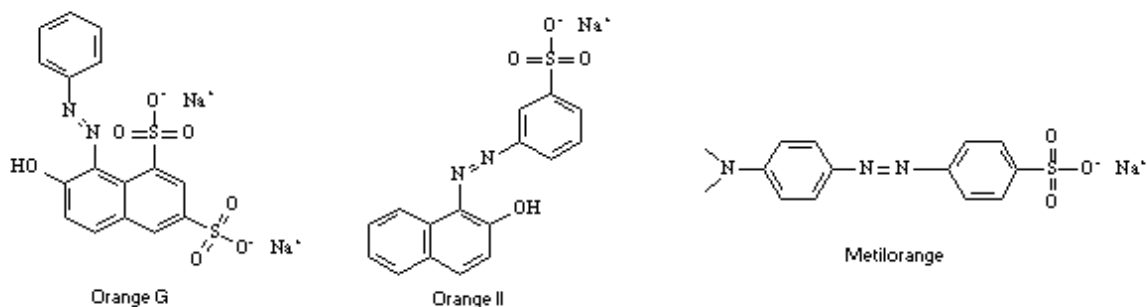


Figure 1 – Structure of the dyes used in the intercalation experiments.

The obtained  $Zn_2Al$ /dyes intercalation compounds were characterized and dispersed into 2 mL of ethanol by sonication (40 kHz) for about 30 minutes (see table 2). Soon afterwards, the ethanolic dispersion of the  $Zn_2Al$ /dyes were added under

vigorous agitation to 0.3 g of PVA ( $M = 72000 \text{ g}\cdot\text{mol}^{-1}$ ; Merck, 98%) previously dissolved in 15 mL of distilled water at 70 °C. After obtaining a homogeneous mixture, the dispersion was transferred to Petri steel dishes (diameter = 6 cm) and the solvent was evaporated in a vacuum oven at 60 °C for 24 hours under a pressure of -400 mmHg. Films were obtained for pure PVA and PVA/Zn<sub>2</sub>Al-dyes with concentrations of 0.5, 1, 2 and 4 wt% in relation to the PVA. For comparison purposes, pure dye salts were also dispersed into PVA in the same proportions as defined by the PVA/Zn<sub>2</sub>Al-dye (table 2).

Table 1 - Chemical proportions used in the synthesis of LDH-orange dyes.

	Mass (g) / Number of mmols.			AEC*	T (°C)
	Al(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Dye salt		
Zn <sub>2</sub> Al/OG	1.875 / 5	2.974 / 10	4.523 / 10	2x	RT**
Zn <sub>2</sub> Al/OII	1.875 / 5	2.974 / 10	7.006 / 20	4x	RT**
Zn <sub>2</sub> Al/MO	1.875 / 5	2.974 / 10	3.273 / 10	2x	60

\*AEC = Excess in relation of the Anionic Exchange capacity; \*\* RT = Room temperature (around 25°C).

Table 2 - Mass of PVA and the filler (LDH-dye) used in the obtaining of PVA films.

Proportion (% - w/w)	PVA (g)	LDH-dye (g)
0.5	0.3	0.0015
1.0	0.3	0.0030
2.0	0.3	0.0060
4.0	0.3	0.0120

The PVA:LDH/dye composite films were characterized by different instrumental techniques such as X-ray diffraction, thermal analysis (TGA/DTA), Fourier-transform infrared spectroscopy (FTIR), Ultraviolet-visible spectroscopy (UV-VIS) and the mechanical properties, emphasizing the results of the last technique in the present work.

Mechanical properties were obtained in tensile mode by using a Instron 5565 equipment. Each experiment used five samples which were kept under controlled humidity conditions (43 % relative air humidity for one week) and average values were considered. Climatic conditions of the equipment room were kept at 43±1 % relative air humidity and 25±1 °C. The samples were cut into 1x4 cm ribbons with average thickness of 0.073±0.009 mm. The initial distance between the instrument grips was kept at 1 cm, while the elongation of the sample was kept at 5 mm·min<sup>-1</sup>.

Using stress/strain curves, the Young's modulus (YM) (from the curve fitting in the initial linear section until 1 % deformation by the least squares method) and the ultimate tensile strength were calculated.

### 3 – RESULTS AND DISCUSSION

Figure 2 shows the photographs of the nanocomposite films obtained by dispersing Zn<sub>2</sub>Al/dye and the pure dye salts into PVA. As can be observed, very homogeneous and transparent nanocomposite films have been obtained in which colour intensity varies proportionally with the concentration pigment (LDH intercalated dye). One important aspect to be noted is the different colours obtained by mixing the same amount of pure dye sodium salts (OG 2%, OII 2% and MO 2%) and the pigments, containing the equivalent amount of the intercalated dye (2%).

Figure 3 shows the Young's modulus with the added filler in the nanocomposites. Pure PVA exhibited Young's modulus value of  $0.73\pm 0.11$  GPa. Addition of 2 % of dye (in relation to the theoretical exchange capacity of the LDH), the Young's modulus increased to  $1.12\pm 0.07$ ,  $1.00\pm 0.18$  and  $1.06\pm 0.07$  GPa for OG, OII and MO, respectively, which was in accordance with earlier reported PVA reinforced LDH-blue dye [11]. These increases of 53.4, 37.0 and 45.2 % in the Young's modulus indicate good interactions/dispersion of the pigment with the polymer molecules, which directly reflect in the mechanical properties of the films.

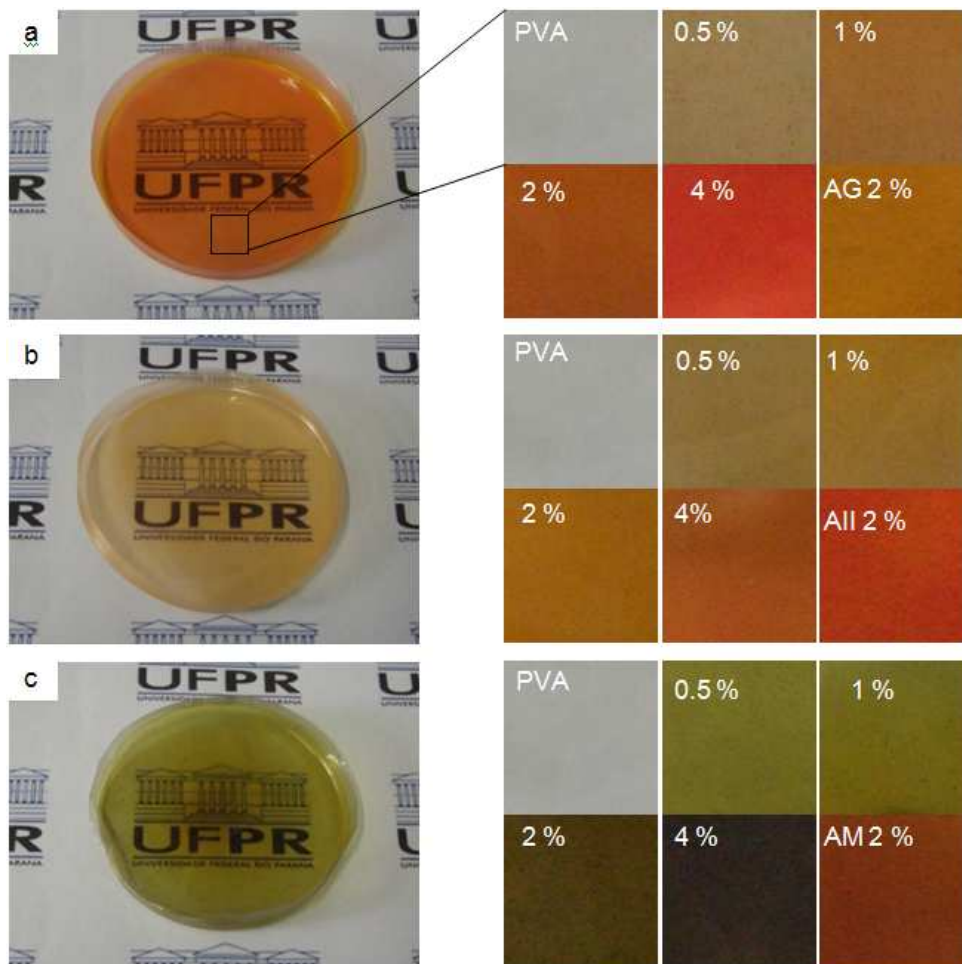


Figure 2 – Photographs of the nanocomposite films obtained by dispersing  $Zn_2Al$ /dye and the pure dyes into PVA. PVA: $Zn_2Al$ /OG (a), PVA: $Zn_2Al$ /OII (b) and PVA: $Zn_2Al$ /MO (c) and details of the films (disks with 6 cm of diameter).

When the intercalation compounds are added to the PVA, the Young's modulus is almost doubled. For example, in PVA:  $Zn_2Al$ /OG, an increase of 98.6 % is observed in Young's modulus ( $1.45\pm 0.08$  GPa) for 0.5 % added charge, while good increases were also observed for the other proportions of fillers. Even for an addition of 4 % of filler, 91.8 % increase in Young's modulus is still observed.

For the nanocomposites derived from PVA: $Zn_2Al$ /OII, a similar behavior as described for blue dye derivatives was observed [11], that is, an increase in the Young's modulus with the added filler, up to 2 %, where after the modulus decreased. The observed modulus values were  $1.40\pm 0.07$ ,  $1.43\pm 0.22$ ,  $1.51\pm 0.18$  and  $1.18\pm 0.19$ , for 0.5, 1, 2 and 4% charge. The highest increase (106.8 %) was observed in the composite with 2 % added filler compared to pure PVA.



The Young's modulus observed for the PVA:Zn<sub>2</sub>Al/MO showed the highest reinforcement values within the orange dye contents tested. For 0.5 % added charge the YM of 1.58±0.14 GPa was observed followed by 1.51±0.09, 1.36±0.27 and 1.19±0.15 for 2%, 1% and 4% of filler, respectively. For OG and MO, the highest values were obtained for 0.5% of filler and for OII, for 2%. The tendency shows that increasing the filler content (see OII and MO), the Young's modulus again decreased. This suggests addition of 0.5 % is sufficient to get a significant reinforcement effect in the PVA films.

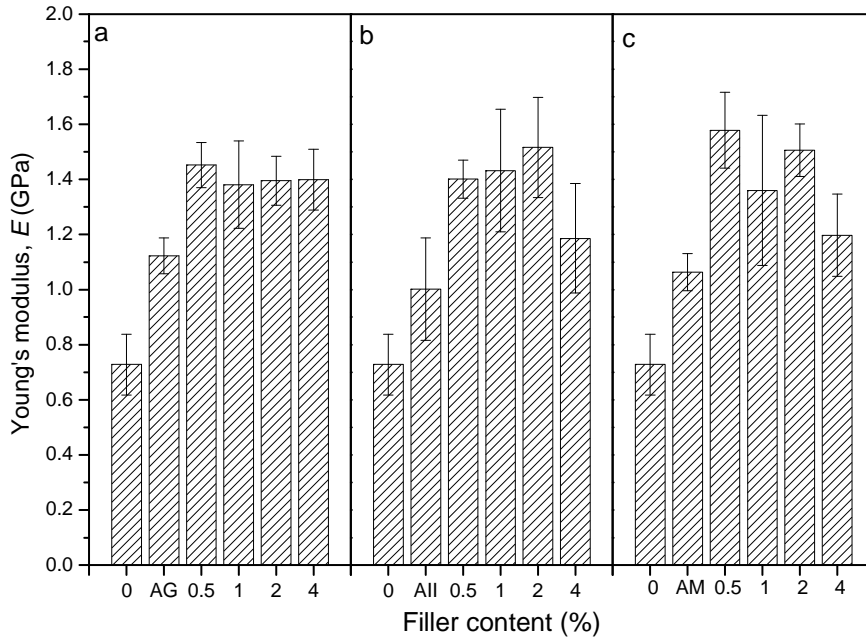


Figure 3 – Young's Modulus ( $E$ ) for PVA:Zn<sub>2</sub>Al/OG (a), PVA:Zn<sub>2</sub>Al/OII (b) and PVA:Zn<sub>2</sub>Al/MO (c). 0 denotes the films prepared with 2 % of the pure dye.

Figure 4 presents the values of ultimate tensile strength ( $\sigma_u$ ) for the PVA nanocomposites with the intercalation compounds LDH-orange dyes. A decrease in the values for  $\sigma_u$  for the PVA-dye compounds is always observed, indicating the negative effect of the dye on the polymer tensile properties. Compared to pure PVA, the dispersion of LDH intercalated with the same dyes showed increase in the maximum fracture strength in all cases, the maximum being concentrated between 0.5 and 1%. The addition of 4 % of Zn<sub>2</sub>Al/MO resulted lower  $\sigma_u$  value than the pure PVA, consistent with the results presented above underlining the negative properties of too high added filler content.

The increase in the maximum tensile strength varies from 6 to 21 %. The average  $\sigma_u$  value for the PVA is 44.22 MPa and the highest increase observed was for the addition of 0.5 % of Zn<sub>2</sub>Al/MO, reaching an average  $\sigma_u$  value of 53.49 MPa. Generally, a plateau between 0.5 and 2 % added filler is observed; however, as already observed in the case of the addition of 4 % of Zn<sub>2</sub>Al/MO, a decreasing tendency of these values with higher amounts of added charge is expected, once the agglomeration of the particles becoming more probable. This results in weak points on the films, leading them more prone to fail at lower values of  $\sigma_u$ . Table 3 presents the values of Young's modulus and ultimate tensile strength for all the compounds studied and discussed above. When dye salts are used as fillers,  $\sigma_u$  values decrease drastically even below the value obtained for pure PVA films (-6.4% for OG and -18.2% for OII).

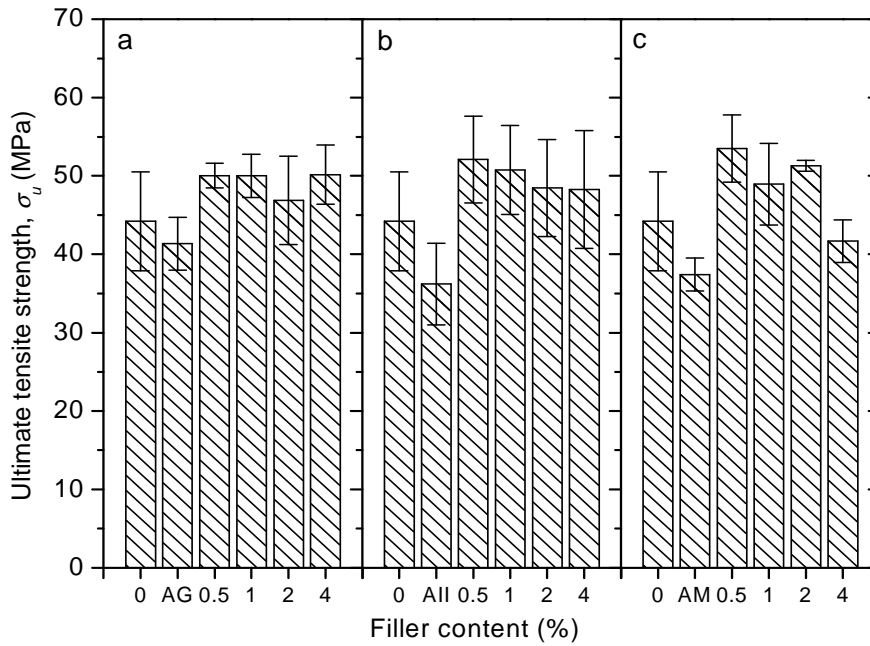


Figure 4 – Ultimate tensile strength ( $\sigma_u$ ) for PVA:Zn<sub>2</sub>Al/OG (a), PVA:Zn<sub>2</sub>Al/Oil (b) and PVA:Zn<sub>2</sub>Al/MO (c). 0 denotes the films prepared with 2 % of the pure dye.

Table 3 - Young's Modulus ( $E$ ) and Ultimate tensile strength ( $\sigma_u$ ) for the nanocomposite films studied.

Content (%)	PVA:Zn <sub>2</sub> Al/OG		PVA:Zn <sub>2</sub> Al/Oil		PVA:Zn <sub>2</sub> Al/MO	
	$E$ (GPa)	%	$E$ (GPa)	%	$E$ (GPa)	%
0	0.73±0.11	-	0.73±0.11	-	0.73±0.11	-
Dye	1.12±0.07	53.4	1.00±0.18	37.0	1.06±0.07	45.2
0.5	1.45±0.08	98.6	1.40±0.07	91.8	1.58±0.14	116.4
1	1.38±0.16	89.0	1.43±0.22	95.9	1.36±0.27	86.3
2	1.39±0.08	90.4	1.51±0.18	106.8	1.51±0.09	106.8
4	1.40±0.11	91.8	1.18±0.19	61.6	1.19±0.15	63.0
	□ (MPa)	%	□ (MPa)	%	□ (MPa)	%
0	44.22±6.29	-	44.22±6.29	-	44.22±6.29	-
Dye	41.37±3.37	-6.4	36.19±5.20	-18.2	37.41±2.10	-15.4
0.5	50.02±1.58	13.1	52.09±5.53	17.8	53.49±4.29	21.0
1	49.98±2.76	13.0	50.75±5.66	14.8	48.94±5.20	10.7
2	46.89±5.64	6.0	48.44±6.17	9.5	51.28±0.70	16.0
4	50.15±3.77	13.4	48.27±7.50	9.2	41.67±2.70	-5.8

The “%” column indicates the mechanical property increase/decrease in relation to pure PVA films; “Dye” represents the dye sodium salt used as filler.

#### 4 – CONCLUSIONS

Zn<sub>2</sub>Al layered double hydroxides were intercalated with the anionic orange dyes through the co-precipitation technique in aqueous alkaline solution. After characterization, the pigments were dispersed in ethanol and the dispersion has been added to the aqueous solution of PVA. After solvent evaporation under mild conditions, homogeneous and transparent nanocomposite films were successfully obtained.

It was observed that the dye molecules generally interact with the polymeric matrix even if intercalated into the inorganic layers. Mechanical reinforcement of the PVA compounded with the dye intercalated-LDHs was achieved, and reasonable increases on Young's modulus and ultimate tensile strength were observed with as little as 0.5 % added filler while larger amount have shown a negative effect of the reinforcement. The further investigation of dye-intercalated LDHs as reinforcement to PVA and other polymers could prove to be a reliable and efficient way to improve both mechanical and colouring properties of the polymers, with vast application ranges.

Currently we are investigating the mechanical properties of nanocomposite films obtained by the compatibilization of the filler with the polymer through an interface created by the chemical modification of the LDH surfaces using silanes and other chemical modifiers.

## 5 – ACKNOWLEDGMENTS

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## 6 – REFERENCES

- [1] Costantino, U.; Coletti, N.; Nocchetti, M.; Aloisi, G.G.; Elisei, F., Anion exchange of methyl orange into Zn-Al synthetic hydrotalcite and photophysical characterization of the intercalates obtained. *Langmuir*, 15, 13, 4454-4460, 1999.
- [2] Costantino, U.; Coletti, N.; Nocchetti, M.; Aloisi, G.G.; Elisei, F.; Latterini, L., Surface uptake and intercalation of fluorescein anions into Zn-Al-hydrotalcite. Photophysical characterization of materials obtained, *Langmuir*, 16, 26, 10351-10358, 2000.
- [3] bin Hussein, M.Z.; Zainal, Z.; Yahaya, A.H.; Aziz, A.B.A., Synthesis of layered organic-inorganic nanohybrid material: an organic dye, naphthol blue black in magnesium-aluminum layered double hydroxide inorganic lamella. *Materials Science and Engineering B-Solid State Materials for Advanced Technology*, 88, 1, 98-102, 2002.
- [4] Bauer, J.; Behrens, P.; Speckbacher, M.; Langhals, H., Composites of perylene chromophores and layered double hydroxides: Direct synthesis, characterization; and photo- and chemical stability. *Advanced Functional Materials*, 13, 3, 241-248, 2003.
- [5] bin Hussein, M.Z.; Yahaya, A.H.; Shamsul, M.; Salleh, H.M.; Yap, T.; Kiu, J., Acid fuchsin-interleaved Mg-Al-layered double hydroxide for the formation of an organic-inorganic hybrid nanocomposite. *Materials Letters*, 58, 3-4, 329-332, 2004.
- [6] bin Hussein, M.Z.; Yahaya, A.H.; Ping, L.M., Dye-interleaved nanocomposite: Evan's Blue in the lamella of Mg-Al-layered double hydroxide. *Dyes and Pigments*, 63, 2, 135-140, 2004.
- [7] Taviot-Gueho, C.; Illaik, A.; Vuillermoz, C.; Commereuc, S.; Verney, V.; Leroux, F., LDH-dye hybrid material as coloured filler into polystyrene: Structural characterization and rheological properties, *Journal of Physics and Chemistry of Solids*, 68, 5-6, 1140-1146, 2007.
- [8] Marangoni, R.; Taviot-Gueho, C.; Illaik, A.; Wypych, F.; Leroux, F., Organic inorganic dye filler for polymer: Blue-coloured layered double hydroxides into polystyrene. *Journal of Colloid and Interface Science*, 326, 2, 366-373, 2008.
- [9] Marangoni, R.; Taviot-Gueho, C.; Illaik, A.; Wypych, F.; Leroux, F., Zn<sub>2</sub>Al layered double hydroxides intercalated and adsorbed with anionic blue dyes: A physico-

chemical characterization. *Journal of Colloid and Interface Science*, 333, 1, 120-127, 2009.

[10] Marangoni, R.; Mikowski, A.; Wypych, F., *Journal of Colloid and Interface Science*, to be published, 2010.

[11] Marangoni, R. PhD Thesis in Chemistry, Federal University of Paraná, 2009.



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