

PVA nanocomposites reinforced with Zn₂Al LDHs, intercalated with orange dyes

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Abstract Zn₂Al-layered double hydroxides (LDH) were intercalated with anions of the dyes Orange G, Orange II, and Methyl Orange by alkaline co-precipitation of aqueous solutions of zinc chloride and aluminum nitrate simultaneously in the presence of dye sodium salts. Transparent, homogeneous, and colored nanocomposite films were obtained by casting after dispersing the dye-intercalated LDHs (pigments) into commercial poly(vinyl alcohol) (PVA). The films were characterized by X-ray diffraction, ultraviolet–visible spectroscopy, thermal analysis (thermogravimetric analysis (TGA)) and differential thermal analysis (DTA)), and mechanical testing. Mechanical reinforcement of the PVA compounded with the dye-intercalated LDHs was achieved, and reasonable increases in Young's modulus and ultimate tensile strength were observed with as little as 0.5% added filler, while larger amounts tended to decrease the reinforcement effect. These results demonstrate the onset of a new range of potential applications for layered

double hydroxide intercalated with dyes in the preparation of polymer composite multifunctional materials.

Keywords Layered double hydroxides · Dye · Intercalation · Nanocomposites · PVA

Introduction

Layered double hydroxides (LDHs) are compounds whose individual layers have a Brucite-like structure. In Brucite (Mg(OH)₂), the layers are electrically neutral with magnesium cations located in the center of a slightly distorted octahedron with six hydroxyl groups at the vertices. The partial isomorphous substitution of magnesium by a trivalent cation 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 $[M_{1-x}^{+2}M_x^{+3}(\text{OH})_2]A_{x/m}^{m-} \cdot n\text{H}_2\text{O}$, where M²⁺ and M³⁺ 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 [1–3]. The intercalated anions can be chosen from a variety of species, from simple inorganic anions to anionic polymers and large colored molecules like anionic dyes. The class of LDHs is widely documented in the literature [4–7]. The pioneering studies of dye intercalation were published in the 1990s when the photophysical properties of the pigments obtained were studied [8–10]. Anionic dyes intercalated into LDHs are especially interesting because of their confinement in the two-dimensional environment of the host structure, the host/guest electrostatic interactions, and high affinity with hydrophilic polymers.

Descriptions of dispersions of pigments in polymers to produce multifunctional polymeric materials are relatively

Dedicated to the 75th birthday of Robert Schöllhorn.

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scarce in the specialized literature, especially papers on the mechanical properties of the resulting micro/nanocomposites [11–13]. This dispersion gives new and desirable properties to the polymer, producing a class of materials called as “multifunctional materials” [14, 15]. Such multifunctionality is described in this paper. Besides varying degrees of color or transparency, thermal stability and mechanical properties can also be improved when the right combination of polymer and pigment is chosen and good dispersion is achieved. The present example describes the intercalation of three orange anionic dyes (Orange G (OG), Orange II (OII), and Methyl Orange (MO)) into Zn_2Al -layered double hydroxides, which after characterization were dispersed into poly(vinyl alcohol) (PVA), producing transparent and homogeneous nanocomposite films. These films were characterized by several instrumental techniques including the investigation of their mechanical properties, by measuring Young’s modulus, or elastic modulus (E), and ultimate tensile strength (σ_u).

Materials and methods

Orange G ($C_{16}H_{10}N_2Na_2O_7S_2$, 7-hydroxy-8-(phenylazo)-1,3-naphthalenedisulfonic acid, disodium salt, Nuclear), denoted OG; Orange II ($C_{16}H_{11}N_2NaO_4S$, *p*-(2-hydroxy-1-naphthylazo)benzenesulfonic acid, sodium salt, Merck), denoted as OII; methyl orange ($C_{14}H_{14}N_3NaO_3S$, 4-[4-(dimethylamino)phenylazo]benzenesulfonic acid, sodium salt, Vetec), denoted MO; and $ZnCl_2 \cdot 5H_2O$ (Vetec, 98%), $Al(NO_3)_3 \cdot 9H_2O$ (Vetec, 99.5%), and NaOH (Vetec, 98%) were used to prepare the intercalation compounds as previously reported [16]. The structure of the dyes can be seen in Fig. 1.

After characterization, the Zn_2Al /dye intercalation compounds obtained were dispersed into 2 mL of ethanol by sonication (40 kHz) for about 30 min. Soon afterwards, the ethanolic dispersion of the Zn_2Al /dye was added under vigorous stirring to 0.3 g of PVA ($M=72,000$ g 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 a steel Petri dish (diameter=6 cm), and the solvent was evaporated in a vacuum oven at 60 °C for 24 h under a pressure of –400 mmHg. Films were obtained for neat PVA and PVA: Zn_2Al /dye with concentrations of 0.5, 1, 2, and 4 wt.% in relation to the PVA. For comparison purposes, pure dyes were also dispersed in PVA in the same proportions as defined for the Zn_2Al /dye [17].

The prepared materials were characterized by different instrumental techniques. X-ray diffraction (XRD) analyses were performed in a Shimadzu XRD-6000 diffractometer with a Cu K_α radiation ($\lambda=1.5418$ Å) between 3.0° and 30.0° 2θ at 30 mA and 40 kV, using a step size of 0.02° and speed of 1° min $^{-1}$. Samples were prepared by deposition of the solid materials onto a glass sample holder or by gluing the polymeric film onto an aluminum sample holder.

Thermal analyses (simultaneous TGA and DTA) were performed with a Mettler Toledo TGA/SDTA 851° device, using 150 μ L Al_2O_3 crucibles under O_2 flow (50 ml min $^{-1}$) at a heating rate of 10 °C min $^{-1}$ between 30 and 1,000 °C.

Mechanical properties were obtained in tensile mode by the use of an Instron model 5565 Universal Assay apparatus. Five samples were tested for each composition. The samples were kept under controlled humidity conditions (43% relative air humidity for 1 week), and average values were considered. The climate of the testing room was kept at $43 \pm 1\%$ relative air humidity and 25 ± 1 °C. The samples were cut into 1×4 cm ribbons with average thickness of 0.073 ± 0.009 mm. The initial distance between the instrument grips was kept at 1 cm, and the elongation tests of the samples were obtained at the speed of 5 mm min $^{-1}$.

The results were evaluated with stress versus strain curves, from which we calculated Young’s modulus (E ; from curve fitting in the initial linear section until 1% deformation by the least squares method) and ultimate tensile strength (σ_u).

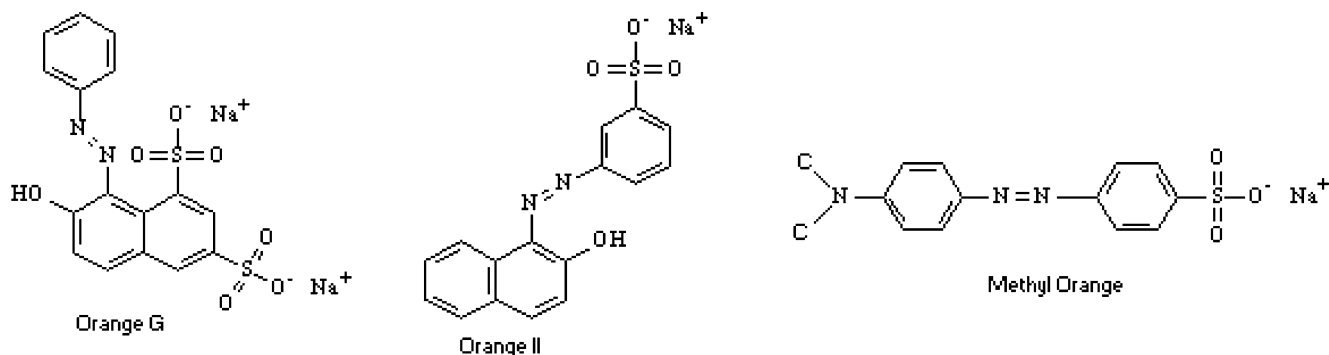
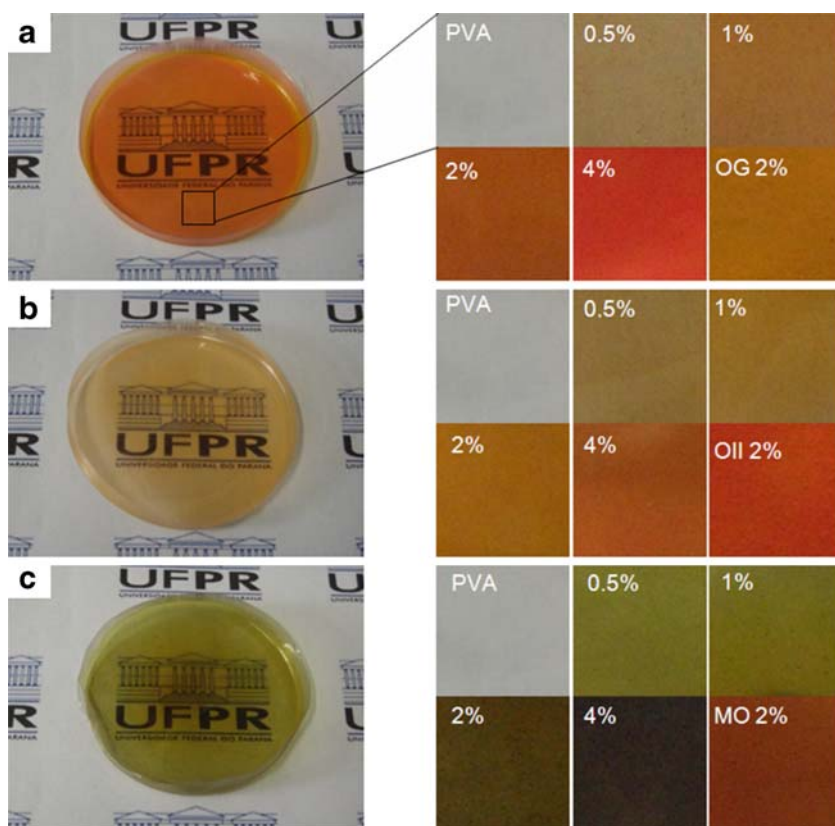


Fig. 1 Structure of the dyes used in the intercalation experiment. Hydrogen atoms were removed to facilitate the visualization

Fig. 2 Nanocomposite films obtained by dispersing Zn₂Al/dye and the pure dyes in PVA. PVA:Zn₂Al/OG (a), PVA:Zn₂Al/OII (b), and PVA:Zn₂Al/MO (c) and details of the films (round films: diameter of 6 cm)



Results and discussion

Figure 2 shows the nanocomposite films obtained by dispersing Zn₂Al/dye and the pure dyes in PVA. As can be observed, very homogeneous and transparent nanocomposite films were obtained in which color intensity varied proportionally to the pigment (LDH intercalated dye) concentration. One important aspect is the different color obtained by mixing the same amount of pure dye (OG 2%, OII 2%, and MO 2%) and the pigments, containing the equivalent amount of the intercalated dye. These color changes are discussed further in the section on characterization by ultraviolet–visible (UV-Vis) spectrometry.

Figure 3 shows the X-ray diffraction patterns of the PVA nanocomposite films. In all nanocomposites, the characteristic PVA matrix diffraction peaks were observed between 18° and 22.5° in 2θ [18].

The diffraction patterns of this series of films show the same tendencies as all films produced. In the lower concentration range (0.5% and 1%), there is no evidence of crystalline phases from the LDH used as filler. However, at 2%, such diffraction peaks start to be observed, and at 4% filler, a broad peak can clearly observed. Basal distances of 17.49, 22.43, and 24.54 Å for PVA:Zn₂Al/OG, PVA:Zn₂Al/OII, and PVA:Zn₂Al/MO were observed, which is consistent with the intercalation of the dye anions into the LDHs, as previously reported [19, 20]. A small

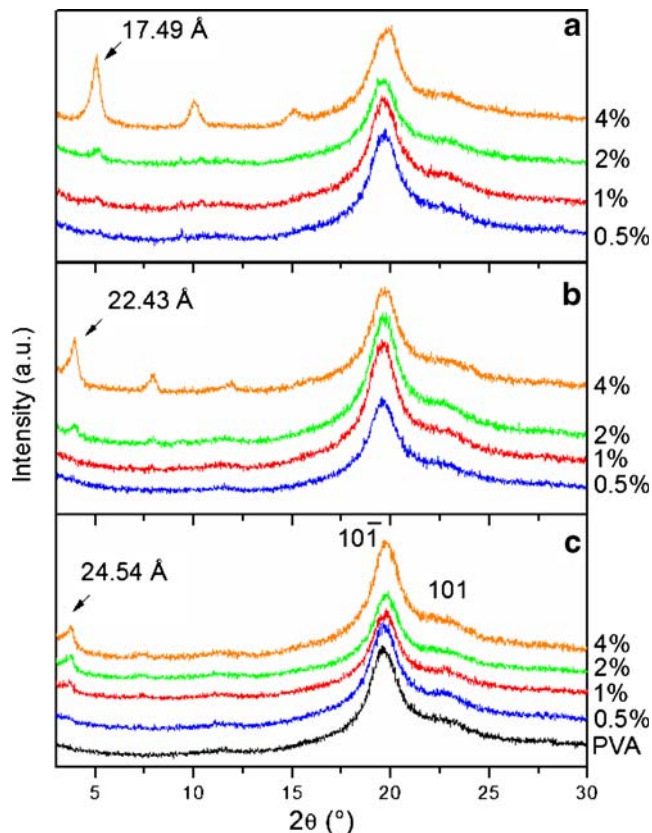


Fig. 3 X-ray diffraction patterns of the PVA nanocomposite films. PVA:Zn₂Al/OG (a), PVA:Zn₂Al/OII (b), and PVA:Zn₂Al/MO (c)

increase in the basal distance in the original intercalated materials is observed, of 0.56, 0.29, and 0.57 Å for PVA:Zn₂Al/OG, PVA:Zn₂Al/OII, and PVA:Zn₂Al/MO, respectively, which most likely indicates a partial co-intercalation of PVA. This effect certainly contributes to the homogeneity of the obtained films [16].

Electronic spectra in the region of UV–visible for the films are presented in Fig. 4. The spectrum for the PVA:Zn₂Al/OG nanocomposite (Fig. 4a) registers that the profile of the intercalation compound added to the PVA presented a 48-nm hypsochromic shift in comparison with the original Zn₂Al/OG (551 nm) (not shown). Bands at 503 and 482 nm were observed, attributed to the tautomeric hydrazone/azo forms of the dye [21]. The same bands are observed in the spectrum of the PVA dye film, suggesting interactions between the co-intercalated molecules of PVA and the dye molecules intercalated into the inorganic matrix. Another possibility is the interactions of the surface and intercalated dye positioned at the borders of the layered crystals, with the polymeric matrix. A shoulder around 551 nm can be observed in the spectra of the films with higher amounts of filler. This indicates that at higher concentrations, part of the pigment is not interacting with the PVA and still

absorbs at higher wavelengths, as in the original intercalation compound.

The nanocomposites derived from Zn₂Al/OII presented absorption maxima around 488 nm (Fig. 4b), a value very close to what is observed in the intercalation compound prior to dispersion in PVA (490 nm). Despite the fact that no clear shift was noticed, there was good dispersion of the filler into the polymeric matrix, as attested by the XRD patterns and by the visual observation of the films. For the PVA containing the pure MO dye (Fig. 4c), a broad absorption band around 452 nm can be observed. This is interesting, since a maximum at 393 nm is observed in the pure dye, while the Zn₂Al/MO intercalation compound presents an absorption maximum at 390 nm, and in the PVA:Zn₂Al/MO composite, the absorption band is very broad and with no clear maximum. This band could be composed from the bands from the pure dye and from the intercalation compound, indicating that the surface methyl orange molecules interact with the PVA while the intercalated molecules do not. Below 350 nm, in the UV region, one can observe absorption bands at 250 and 332 nm for the Zn₂Al/OG, at 232, 268, and 314 nm for the Zn₂Al/OII, and at 283 nm for the Zn₂Al/MO compounds, which overlap at higher concentrations with the PVA bands at 284 and 331 nm. These bands from the filler are, however, of higher intensity than the ones from the PVA and increase the absorption capacity of the nanocomposite films in the UV-A, B, and C regions in relation to the neat polymer.

The thermal behavior of the nanocomposite films from Zn₂Al/OG was evaluated and is presented in Fig. 5a, b.

Thermal behavior of the different films is very similar up to 150 °C, when adsorbed water is eliminated, with around 7.1% mass loss. From 210 °C onwards, the PVA begins to decompose (endothermic DTA event). This temperature varies, however, up to 218 °C, with the increase in added filler.

After 233 °C, the decomposition of the PVA accelerates due to a dehydroxylation process. This onset temperature tends to decrease with increasing added filler in the nanocomposites. If one considers the temperature needed to achieve a 10% mass loss, the neat PVA reaches 233 °C, while the composites with 2% and 4% filler reach 236 °C, and higher temperatures are reached for the films with 0.5% (241 °C) and 1% (248 °C). This represents a 15 °C higher stability temperature for the nanocomposite film formed with 1% filler to reach 10% mass loss. A variable mass loss is observed at higher temperatures within the different nanocomposites, 52% residue at 298 °C for 4% added filler; 40% residue at 308 °C for 1% added filler; 38% residue at 321 °C for 0.5% added filler; and 45% residue at 323 °C for 2% added filler. This decomposition occurs more slowly in the neat PVA, where a 37.8% residue is obtained at 387 °C [22].

A relative stabilization of the system occurs after that, until a sudden, very fast burning process is observed in

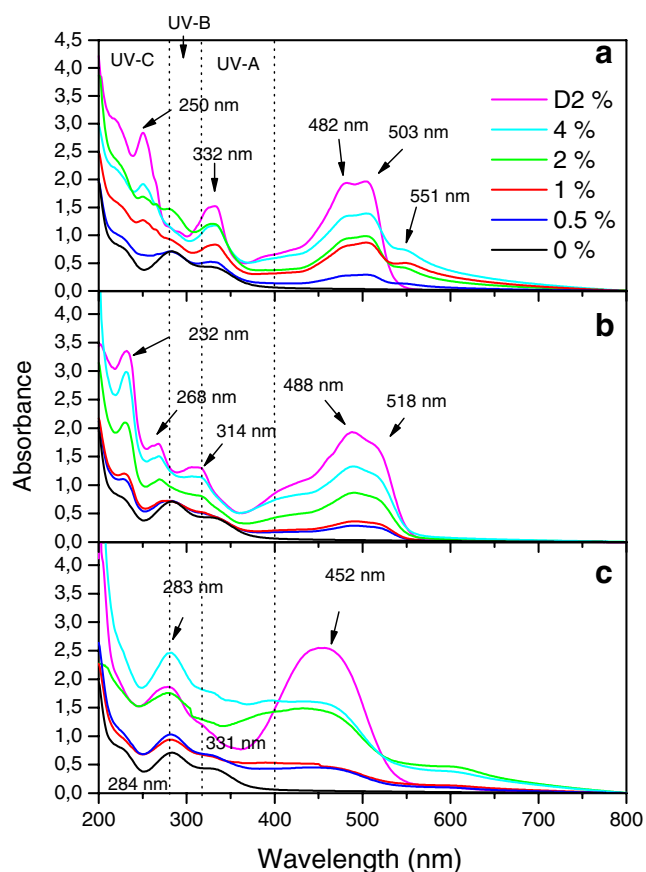


Fig. 4 UV–visible absorption spectra for the nanocomposite films: PVA:Zn₂Al/OG (a), PVA:Zn₂Al/OII (b), and PVA:Zn₂Al/MO (c). D2% stands for a PVA film doped with 2% pure dye

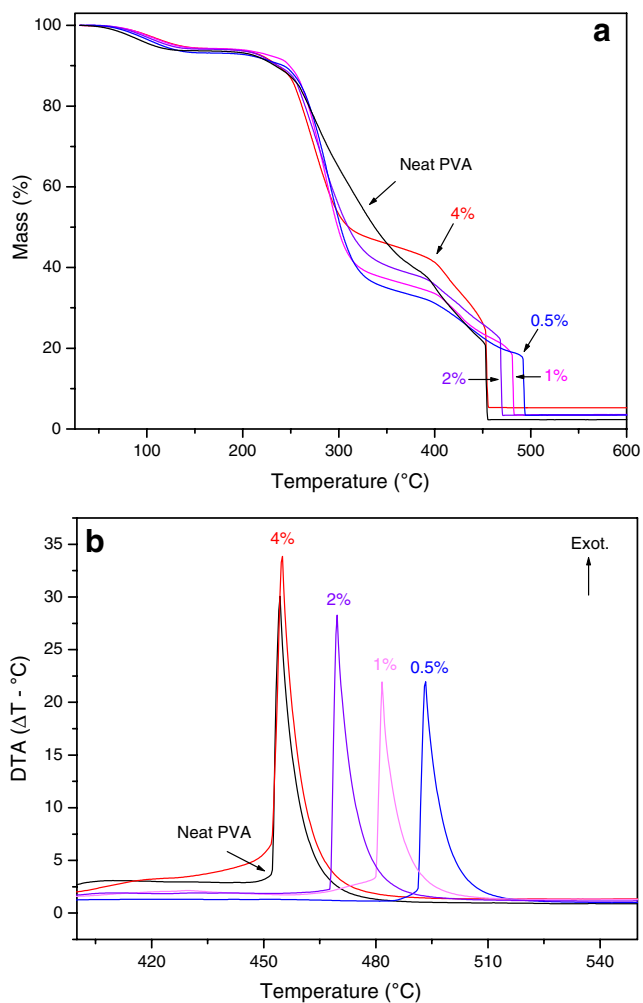


Fig. 5 Thermal analysis curves (TGA (a) and DTA (b)) for the nanocomposite PVA:Zn₂Al/OG with different pigment concentrations. Curve (b) restricted to a smaller range of temperature to show the effect of the DTA peak shift

conjunction with a very intense exothermic DTA peak. In agreement with the results of the former decomposition steps, the composites with lower added filler presented higher decomposition end-temperatures. For 0.5% added filler, the maximum temperature of the DTA peak occurs at 494 °C, while in the neat PVA, the peaks is observed at 453 °C. Even presenting a fast initial decomposition, this composite needed a 41 °C hotter environment to totally decompose in relation to the neat PVA. The aggregation of LDH nanoparticles at higher concentration of filler and decrease of relative contact surface area could inhibit radical reactions and consequently explain the increase of thermal stability at lower concentration of filler and its successive decrease with increase of amount of filler [23].

The stress/strain curves for the PVA:Zn₂Al/OII nanocomposite films are presented in Fig. 6. Each of the curves was chosen as being the most representative from within all samples analyzed, presenting average values of Young’s

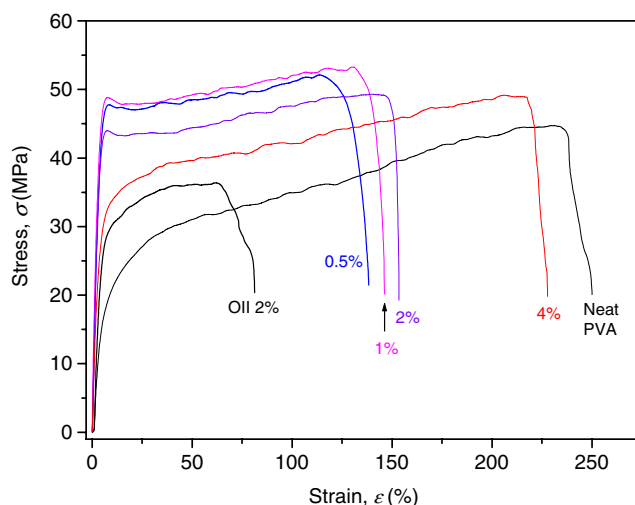


Fig. 6 Stress/strain curves of the PVA:Zn₂Al/OII nanocomposite films

modulus and maximum stress. In general, more traction-resistant films were obtained from adding the intercalated compounds to the PVA. There was an increase in both Young’s modulus and ultimate tensile strength of the nanocomposites.

Figure 7 shows Young’s modulus with the added filler in the nanocomposites. Neat PVA presented a Young’s modulus value of 0.73 ± 0.11 GPa. In accordance with what was formerly reported on the reinforcement of PVA with LDH blue dye [24], adding 2% of dye (in relation to the theoretical exchange capacity of the LDH) caused Young’s modulus to increase to 1.12 ± 0.07 , 1.00 ± 0.18 , and 1.06 ± 0.07 GPa for OG, OII, and MO, respectively. These increases of 53.4%, 37.0%, and 45.2% in Young’s modulus

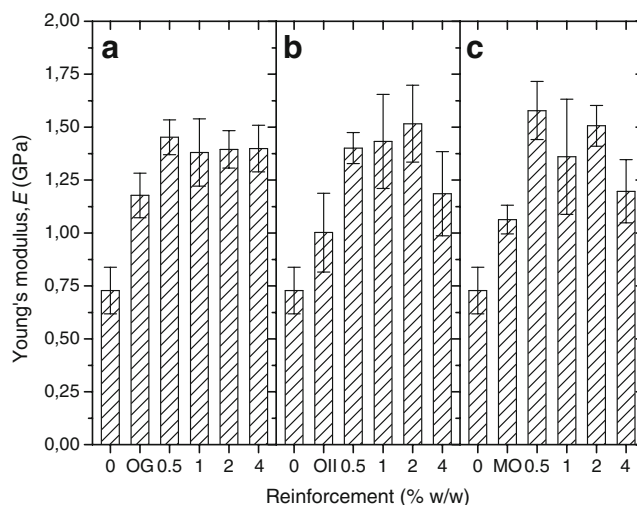


Fig. 7 Young’s modulus (E) obtained from mechanical tests of PVA: Zn₂Al/OG (a), PVA:Zn₂Al/OII (b), and PVA:Zn₂Al/MO (c). OG, OII, and MO denote films prepared from PVA and 2% pure dye

indicate the strong hydrogen bond interactions of the pigment with the polymer molecules, which are directly reflected in the films' mechanical properties.

When the intercalation compounds are added to the PVA, Young's modulus almost doubles. For the PVA: Zn₂Al/OG, an increase of 98.6% is observed (1.45 ± 0.08 GPa) for 0.5% added filler, with slightly lower increases for the other reinforcement proportions. Even with an added filler of 4%, increases of 91.8% in Young's modulus are still observed. It is possible that at higher values of added filler, the modulus will tend to decrease due to the expected filler particles' aggregations. For the nanocomposites derived from PVA:Zn₂Al/OII, a similar behavior to blue dye derivatives was observed [24], that is, an increase in the elastic modulus with the added filler, up to a 4% added filler, after which the modulus decreases. The Young's modulus values were 1.40 ± 0.07 , 1.43 ± 0.22 , 1.51 ± 0.18 , and 1.18 ± 0.19 for 0.5%, 1%, 2%, and 4% of added filler. The greatest increase was observed in the composite with 2% added filler, 106.8% in comparison to neat PVA. The Young's modulus observed for the PVA: Zn₂Al/MO presented the best reinforcement values among the orange dyes tested. An increase of 116.4% for 0.5% added filler (1.58 ± 0.14 GPa), followed by 1.51 ± 0.09 (2%), 1.36 ± 0.27 (1%), and 1.19 ± 0.15 (4%). Despite this inversion in the sequence, the composite with the highest added filler still presented the smallest reinforcement increase, and an addition of 0.5% proved to be enough for a significant reinforcement of the PVA films.

Figure 8 presents the ultimate tensile strength (σ_u) values for the PVA nanocomposites with the LDH/orange dye intercalation compounds. A decrease in the σ_u values for the PVA-dye compounds is always observed, signaling the

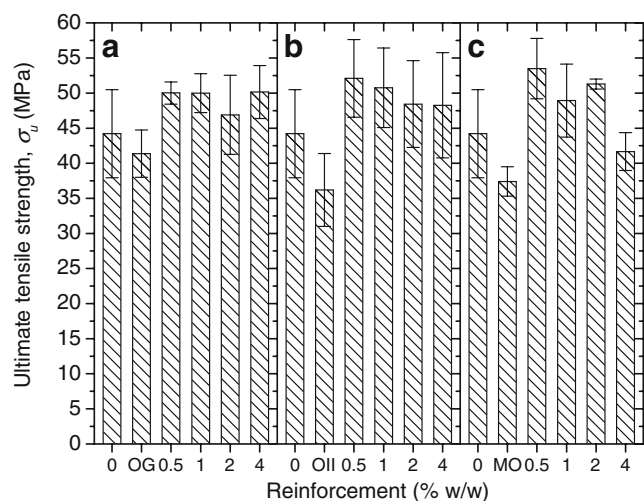


Fig. 8 Ultimate tensile strength (σ_u) obtained from mechanical assays for PVA:Zn₂Al/OG (a), PVA:Zn₂Al/OII (b), and PVA:Zn₂Al/MO (c). OG, OII, and MO denote films prepared from PVA and 2% pure dye

Table 1 Young's modulus (E) and ultimate tensile strength (σ_u) for the nanocomposite films studied

Filler (wt.%)	PVA:Zn ₂ Al/OG			PVA:Zn ₂ Al/OII			PVA:Zn ₂ Al/MO		
	E (GPa)	σ_u (MPa)	%	E (GPa)	σ_u (MPa)	%	E (GPa)	σ_u (MPa)	%
0	0.73±0.11	44.22±6.29	–	0.73±0.11	44.22±6.29	–	0.73±0.11	44.22±6.29	–
Dye	1.12±0.07	41.37±3.37	–6.4	1.00±0.18	37.0	–18.2	1.06±0.07	37.41±2.10	–15.4
0.5	1.45±0.08	50.02±1.58	13.1	1.40±0.07	91.8	17.8	1.58±0.14	53.49±4.29	21.0
1	1.38±0.16	49.98±2.76	13.0	1.43±0.22	95.9	14.8	1.36±0.27	48.94±5.20	10.7
2	1.39±0.08	46.89±5.64	6.0	1.51±0.18	106.8	9.5	1.51±0.09	51.28±0.70	16.0
4	1.40±0.11	50.15±3.77	13.4	1.18±0.19	61.6	9.2	1.19±0.15	41.67±2.70	–5.8

The percent column indicates the mechanical properties' increase (+) or decrease (–), in relation to neat PVA

negative effect of the dye on the polymer mechanical properties. On the other hand, the reinforcement with LDH intercalated with the same dyes proved to increase the tensile strength in all cases. Only the addition of 4% Zn₂Al/MO caused a σ_u value lower than the neat PVA, although this value is within the experimental error. This is consistent with the results presented above, relating the negative properties of an overly high added filler. The average σ_u value for the PVA is 44.22 MPa, and the best increase observed is achieved with the addition of 0.5% Zn₂Al/MO, reaching an average σ_u value of 53.49 MPa. Generally, a plateau between 0.5% and 2% added filler is observed. However, as already shown by the addition of 4% Zn₂Al/MO, a tendency of these values to decrease with higher amounts of added filler is expected since the agglomeration of the particles will be more frequent, causing weak points in the films, making them more prone to fail at lower values of σ_u . Table 1 presents the values of Young's modulus (E) and ultimate tensile strength (σ_u) for all the compounds studied and discussed above.

In the literature, Young's modulus and tensile strength of PVA are between the ranges of 1.4 and 5.6 GPa and 15.7 and 83 MPa, respectively [12, 24–26]. The Young's modulus and tensile strength values of neat PVA films obtained in this work, 0.73 ± 0.11 GPa and 44.22 ± 6.29 MPa, respectively, are within the range observed in the literature. The mechanical properties of polymers vary according to the molecular weight (degree of polymerization), crystallinity index, and the thermal history of the sample used, which makes an absolute comparison difficult.

Even so, the results obtained for the PVA:Zn₂Al/dyes nanocomposites are in the same range as previously reported, where the improvements occur in relation to neat PVA (the increase of Young's modulus and tensile strength of PVA are, respectively, 116.4% for PVA:0.5 wt.% of Zn₂Al/MO and 21.0% for the same sample). Similar PVA films reinforced with different layered double hydroxides reported in the literature [12] have shown both Young's modulus and tensile strength of the PVA nanocomposites below the values of neat PVA, attesting the positive results obtained in the present work.

Table 2 presents Young's modulus (E) and ultimate tensile strength (σ_u) of PVA and the different composites using PVA as matrix, as reported in the literature [12, 24–26].

The mechanical property results obtained for Zn₂Al/dyes are not as good as those obtained for carbon nanotubes but are similar to those obtained for PVA reinforced with sodium montmorillonite, a traditional reinforcement in polymer nanocomposites [27]. In the case of carbon nanotubes, it is important to comment that these materials are much more expensive and difficult to obtain in large scale than LDHs and also produces a black color in the samples, which can be a problem for certain applications.

One strategy to improve the mechanical properties is the process of functionalization, as can be seen in Table 2. This is recommended in the literature to allow compatibilization of the reinforcement with the polymeric matrix, maximize the dispersion and consequently the mechanical properties [28]. Experiments are under way to use Zn₂Al/dyes as

Table 2 Summary of mechanical properties of PVA and composites from the literature [12, 24–26]

Sample	E (GPa)	%	σ_u (MPa)	%	Ref.
PVA	1.41	–	75	–	[12]
PVA/APP/Zn–Al 0.3 wt%	0.88	–37.6	58.3	–22.3	
PVA/APP/Ni–Al 0.3 wt%	1.08	–23.4	65.8	–12.3	
PVA/APP/Ni–Fe 0.3 wt%	1.08	–23.4	61.7	–17.7	
PVA/APP/Zn–Fe 0.3 wt%	0.93	–34.0	57.4	–23.5	
PVA	4.34	–	80.49	–	[24]
PVA/FWNTS 0.2 wt%	5.31	22.4	104.55	29.9	
PVA/fFWNTS 0.2 wt%	6.33	45.9	122.45	52.1	
PVA/fFWNTS 0.5 wt%	6.8	56.7	127.27	58.1	
PVA/fFWNTS 1 wt%	7.10	63.6	132.57	64.7	
PVA	5.6	–	15.7	–	[25]
PVA/MWNTS 0.91 wt%	7.2	28.6	19.5	24.2	
PVA/MWNTS 2.4 wt%	12.5	123.2	22.1	40.8	
PVA/MWNTS 9.1 wt%	25.3	351.4	42.3	169.4	
PVA	4.0	–	83	–	[26]
PVA/fSWNT 2.5 wt%	5.6	40	97	16.9	
PVA/fSWNT 5 wt%	6.2	55	128	54.2	
PVA/pure SWNT 2.5 wt%	5.4	35	79	–4.8	

The percent column indicates the mechanical properties increase (+) or decrease (–), in relation to neat PVA

APP ammonium polyphosphate, FWNTS few-walled carbon nanotubes, fFWNTS functionalized few-walled carbon nanotubes, MWNTS multiwall carbon nanotubes, fSWNT functionalized single-walled carbon nanotubes

fillers in other hydrophilic and hydrophobic synthetic polymers.

Conclusions

Zn₂Al-layered double hydroxides were intercalated with anionic orange dyes through the co-precipitation technique in aqueous alkaline solution. After characterization, the pigments (LDH intercalated dyes) were dispersed in ethanol, which was added to the aqueous solution of PVA. After solvent evaporation under mild conditions, homogeneous and transparent nanocomposite films were obtained. The films were characterized by XRD, UV-Vis spectroscopy, thermal analysis (TGA/DTA), and mechanical testing. It was observed in the UV-Vis spectra that some intercalated dye molecules (probably those positioned at the borders of the layered crystals) can interact with the co-intercalated PVA molecules. In addition, the adsorbed dye molecules can also interact with the polymeric matrix. Mechanical reinforcement of the PVA compounded with the dye-intercalated LDH was achieved, and reasonable increases in Young's modulus and ultimate tensile strength were observed with as little as 0.5% added filler, while larger amounts tended to decrease the reinforcement effect. The obtained PVA:Zn₂Al/dyes nanocomposites are transparent, colored, with improved mechanical properties and thermal stability, and capable of absorbing UV radiation. These findings open up a new venue for the potential applications of this remarkable class of compounds as multifunctional-layered nanocomposite materials.

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