Influence of Organic-Modified Inorganic Matrices on the Optical Properties of Palygorskite–Curcumin-Type Hybrid Materials

Florentina Monica Raduly, Valentin Rădițoiu *, Radu Claudiu Fierăscu, Alina Rădițoiu, Cristian Andi Nicolae and Violeta Purcar

National Research and Development Institute for Chemistry and Petrochemistry—ICECHIM, 202 Splaiul Independentei, 6th District, 060021 Bucharest, Romania; monica.raduly@icechim.ro (F.M.R.); fierascu.radu@icechim.ro (R.C.F.); coloranti@icechim.ro (A.R.); ca_nicolae@yahoo.com (C.A.N.); violeta.purcar@icechim.ro (V.P.)

* Correspondence: vraditoiu@icechim.ro

Abstract: Clays are very important from an economic and application point of view, as they are suitable hosts for organic compounds. In order to diversify the fields of application, they are structurally modified by physical or chemical methods with cationic species, and/or different bifunctional compounds, such as organosilanes. In this study, palygorskite was modified with (3-Aminopropyl) triethoxysilane, which was subsequently modified at the amino group by grafting an acetate residue. By using this strategy, two types of host hybrid materials were obtained on which curcumin derivatives were deposited. The composites obtained were structurally characterized and their photophysical properties were investigated in relation to the structure of the host matrices and interactions with curcumin-type visiting species. The hybrid composites have different colors (orange, yellow, pink), depending on the polarity of the inorganic matrices modulated by different organic groups grafted at the surface. Fluorescence emission in the visible range is characterized by the presence of two emission maxima, one belonging to the chromophore and the other influenced by the physical interactions between auxochromes and host matrices. These hybrid materials, compared to other composite structures, are obtained by a simple adsorption process. They are temperature stable in aggressive environments (acid/base) and render the fluorescent properties of dyes redundant, with improved luminescent performance compared to them.

Keywords: hybrid materials; palygorskite; curcumin derivatives; X-ray diffraction; fluorescence emission

1. Introduction

Hybrid materials, consisting of carrier matrices of inorganic origin and an active compound of organic/inorganic type, are more and more common in current studies, especially in fields such as medicine, environmental protection or catalysis [1–5]. Inorganic matrices, such as clays, are very often used due to availability, low price, structural diversity and the possibility of recycling [6,7]. These are found as support matrices for two categories of materials, some that act as a collection vehicle and others as a transport and/or release of organic compounds. Of these, the former acts as an adsorbent and is usually used in water purification processes. In this case, the clays are conditioned by different methods so that the adsorption processes of organic/inorganic compounds that pollute the water are as efficient as possible [1,6]. These types of supports have been modified according to the nature of the active substances transported, the structure of clay-based matrices becoming much more complex. In this sense, the clays were modified with layer swelling compounds or organic substances with high affinity for bio-active compounds, so as to increase their adsorption capacity [7–10]. In some studies, palygorskite (attapulgite, (Mg, Al)2Si4O10 (OH) 4 (H2O)), a magnesium aluminum phyllosilicate with a fibrillar structure, in monoclinic crystalline
systems [11–13], is preferred for such applications. At the same time, palygorskite is known to be one of the oldest clays used to make hybrid materials (Maya blue pigment) obtained by the adsorption of natural indigo [14,15].

Palygorskite is currently treated with cationic substances [16,17], hydroxylamine derivatives [18] or silanes [19–22] to promote the adsorption of naturally occurring or synthesized organic compounds. Most often, these are essential oils [23], dyes [24–26] or enzymes [27] loaded on the inorganic matrices, resulting in hybrid materials that preserve their original properties in different environments, in which factors, such as light, temperature, or pH, can degrade organic compounds. The processes of loading inorganic matrices with bioactive compounds take place through ion exchange processes, adsorption at microwaves or ultrasound-assisted processes [20,28,29]. Such hybrid materials usually have antioxidant or antimicrobial properties and are used in the food and pharmaceutical industry [30–33].

One of the most sought after natural sources of antioxidant compounds is turmeric (Curcuma longa), whose main compounds are curcumin, demethoxy and bisdemethoxy derivatives. These phenolic compounds are found in studies that confirm their antioxidant, anti-inflammatory or antimicrobial properties [34–37]. Given these properties, we are currently trying to develop new and modern applications in areas related to human health. Thus, through various methods of conditioning with nanoparticles, natural polymers or clays, curcumin derivatives have found applications in the form of hybrid materials, in areas, such as food packaging, food additives, sensors, bioactive coatings and skin cosmetic products [38].

The aim of this study was to obtain hybrid materials made by depositing curcumin (CC) and a curcumin derivative (CCN) obtained by synthesis, on two types of silane-modified palygorskite. The hybrid materials obtained were structurally analyzed and the optical properties were evaluated. The influence of the structure of the modified inorganic support with different organic molecules having different polarities on the optical properties of the curcuminoids deposited on them was analyzed.

2. Materials and Methods

2.1. Materials

2.1.1. The Host Inorganic Matrix

The Palygorskite (PAL) clay used in this study was obtained from SERVA (Germany) with the chemical compositions presented in Table 1 (by X-ray fluorescence, XRF). The clay was activated in hydrochloric acid (5 N, HCl, Chimreactiv, Bucharest, Romania) and modified with (3-Aminopropyl)triethoxysilane (99%, APTES, Aldrich, St. Louis, MO, USA) and sodium chloroacetate 98%, ACD, Aldrich, St. Louis, MO, USA) using ethanol (96%, EtOH, Chimreactiv, Bucharest, Romania) as solvent.

<table>
<thead>
<tr>
<th>Element</th>
<th>Si</th>
<th>Al</th>
<th>Fe</th>
<th>Mg</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>L.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw (wt%)</td>
<td>25.79</td>
<td>3.65</td>
<td>4.19</td>
<td>3.7</td>
<td>0.48</td>
<td>4.02</td>
<td>0.63</td>
<td>56.74</td>
</tr>
<tr>
<td></td>
<td>(+0.48)</td>
<td>(+0.21)</td>
<td>(+0.09)</td>
<td>(+1.2)</td>
<td>(+0.02)</td>
<td>(+0.07)</td>
<td>(+0.05)</td>
<td>(+0.9)</td>
</tr>
</tbody>
</table>

L.E.—light elements (not detectable by XRF).

2.1.2. Curcumin Dyes

The curcumin dye (Figure 1) was synthesized at microwaves and purified using a method already published by our group [39]. Briefly, a mixture of boron trioxide (4 mmol), acetylacetone (8 mmol) and tributyl borate (3.2 mmol) was introduced in a porcelain capsule and was irradiated in a microwave oven at 300 W for 10 min. After the formation of the boron complex of acetylacetone, vanillin or 4-N,N-diethyl-benzaldehyde (7 mmol) and dodecylamine (0.162 mmol) were added, and the mixture was irradiated for another 20 min at 100 W. An aqueous solution of acetic acid (10% by weight) was added to the reaction mixture, the obtained suspension was filtered off, and the solid product was washed with
cold water, and then dried. The obtained product was purified by recrystallization from a mixture of ethyl-acetate:methanol = 3:2 (v/v).

Figure 1. Keto-enol tautomeric forms of curcumin derivatives.

2.2. Methods

2.2.1. Obtaining the Palygorskite Functionalization

The clay was activated in a 5 M HCl solution at 100 °C for 4 h. The gelled composition was centrifuged, filtered, and then washed with water until neutral pH. Afterwards, the crude product was dried at 110 °C for 5 h in order to obtain activated PALs, which was dispersed into anhydrous ethanol, and the silane (APTES) was added to the mixture (1:1 mass/volume ratio) with vigorous stirring for 2 h at 45 °C. The product was filtered, washed with ethanol and dried at 110 °C. The modified clay with APTES (S1) was further treated with the sodium salt of chloroacetic acid (1:1 mass ratio) at 70 °C, for 4 h, then product (S2) was filtered, washed with ethanol and dried at 110 °C.

2.2.2. Obtaining the Colored Hybrid Materials

Onto every modified substrate (S1, S2) the curcuminoid dye was deposited (CC or CCN), obtaining hybrid materials. Thus, 1 g of clay was suspended in 50 mL dye alcoholic solution 0.54 g/L for 4 h at room temperature. It was the optimal concentration used to obtain colored composite materials whose optical properties do not vary significantly, compared to the use of higher concentrations of dye. The dispersion was filtered and the composite material dried at 105 °C.

2.2.3. Characterization

The elemental analysis of the material was performed using a Vanta C series handheld XRF (Olympus, Waltham, MA, USA), equipped with 40 kV X-ray tube with rhodium anode, Silicon Drift Detector, in the pre-calibrated GeoChem mode, and acquisition time 60 s for each beam. The equipment uses two different energy beams for the quantification of the elements: beam 2 (10 kV) for light elements (Mg, Al, Si, P, S, K, Ca, Ti, Mn) and beam 1 (40 kV) for the rest of the detectable elements.

XRD analyses were performed using a Rigaku SmartLab equipment (Rigaku Corporation, Tokyo, Japan), in 2θ/θ configuration, XRD diffractograms being recorded in the 2θ range 2–90°. The collected data were interpreted using the PDXL software (ver. 2.7.2.0, Rigaku Corporation, Tokyo, Japan), provided by Rigaku, and the identification of the phases present was performed by comparison with the ICDD (International Centre for Diffraction Data) database entries.

The structural differences of the host matrices were analyzed by FTIR measurements, recorded with a JASCO FT-IR 6300 instrument (Jasco Int. Co. Ltd., Tokyo, Japan), equipped...
with a Specac ATR Golden Gate (Specac Ltd., Orpington, UK) with KRS5 lens, in the range of 400 to 4000 cm\(^{-1}\) (128 accumulations at a resolution of 4 cm\(^{-1}\)).

Characterization of porous materials by surface area, pore volume and size measurements was performed using Nova 2200e Quantachrome (Quantachrome Instruments Corporate Drive, Boynton Beach, FL, USA) automated gas adsorption system. All the samples were out gassed at 110 °C for 4 h, after \(N_2\) adsorption–desorption isotherms were measured at −196 °C. The specific surface areas (\(S_{\text{BET}}\)) and total pore volumes (\(V_{\text{total}}\)) of the samples were determined by BET (Brunauer–Emmett–Teller) and BJH (Barrett–Joyner–Halenda) methods, respectively.

The obtained results were interpreted and graphically presented using OriginPro 2018 data analysis software (ver. 9.5, OriginLab corporation, Northampton, MA, USA).

Thermogravimetric analysis (TGA) of the hybrid materials obtained was performed with a TGA Q5000IR instrument (TA Instruments, New Castle, DE, USA). The 5–9 mg samples were analyzed in platinum pans under the following conditions: heating ramp 10 °C/min up to 700 °C, Nitrogen 5.0 (99.999%), used as purge gas at a 50 mL/min flow rate.

Total color differences in CIELAB system, using a 10° standard observer and illuminant D65, and diffuse reflectance spectra, were measured with a V570 UV-VIS-NIR (Jasco Int. Co. Ltd., Tokyo, Japan) spectrophotometer equipped with a JASCO ILN-472 (150 mm) integrating sphere, using Spectralon as reference.

Evaluation of the fluorescence properties of hybrid materials was analyzed by recording steady-state fluorescence spectra on a JASCO FP 6500 spectrofluorimeter (Jasco Int. Co. Ltd., Tokyo, Japan) at 25 °C.

2.2.4. Evaluation of Resistance to Low Temperature, Acid, Alkali and Saline Solution

To evaluate the resistance of the hybrid materials to low temperature, the samples used to measure the specific surface area (cooled with liquid nitrogen, approximately 9 h) were investigated by recording their diffuse reflectance spectra using a UV-Vis spectrophotometer. For the other tests, 0.5 g of each hybrid material was placed in a paper cartridge and immersed in 25 mL 1.0 mol/L HCl or 1.0 mol/L NaOH or 1.0 mol/L NaCl solutions at room temperature for 24 h. The cartridges were then dried at 110 °C, and the diffuse reflectance spectra were measured for each hybrid material.

3. Results and Discussion

Following the adsorption process of curcumin derivatives on the inorganic matrix, decorated only with amino groups or with glycine residues, four types of hybrid materials of palygorskite-curcumin, were obtained. The degree of dye sorption on the two types of modified inorganic matrices was calculated using formula (1):

\[
\text{Sorption degree} = \left(\frac{C_0 - C_1}{C_0}\right) \times 100 \%
\]

where \(C_0\) represent the initial and \(C_1\) final concentrations (mg/L), respectively.

Depending on the design of the fibrous surface of the attapulgite clay, the optical properties of the hybrid materials obtained by the deposition of curcumin derivatives were investigated. For this purpose, the clay was decorated with amino groups, by treatment with (3-aminopropyl)triethoxysilanes. The treatment of S1 with sodium chloroacetate was performed in order to graft amphionic groups onto the structure of palygorskite (S2). Thus, the creation of the amphoteric character of the inorganic matrix aimed at improving the adsorption capacity of curcumin derivatives (Figure 2).
3.1. Analytical Characterization of the Materials

3.1.1. XRD Analysis of Hybrid Materials

The X-ray diffractograms of the modified palygorskite, with organic molecules and composite materials obtained by depositing curcumin derivatives on the modified clays, are presented in Figures 3 and 4, respectively. The identification peaks corresponding to the palygorskite structure (ICCD 21-0958) are presented in the Supplementary Materials in the Table S1, as observed in other studies [7,9].

In the XRD pattern of palygorskite (PAL), the peak characteristic of the stratified structure can be found at a value of 2θ = 8.58°. By reacting with APTS, the substrate is silanized and functionalized with aminopropyl groups (S1). These groups intercalate in the interstitial space and cause a displacement of the peak at a value of 2θ = 8.38°. The reaction of the amino group with sodium chloroacetate leads to functionalization with a glycine residue (S2), in this case, the displacement of the peak taking place up to the value 2θ = 8.20°. The disappearance of this peak in the case of adsorption of CC and CCN dyes, which have larger molecules, indicates exfoliation, confirmed by the appearance of a wide band characteristic of amorphous phase, centered at 2θ = 22°.

This case is supported by the measurements of the curcumin molecule size, which is situated around the values 0.89–1.16 nm, depending on the conformation (cis-cis, cis-trans or trans-trans), with the highest most probable size of 1.05 nm, as already reported [9,40]. The values are around the distance d = 1.04 nm obtained from the characteristic (110) reflection of S1 and d = 1.02 nm in the case of S2.

Upon grafting, the X-ray diffractograms suffer some alterations (Figure 3), the most visible being for the APTES grafting, the decrease in intensity of peaks at 39.46° and 60.56° (2θ), peaks associated with the presence of quartz and, to a lesser extent, to those at 29.44°, 30.86° (2θ), the increase in intensity of the peaks at 21.32° and 25.72° (2θ), as well as the appearance of a supplemental peak at 22.28°(2θ), most probably due to an increase in the relative concentration of some minor phase upon purification. After the treatment of the APTES grafted sample with sodium chloroacetate, some minor changes in the X-ray diffractogram can be noticed, respectively, the increase in intensity of peaks at 8.58°, 27.52°, 57.34°, as well as the appearance of supplementary peaks at 31.75°, 33.18°, 45.56° and 56.62° (2θ), which could be assigned to the presence of acetate group.

After, the deposition of curcumin on the obtained samples, some changes can be observed on the X-ray diffractograms. Figure 4 presents the X-ray diffractograms obtained for the deposition of curcumin (S1-CC) and curcumin derivative (S1-CCN) on modified clay, respectively (Figure 4a). The major changes observed are the disappearance of some minor peaks associated with the palygorskite phase (i.e., at 2θ 29.44, 30.86, 57.34°), associated with the increase/apparition of some peaks corresponding to the curcumin phase: (S1-CC)-13.82°-(1,1,0), 20.83°-(2,1,−2), 26.63°-(5,1,−1), 36.48°-(6,1,−3), 50.13°-(6,3,−2), 81.54°-(5,2,9), (S1-CCN)-13.82°-(1,1,0), 17.77°-(4,0,0), 20.83°-(2,1,−2), 25.70°-(5,1,−1),
26.63°-(5,1,−1), 36.48°-(6,1, −3), 50.13°-(6,3,−2), 81.54°-(5,2,9). Major differences are recorded upon the deposition of dye on support S3 (Figure 4b). It can be observed that the intensity of some peaks associated with the presence of curcumin has increased, i.e., at 26.62°-(2,1,3), 60.09°-(10,0,−6), 68.25°-(5,0,−9), 79.93°-(1,6,0) and 81.46°-(17,1,0). However, the major change visible from the diffractogram is the apparition of a specific broad “hump”, centered around 22° (2θ), which suggests the apparition of an amorphous phase at the surface of the material, following the interaction curcumin/support material.

Figure 3. XRD patterns of the support materials.
Nitrogen adsorption–desorption isotherms of modified clay and colored nanocomposites at 77 K are type II in concordance IUPAC classification. These isotherms show hysteresis with large loops, characteristic to mesoporous materials, thus confirming the textural change of the clay. The treatment of clay with APTES, leads to the decrease in the specific surface and the formation of meso- and macroporous surfaces, with an average pore diameter of 30 nm. After the modification of the composite with sodium chloroacetate, the characteristics mentioned above become more pronounced. Thus, the hybrid materials obtained have an even smaller specific surface area, but the pore volume increases (Table 2). The modification of the amino groups with acetate groups led to the increase in the interstitial volume in the structure of the palygorskite–APTES hybrid, the pore diameter obtained being in the range of 10–50 nm (Figure 5). The process of adsorbing the dye on the modified clay is influenced by the texture of the substrate, but at the same time it depends a lot on the chemical structure of the dye.

This is evident in the deposition of curcumin on the two types of hybrid materials, through which colored composites were obtained with a smaller pore volume than the S1 hybrid support, where we assume that the adsorption of the dye took place mainly in mesopores of the support structure. The adsorption of the CCN dye, which has in its chemical structure voluminous N-diethyl amine groups, leads to composite materials with a higher pore volume than that of the support. These results were most likely obtained by the partial adsorption of the dye in the structure of the hybrid material, confirmed by the increase in the specific surface area at 97 m²/g. In the case of S2 support, the chemical and textural structure increases the affinity for curcumin derivatives. The adsorption process is favored by the amphoteric character of the support, and the dyes interact more intensely with it through the physical bonds established with the acetate and amino groups grafted on the surface. The presence of smaller pores of 3–5 nm in the structure of the S2–CCN hybrid material is probably due to the aggregation phenomena between the dye molecules. The structural aggregates of the dyes, deposited on the S2 support, lead to amorphous structures, confirmed by XRD analyzes.
At the same time, the appearance of new peaks at 1590 cm$^{-1}$ confirms the interactions between the dye and the modified clay. The range 1800–1300 cm$^{-1}$ is representative for the identification of the vibration bands of the bonds in the organic compounds grafted onto the hybrid materials. Peaks characteristic to inorganic matrices in this interval are found around values of 1650 cm$^{-1}$, this being the characteristic to the vibration band of the bending and stretching of water molecules. The spectra for the modified polygorskite includes the bands at 3610 and 3290 cm$^{-1}$, corresponding to the stretching vibrations of the OH groups related to Al, Mg or Si of the network. The band in the range 1050–914 cm$^{-1}$ was assigned to the Si-O stretching vibration, respectively, and the band at 796 cm$^{-1}$, to the Si-O-Si vibration.

The presence of organic molecules on the inorganic structure is confirmed by the presence of smaller pores of mesopores of the support structure. The presence of organic molecules on the inorganic structure is confirmed by the presence of smaller pores of mesopores of the support structure.

### Table 2. Specific surface area, pore volume and average pore diameter of PAL and organic–inorganic hybrids.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V_{total}$ (cm$^3$/g)</th>
<th>$D_{med}$ pore (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAL</td>
<td>117</td>
<td>0.327</td>
<td>13</td>
</tr>
<tr>
<td>S1</td>
<td>86</td>
<td>0.281</td>
<td>30</td>
</tr>
<tr>
<td>S1-CC</td>
<td>81</td>
<td>0.193</td>
<td>10</td>
</tr>
<tr>
<td>S1-CCN</td>
<td>97</td>
<td>0.298</td>
<td>13</td>
</tr>
<tr>
<td>S2</td>
<td>36</td>
<td>0.319</td>
<td>15</td>
</tr>
<tr>
<td>S2-CC</td>
<td>40</td>
<td>0.167</td>
<td>17</td>
</tr>
<tr>
<td>S2-CCN</td>
<td>24</td>
<td>0.272</td>
<td>3</td>
</tr>
</tbody>
</table>

![Figure 5. Pore-size distribution of the hybrid materials.](image)

#### 3.1.3. Characterization of Hybrid Materials by ATR-FTIR Spectra

Figure 6 shows the FTIR spectra of organically modified clays and colored composites. The range 1800–1300 cm$^{-1}$ is representative for the identification of the vibration bands of the bonds in the organic compounds grafted onto the hybrid materials. Peaks characteristic to inorganic matrices in this interval are found around values of 1650 cm$^{-1}$, this being the characteristic to the vibration band of the bending and stretching of water molecules. The spectra for the modified polygorskite includes the bands at 3610 and 3290 cm$^{-1}$, corresponding to the stretching vibrations of the OH groups related to Al, Mg or Si of the network. The band in the range 1050–914 cm$^{-1}$ was assigned to the Si-O stretching vibration, respectively, and the band at 796 cm$^{-1}$, to the Si-O-Si vibration.

The presence of organic molecules on the inorganic structure is confirmed by the bands from 1560 cm$^{-1}$, 1490 cm$^{-1}$ and 1430 cm$^{-1}$ attributed to the stretching vibration of the $\equiv$NH$_2$ and C–N bonds of APTES, respectively. The wide band at 1650 cm$^{-1}$ is displaced and is attributed to the C = C bonds in the chemical structure of the dye that overlaps with the vibration band of the water molecules in the inorganic network (Figure 6a). Curcumin-colored hybrid materials (S1-CC), due to the low adsorption of the dye, are characterized by low intensities of the characteristic vibration bands. On the other hand, the molecular structure of the CCN dye (in the Supplementary Materials, Figure S1) deposited on the S1 support contributes to the intensification of the vibration bands characteristic of amines. At the same time, the appearance of new peaks at 1590 cm$^{-1}$ and 1520 cm$^{-1}$ attributed to secondary amines, respectively, means the NH band confirms the interactions between the dye and the modified clay.
characteristic to inorganic matrices in this interval are found around values of 1650 cm\(^{-1}\), this being the characteristic to the vibration band of the bending and stretching of water molecules.

The spectra for the modified palygorskite includes the bands at 3610 and 3290 cm\(^{-1}\), corresponding to the stretching vibrations of the OH groups related to Al, Mg or Si of the network. The band in the range 1050–914 cm\(^{-1}\) was assigned to the Si-O stretching vibration, respectively, and the band at 796 cm\(^{-1}\), to the Si-O-Si vibration.

\[\text{(a)}\]

**Figure 6.** FTIR spectra of the hybrid materials modified with aminopropyl groups (a) and glycine residue (b).

For hybrid materials treated with sodium chloroacetate, the molecular structures formed are more complex. The FTIR spectra confirm the grafting of the carboxyl groups by the presence of bands from 1740 cm\(^{-1}\) attributed to the stretching vibration C = O. Due to the multiple interactions between atoms of the amino groups, acetate and hydroxy, their characteristic peaks are overlapped. Thus, the hybrid materials are characterized by the presence of wide bands with obvious displacements of the absorption maxima for the colored composites compared to the modified clays (Figure 6b).

3.1.4. Thermogravimetric Analysis of Composite Materials

To evaluate the thermal stability and decomposition of hybrid materials, TG curves were recorded for the inorganic matrix modified with organic groups, and then loaded with curcumin dyes (Figure 7). At the same time, the decomposition temperatures and mass losses characteristic to the analyzed hybrid materials are presented in Table 3.
Table 3. Characteristic decomposition temperatures and mass losses of hybrid materials and curcumin dyes.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. Loss (%)</td>
<td>Wt. Loss (%)</td>
<td>Tmax (°C)</td>
<td>Wt. Loss (%)</td>
<td>Tmax (°C)</td>
<td>Wt. Loss (%)</td>
</tr>
<tr>
<td>S1</td>
<td>5.89</td>
<td>1.74</td>
<td>248.8</td>
<td>7.05</td>
<td>-</td>
</tr>
<tr>
<td>S2</td>
<td>3.66</td>
<td>9.63</td>
<td>213.2</td>
<td>15.90</td>
<td>429.2</td>
</tr>
<tr>
<td>S1-CC</td>
<td>5.52</td>
<td>3.77</td>
<td>190.7</td>
<td>4.12</td>
<td>8.08</td>
</tr>
<tr>
<td>S2-CC</td>
<td>2.82</td>
<td>4.27</td>
<td>223.2</td>
<td>3.63</td>
<td>9.55</td>
</tr>
<tr>
<td>CC</td>
<td>1.53</td>
<td>27.11</td>
<td>271.5</td>
<td>15.96</td>
<td>333.0</td>
</tr>
<tr>
<td>S1-CCN</td>
<td>5.79</td>
<td>1.87</td>
<td>197.4</td>
<td>2.94</td>
<td>279.1</td>
</tr>
<tr>
<td>S2-CCN</td>
<td>3.34</td>
<td>1.90</td>
<td>202.1</td>
<td>5.11</td>
<td>281.7</td>
</tr>
<tr>
<td>CCN</td>
<td>0.23</td>
<td>2.44</td>
<td>179.7</td>
<td>46.07</td>
<td>296.9</td>
</tr>
</tbody>
</table>

Figure 7. Thermogravimetric curves of hybrid materials modified with aminopropyl groups and CC dye (a) and hybrid materials modified with glycine residue and CCN dye (b).

By comparing the TG curves of composite materials, there can be observed a first stage of constant mass loss around 5.5% (±0.3) for modified materials with APTES (with and without dye), and 3.3% (±0.3) for those modified with glycine residue, respectively. This process takes place in the temperature range of 50–140 °C and can be attributed to the desorption of water adsorbed on the surface and of zeolitic water, existing in the channels of the inorganic matrix. The second stage of thermal decomposition, which involves mass loss, takes place differently and depends on the molecular structure of the dye loaded on the support. It can also be seen that the mass loss differs for the two types of modified substrate. For S2, the thermal effects are more dynamic, reaching a maximum temperature of 213 °C. For this temperature range, the mass loss for S2, around 9.6% is attributed to the decomposition of the organic residues grafted on PAL, a process that continues up to 429 °C, the stage in which the mass loss is 15.9%. The mass loss, is almost double for S2, compared to S1 and is due to the additional load on the inorganic matrix with the rest of glycine, confirmed by XRD and FTIR analyses.

However, when the two types of support matrix are loaded with CC, the mass losses are comparative (~4%). The maximum decomposition temperature at 119 °C for S1-CC can be attributed to the weak interactions between the dye and the host matrix. In comparison, it can be seen that the mass loss for S2-CC occurs at a higher temperature (223 °C) and can be attributed to the stronger interactions between the amphoteric support and the dye. For hybrid materials loaded with CCN, the thermal decomposition effects that take place in the second stage are similar and the mass losses are less than 2%. These thermal events continue in the next temperature range 285–410 °C. At this stage, S2-CCN has a higher mass loss than S1-CCN, motivated by the decomposition of the dye bound to the PAL...
surface modified with glycine residues, as confirmed by XRD and BET analysis. In the last temperature range of 410−700 °C, the composite materials have a mass loss between 8−13%. These thermal effects occur around the temperature of 400 °C and are attributed to the loss of water due to the aluminol and silanol groups condensation [9,10].

3.2. Photophysical Studies

3.2.1. Spectrophotometric Properties of Hybrid Materials

In order to evaluate the chromatic characteristics of the colored hybrid materials (Figure 8a), the color coordinates L*, a*, b* were compared. The results of total color differences in the CIELAB system of materials colored with curcumin dyes showed that the structure of the inorganic material greatly influences the final color of the composites. In S1–dye hybrids, dyes interact with the support on which amino groups are grafted, by predominantly polar bonds (CCN) and less by hydrogen bonds (CC).

The coordinates are comparable, the brightness L* being slightly lower and a* slightly higher for S1-CC (Figure 9a), this leading to a darker orange shade than S1-CCN (Figure 9c). For the inorganic support decorated with both amino and acetate groups, the parameters of colored hybrid materials differ significantly. The polarity of the inorganic support increases the polar interactions with the dye. In the case of the S2–CC type hybrid, the polar physical bonds between the dye and the support lead to a drastic decrease in its a* value and increase in the brightness, obtaining a yellow composite (Figure 9b). For the CCN composite, the presence of acetate groups has the effect of decreasing the value of b*, the shift to red having the effect of changing the color to pink (Figure 9d).

The resistance of colored composites to low temperature, alkaline, acidic and saline environments was assessed by color measurements for the exposed samples. By comparing the color parameters, it can be seen that the hybrid materials have good stability at low temperatures, and in the case of S1-CC, a more pronounced hypsochromic process takes place. In an alkaline environment, the bonds between the dye and the substrate are affected, which leads to the release of the dye from the surface of the modified clay. In acidic environments, the hybrid materials show stability, but with a color change to yellow for S1-CC and red for S2-CCN, respectively, most likely determined by the tautomeric structures of the dye. In the saline environment, the composite materials did not have essential changes, except for S2-CCN, which had a bathochromic displacement. However,
the evaluation of resistance is done by calculating the total color differences, which in turn can be broken down into components related to the influence of hue, chroma and lightness, as it can be seen in Table S2 (in the Supplementary Materials). The stability of the colored materials was evaluated by measuring color differences ($\Delta E^*$) between the sample before and after performing tests on various environmental factors. It was observed by comparing the total color differences, $\Delta E^*$, that the smallest variations were recorded for the S2-CCN sample, which is further evidence of the strong interactions established between the curcumin derivative and the host matrix.

![Figure 9. Color parameters in the CIELAB system for colored nanocomposites (S1-CC (a), S2-CC (b), S1-CCN (c), S2-CCN (d)) and after testing their resistance to low temperature (t), alkaline (a), acid (H+) and saline (s) solutions.](image)

3.2.2. Fluorescent Properties of Hybrid Materials

The fluorescent properties of the colored hybrid materials are shown in Figure 8b. All spectra of hybrid materials and solid dyes, respectively, show two emission maxima (Figure 10). The first maximum of fluorescence emission at 480 nm is characteristic to the curcumin type (H+) and saline (s) solutions. For the CCN composite, the presence of acetate groups (CC) results in a maximum emission at 590 nm, with an increased intensity compared to the peak at 480 nm. The attachment of amino groups (CCN) on aromatic rings has the effect of extending the conjugation and moving the second maximum of fluorescence emission to a longer wavelength (685 nm). The explanation for the allure of the fluorescence emission spectra is related to the presence of the basic aminopropyl groups in S1, respectively, the amphionic groups of the glycine residue in S2, groups that interact differently with the terminal groups of curcuminoid dyes, phenolic for CC and dialkylarylamine for CCN. All these interactions between the dye and the host matrix lead to the increased fluorescence intensity of hybrid materials compared to that of the curcumin dyes (Figure 10). From the variation of the basic/acid character of the four groups, there are interactions through hydrogen bonds that can lead as far as the formation of ions, as in the case of the S2-CCN system, which has a very intense emission band displaced hypsochromic at 580 nm. At the same time, for the S2-CC system, the same emission band is found at 515 nm and the hypsochromic change can be attributed to the
dye that acts as a proton acceptor [41]. Interactions, such as hydrogen bonds between the dye and the host matrix, also affect the chromophore and a hypsochromic shift at 425 nm is observed. In the case of CCN, only the intensities of these bands are influenced due to the surrounding environment of the matrices. In accordance to the results obtained for the color parameters, the S1–CC hybrid, in whose structure hydrogen bonds are established, in addition to the polar interactions, has the lowest intensity of fluorescence emission. By establishing hydrogen bonds, a strong path for quenching fluorescence emission is created, thus explaining the noted effect.

![Fluorescence emission spectra](image)

**Figure 10.** Fluorescence emission spectra of colored nanocomposites (a) and curcumin derivative (b).

In the case of hybrids loaded with CCN, the maximum emission characteristic to the curcumin chromophore is unchanged at 480 nm, while the polar interactions between the chromophore and the support determined a peak at 565 nm for the modified support with APTES. The strongly blue shift of 120 nm is probably due to the steric effects that modify the planarity of the dye molecules and the extended interaction with the support. Increasing the polarity of the inorganic matrix by grafting acetate groups leads to an increase in fluorescence intensity for the entire composite system. In particular, the addition of anionic groups produces, besides the intensification of the fluorescence emission, a 105 nm hypsochromic shift of the long wavelength emission band compared to that of the bulk dye.

4. Conclusions

In this study, the structural modifications of palygorskite with organic groups were made in order to obtain hybrid materials compatible with curcumin-derived dyes. The morphostructural characteristics and optical properties of the colored hybrid materials were studied in relation to the design of modified clay hosting material. The adsorption capacity of two curcuminoid dyes on two types of hybrid matrices derived from palygorskite were studied, noting that the degree of sorption is higher in the case of dye with basic peripheral groups and amphionic modifier grafted onto the palygorskite network. According to XRD data, the introduction of curcuminoid dyes into the palygorskite network leads to exfoliation, in the case of the host network modified with glycine residues. The presence of acid or basic groups grafted onto the surface of palygorskite that interact differently with the terminal residues of curcuminoid dyes leads to large Stokes shifts. Following the characterization–structure characteristics, dye-loaded composites can be used in various fields, such as sensor materials.

**Supplementary Materials:** The following supporting information can be downloaded at: [https://www.mdpi.com/article/10.3390/cryst12071005/s1](https://www.mdpi.com/article/10.3390/cryst12071005/s1); Figure S1: FTIR spectra of the curcumin dyes [39]; Table S1: The XRD peaks corresponding to the palygorskite structure; Table S2: Color differences for hybrid colored materials, exposed to various environmental factors.

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