

Article

Mechanism of Sodium Dodecyl Diphenyl Ether Disulfonate Filled Hydrotalcite Inhibiting the Photo-Degradation of Polyvinyl Chloride under Different Ranges of Ultraviolet Wavelength Irradiation

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Abstract: This content introduces a novel Ultraviolet (UV)-shielding material, Zn₂Al-MADS-LDH (MADS-LDH), which was synthesized through co-precipitation method to insert sodium dodecyl diphenyl ether disulfonate (MADS) into the interlayer of Zn₂Al-LDH layered double hydroxide (LDH), to improve the photoaging resistance of polyvinyl chloride (PVC). The characterization results indicated that MADS-LDH had a host-guest interaction between the LDH host layer and MADS guest anion, and it exhibited superior UV absorption capabilities than Zn₂Al-CO₃-LDH (CO₃-LDH) and a broader absorption spectrum compared to MADS. A series of LDHs/PVC film composite materials containing LDHs nanosheets were prepared by incorporating the prepared LDHs into a PVC matrix via a solvent casting method. As expected, the MADS-LDH/PVC film composite materials exhibited enhanced photoaging resistance. The results of photoaging tests indicated that MADS-LDH inhibits the rate of carbonyl generation during photoaging of MADS-LDH/PVC film composite materials, resulting in a decrease in the carbonyl index (ΔCI) and relative degradation rate (RDR) compared to pristine PVC film and CO₃-LDH/PVC film composite materials. Furthermore, the study evaluated the influence of different UV light wavelength ranges, such as UVB (280~315 nm), UVC (200~280 nm), and UV (200~400 nm), on the aging performance of PVC film and LDHs/PVC film composite materials. The results demonstrated that UV had the highest aging effect on PVC composite films, followed by UVC and UVB. Therefore, the MADS-LDH is a highly efficient and promising UV-shielding material with excellent potential for wide applications in the field of PVC.

Keywords: hydrotalcite; polyvinyl chloride; intercalation; UV-shielding materials; film composite materials



Citation: Zhou, E.; Liu, Y.; Yuan, H.; Cheng, X.; Zhong, Y.; He, J.; Lu, X. Mechanism of Sodium Dodecyl Diphenyl Ether Disulfonate Filled Hydrotalcite Inhibiting the Photo-Degradation of Polyvinyl Chloride under Different Ranges of Ultraviolet Wavelength Irradiation. *Coatings* **2023**, *13*, 985. <https://doi.org/10.3390/coatings13060985>

Academic Editor: Dimitrios Tasis

Received: 30 March 2023

Revised: 17 May 2023

Accepted: 19 May 2023

Published: 25 May 2023



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1. Introduction

Polyvinyl chloride (PVC) is a highly versatile and commonly used polymer materials in modern industries [1,2]. However, as a polymer material, PVC is susceptible to degradation and aging under the influence of external factors such as light, water, heat, and oxygen. This degradation can lead to discoloration, brittleness, and hardening, which ultimately reduces its physical properties [3,4]. Research has shown that UV light from sunlight is the primary contributor to the aging of polymer materials [3,5]. Therefore, incorporating UV-shielding materials is crucial to improve the stability of PVC film composite materials.

In recent years, there has been a growing interest in the development and utilization of inorganic-organic hybrid nanomaterials, such as hydrotalcite, due to their unique properties

that arise from the interaction between the inorganic matrix and the organic material. Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds or anionic clays, are a diverse group of layered materials that can be either natural or synthetic. LDHs are characterized by the general formula: $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} represent divalent and trivalent metal cations, respectively, and A^{n-} represents exchangeable anions with negative charge n , which can be organic or inorganic in nature [6].

By regulating its plate and interlayer structure, hydrotalcite can be customized for various functional purposes. It has important applications in various fields including catalysis, environmental protection [7–10], electrochemistry [11,12], and polymer additives [13,14].

The use of organic UV absorbers and inorganic nanoparticles to delay the photoaging degradation of polymeric materials, such as PVC, is common. However, these materials have certain limitations, such as high lipophilicity [15] and a narrow range of UV wavelengths shielding ability [16]. Moreover, the UV absorption ability of anionic surfactant intercalated hydrotalcite, containing a conjugated structure and dodecyl chain length as UV-shielding materials, is insufficiently studied. Existing studies mainly focus on the adsorption capacity of such anionic surfactants after intercalation of hydrotalcite. They can adsorb heavy metals or organic pollutants through hydrogen bonding and electrostatic interactions after anion insertion into hydrotalcite, and physical adsorption by increased layer spacing [9,17–21].

Although numerous studies have examined the effect of single UV wavelength range on the photoaging of PVC films [22,23], there is a lack of comparison between the results obtained and different wavelength ranges. Additionally, when adding intercalated hydrotalcite powders to polymers, it is important to consider their compatibility and interlayer crystalline water content, a factor that has not been thoroughly explored in previous studies.

To address these gaps in knowledge, this study investigates the mechanism of MADS-LDH fillers to inhibit the photoaging degradation of PVC film composite materials under different UV wavelength range irradiation. This is based on the existing oxidation reaction mechanism of photo-oxidation reaction generating carbonyl during PVC aging [24]. As a result, the objectives of this study are to: (1) study and compare the UV absorption range and absorption intensity between CO_3 -LDH and MADS-LDH; (2) analyze and discuss the desorption behavior of adsorbed water and crystalline water during the thermal decomposition of MADS-LDH; (3) analyze the morphology and pore size of MADS-LDH fillers, and their effect on structure and compatibility of PVC; (4) investigate the influence of different wavelength ranges of UV light on the MADS-LDH/PVC film composite materials' irradiation aging behavior, and the mechanism by which MADS-LDH inhibits the photoaging degradation of MADS-LDH/PVC film composite materials.

2. Materials and Methods

2.1. Materials

$ZnCl_2$ (98.0%), $AlCl_3 \cdot 6H_2O$ (97.0%), and NaOH (96.0%) were supplied by Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China), Sodium dodecyl diphenyl ether disulfonate (45% aqueous solution) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China), and ethanol (99.7%) was supplied by Anhui Zesheng Technology Co., Ltd. (Anqing, China). Further, 1, 2-dichloroethane (99.5%) was purchased from Meryer (Shanghai) Biochemical Technology Co., Ltd. (Shanghai, China). PVC (99.0%) and was supplied by Zhangmutou Ruixiang Polymer Materials Business Department, Dongguan City (Dongguan, China). Deionized water was decarbonized by boiling for 5 min before use.

2.2. Preparation of MADS Anion-Intercalated LDH

MADS-LDH was prepared by co-precipitation method as follows: a mixture of 0.625 M $ZnCl_2$ and 0.313 M $AlCl_3 \cdot 6H_2O$ (Zn/Al molar ratio = 2:1) was slowly added to 100 mL of MADS solution (0.125 M) with stirring in N_2 atmosphere. The pH of the reaction solution

was adjusted to 9.0 by dropwise addition of 1 M NaOH alkaline solution. The resulting slurry was crystallized at 70 °C for 24 h. The white precipitates were filtered and separated. They were rinsed with hot decarbonated deionized water and anhydrous ethanol until reaching a state of neutrality. Finally, the sample was subjected to a 24 h drying process at 100 °C, followed by grinding and sieving. Instead of MADS, Na₂CO₃ was utilized as the precursor. Meanwhile, the preparation of CO₃-LDH was exactly following the same method.

2.3. Preparation of LDHs/PVC Composite Materials

Prepared MADS-LDH of 1.0 g dry weight was added to a round bottom flask containing 100 mL of 1,2-dichloroethane for dispersion and stirring for 30 min to ensure uniform dispersion. Then, 10.0 g of PVC was added to the same round-bottom flask and stirred at 25 °C for 2 h. The resulting dispersion system of MADS-LDH and PVC was defoamed and poured onto a flat and smooth glass plate. The dispersion system solution was immediately scraped with a wet applicator and placed in a fume hood for static drying. The resulting film was then cut into dimensions of length × width × height = 30 mm × 20 mm × 0.1 mm and was used for subsequent testing. The reference samples of pure PVC and 10.0 wt% CO₃-LDH/PVC film materials were also prepared using the same method described above.

2.4. UV Photoaging Test

The UV photoaging tests were performed in a custom-made UV-aging chamber that was equipped with individually controllable UVA (315~400 nm, 8 W), UVB (280~315 nm, 8 W), and UVC (200~280 nm, 8 W) lamps. The chamber was designed to have a cooling system to eliminate the influence of thermal aging during the photoaging test of PVC films. The PVC films were subjected to photoaging treatment three times with a total UV exposure time of 144 h.

2.5. Characterization

The X-ray diffraction (XRD) patterns were analyzed using a Shimadzu XRD-6000 diffractometer (Shimadzu Corporation, Japan) with monochromatic Cu K α radiation ($\lambda = 0.15406$ nm, 40 kV, 40 mA) from 2 to 70° at a scan speed of 10°·min⁻¹. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Vector 22 infrared spectrophotometer (Bruker Corporation, Billerica, MA, USA) with a scan range of 4000~400 cm⁻¹ and a resolution of 1 cm⁻¹. The surface and internal morphology of the sample were examined using scanning electron microscope (TESCAN MIRA LMS SEM, TESCAN Orsay Holding, a.s., Brno, Czech Republic) and transmission Electron Microscope (Hitachi HT7700 TEM, Hitachi High Technologies Corporation, Tokyo, Japan). Thermogravimetric analysis (TGA) was carried out on a PCT-IA instrument (Thermal Analysis Instruments, Inc., New Castle, DE, USA) in the range of 25~800 °C with a heating rate of 10 °C·min⁻¹ under N₂ atmosphere. BET analysis was performed on a Micromeritics ASAP 2460 instrument (Micromeritics Instrument Corporation, Norcross, GA, USA). The ultraviolet–visible (UV-vis) absorption spectra were obtained using a Shimadzu UV-2501 PC instrument (Shimadzu Corporation, Kyoto, Japan).

3. Results and Discussion

3.1. XRD Analysis

The XRD patterns of powder CO₃-LDH and MADS-LDH are shown in Figure 1. These two samples have characteristic diffraction peaks of LDHs materials. From Table 1, the planar spacing of LDHs (003), (006), and (009) showed good multiplicative relationships, with ($d_{003} = 2(d_{006}) = 3(d_{009})$) [25], confirming the successful preparation of LDHs materials. The XRD spectrum LDH of MADS-LDH (Figure 1) shows only one set of typical (00 l) ($l = 3, 6, 9$) Bragg reflections, indicating the successful intercalation of MADS into the interlayer of Zn₂Al-LDH with only a single crystalline phase. The basal spacings (d_{003}) of CO₃-LDH and MADS-LDH are approximately 0.75 and 2.87 nm, respectively. Subtracting the LDH

plate layer thickness of 0.48 nm [26], the interlayer spacings of CO₃-LDH and MADS-LDH are approximately 0.27 and 2.39 nm, respectively. Additionally, we propose a possible orientation for MADS intercalated in Zn₂Al-LDH interlayer (Figure 2).

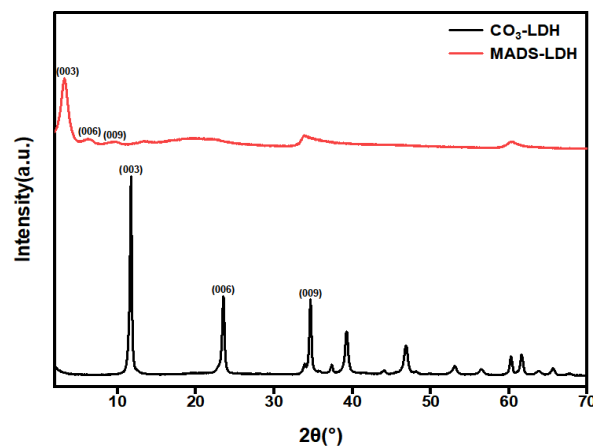


Figure 1. XRD patterns of CO₃-LDH and MADS-LDH.

Table 1. Crystal spacing for CO₃-LDH and MADS-LDH.

Parameter (nm)	CO ₃ -LDH	MADS-LDH
d_{003}	0.75	2.87
d_{006}	0.38	1.41
d_{009}	0.26	0.93
d_{110}	0.15	0.15

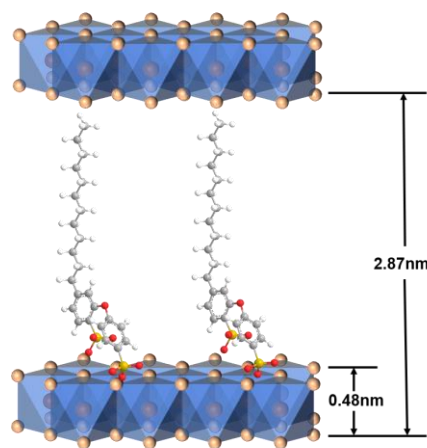


Figure 2. The probable orientation of MADS intercalated in Zn₂Al-LDH interlayer.

It has been reported by Yanjun Lin et al. [27] that an increase in LDHs layer spacing can improve the stability of PVC films. This is because a larger interlayer spacing facilitates the entry of Cl[−] into the LDHs interlayer channels, thereby inhibiting the autocatalytic dechlorination decomposition of PVC by Cl[−]. Therefore, MADS-LDH, with a layer spacing of 2.39 nm, is expected to improve the UV aging resistance of PVC.

3.2. FT-IR Analysis

The resulting FT-IR spectra of CO₃-LDH, MADS-LDH, and MADS are shown in Figure 3. The broad absorption band near 3430 cm^{−1} in the spectra of CO₃-LDH and MADS-LDH can be attributed to the O-H stretching vibration of the LDH plate layer and interlayer water molecules [18,20]. The intense band at very low wavenumber (428 cm^{−1})

was only observed for CO₃-LDH and MADS-LDH, which is attributed to the Zn-O-bound for LDH structures [28,29]. The absence of CO₃^{2−} groups at 1360 cm^{−1} indicates that there were no CO₃^{2−} anions in the interlayer of MADS-LDH [30]. The C-H of alkyl chains formed strong peaks at 2958, 2928, and 2858 cm^{−1}, while the C-C of diphenoxy produced strong peaks at 1590 and 1482 cm^{−1}, and the -O- of diphenoxy resulted in a peak at 1245 cm^{−1} [31,32].

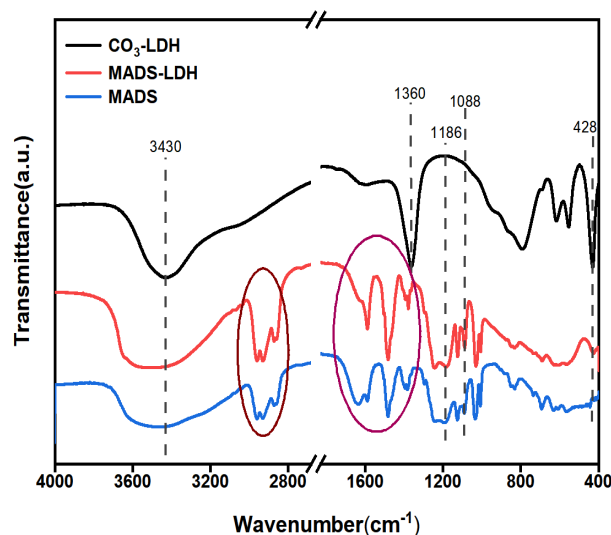


Figure 3. FT-IR spectra of CO₃-LDH, MADS-LDH and MADS.

In the FT-IR spectra of MADS-LDH, most of the characteristic absorption bands of MADS were observed, indicating that MADS was successfully intercalated into the interlayer of Zn₂Al-LDH. However, some subtle differences were observed between MADS-LDH and MADS. The asymmetric and symmetric vibrational absorption peaks of the -SO₃[−] groups of MADS were shifted from 1190 and 1092 cm^{−1} to 1186 and 1088 cm^{−1}, respectively, due to the host-guest interaction between the Zn₂Al-LDH layer and interlayer MADS anion [31]. These shifts suggest that the environment experienced by MADS anion in the interlayer gallery of LDHs is distinct from that of UV absorber. The successful preparation of a new organic-inorganic UV shielding material, MADS-LDH, is confirmed by XRD and FT-IR analyses. Similarly, the XRD and FT-IR spectra of CO₃-LDH (Figures 1 and 3) verified the successful intercalation of CO₃^{2−} into Zn₂Al-LDH.

3.3. SEM and TEM Analysis

Figure 4 illustrates the SEM images of CO₃-LDH and MADS-LDH. The obtained CO₃-LDH exhibited flaky morphological features, while the SEM image of MADS-LDH showed aggregation of irregular flaky particles. This aggregation is attributed to the intercalation of MADS anions, which leads to the aggregation of Zn₂Al-LDH crystals [33]. To further confirm the successful intercalation of MADS anion into Zn₂Al-LDH, transmission electron microscopy (TEM) was used, and the obtained TEM image of MADS-LDH was displayed in Figure 5. Clusters with irregularly shaped MADS-LDH nanosheets stacked in the TEM images were observed. The surfactant intercalated samples exhibit a rather different morphology. The agglomeration of MADS-LDH resulted in a decrease in its crystallinity, which is consistent with the XRD results.

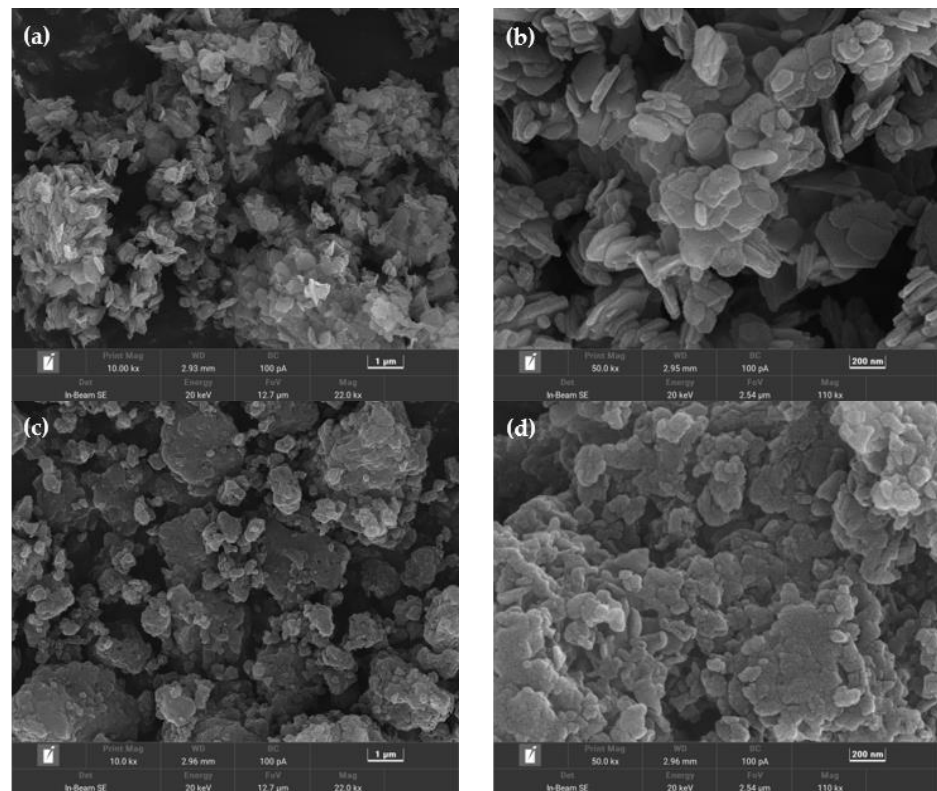


Figure 4. SEM images of (a,b) CO₃-LDH and (c,d) MADS-LDH.

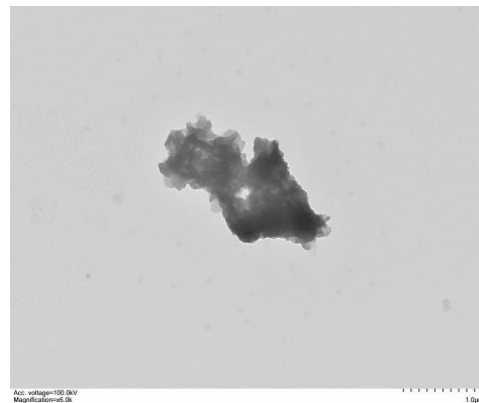


Figure 5. TEM image of MADS-LDH.

3.4. BET Analysis

Figure 6 shows the N₂ adsorption–desorption isotherms of CO₃-LDH and MADS-LDH. The nitrogen adsorption method revealed that both CO₃-LDH and MADS-LDH are mesoporous materials with type IV isotherms and H3 hysteresis loops [34]. The BET surface areas were calculated to be 30.430 m²/g for CO₃-LDH and 23.927 m²/g for MADS-LDH [35]. The decrease in the specific surface area of MADS-LDH after MADS anion intercalation is consistent with the increase in the unit mass of MADS-LDH due to agglomeration [36], which further confirms the successful intercalation of MADS anion into Zn₂Al-LDH.

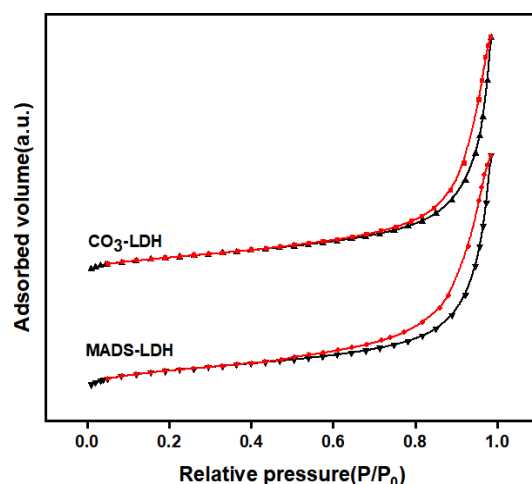


Figure 6. N_2 adsorption–desorption isotherms of CO_3 -LDH and MADS-LDH.

Figure 7 presents the pore diameter distribution of CO_3 -LDH and MADS-LDH. The results show that MADS-LDH has a narrower pore diameter distribution with a maximum effective pore diameter of 4.6 nm compared to CO_3 -LDH. These findings are consistent with the adsorption isotherm results, which indicate that both CO_3 -LDH and MADS-LDH have a mesoporous structure with pore diameters ranging from 2 nm to 50 nm. These findings are crucial in the development of new UV-shielding materials based on MADS-LDH, as they provide insights into the specific surface area and porosity of the materials.

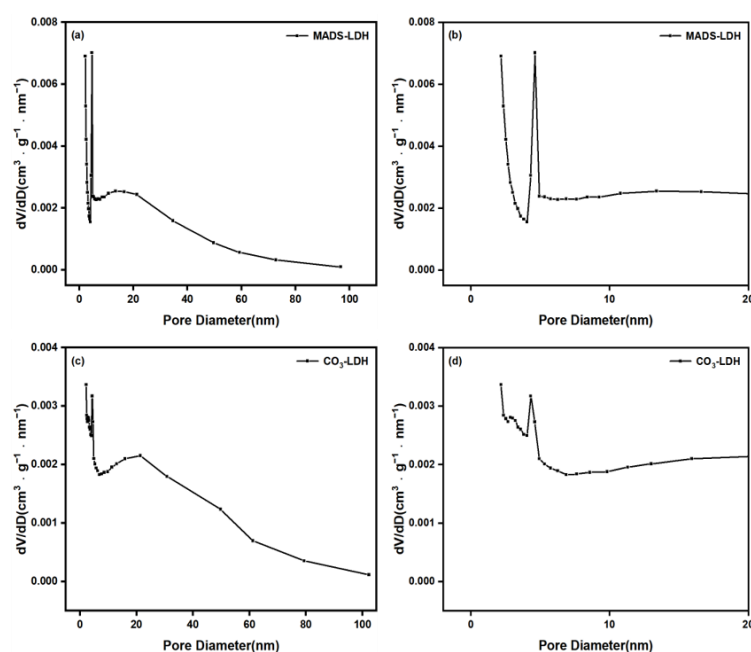


Figure 7. Pore diameter distribution curves of the (a,b) MADS-LDH and (c,d) CO_3 -LDH.

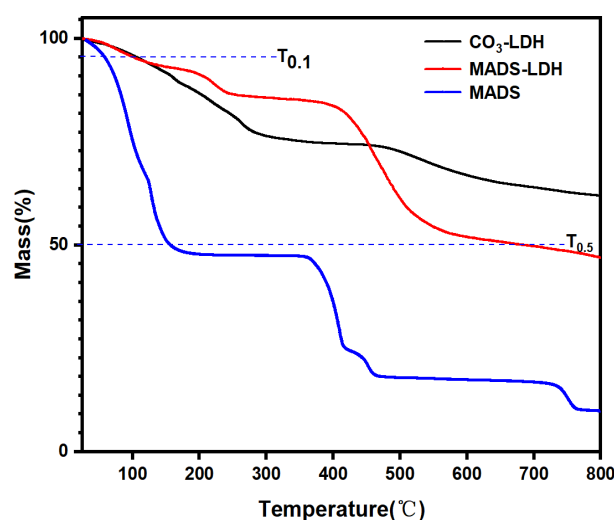
Table 2 shows Constitutive properties of CO_3 -LDH and MADS-LDH. As shown in Table 2, the specific surface area of CO_3 -LDH ($S_{BET} = 30.430 \text{ m}^2/\text{g}$) is much larger than that of MADS-LDH ($S_{BET} = 23.927 \text{ m}^2/\text{g}$). Meanwhile, the pore volume V_p and the pore diameter D_p of both were almost equal. This indicates that the MADS anion intercalation into the interlayer of Zn_2Al -LDH has the greatest effect on its specific surface area.

Table 2. Constitutive properties of CO₃-LDH and MADS-LDH.

Sample	S _{BET} (m ² /g)	V _p (cm ³ /g)	D _p (nm)
CO ₃ -LDH	30.430	0.119	16.610
MADS-LDH	23.927	0.117	16.187

3.5. TGA Analysis

Thermogravimetric analysis (TGA) was utilized to assess the thermal stability of the prepared LDHs. Figure 8 displays the TG curves of CO₃-LDH, MADS-LDH, and MADS. The mass loss stage for MADS occurred within the range of 25~765 °C, with 10% mass loss temperature (T_{0.1}) and 50% mass loss temperature (T_{0.5}) at 58 and 156 °C, respectively. In comparison, the weight loss rate of LDHs was substantially lower than that of MADS within the thermal decomposition temperature of 25~800 °C, indicating a better thermal stability.

**Figure 8.** TG curves of CO₃-LDH, MADS-LDH, and MADS.

Specifically, the weight loss rate of MADS-LDH between 120~452 °C was lower than that of CO₃-LDH. At this stage, the weight loss for LDHs is primarily caused by the desorption of water of crystallization between its layers [18]. The hydrophobic environment created by the alkyl chain of the MADS anion within the MADS-LDH interlayer made it difficult for water molecules to enter and form crystalline water [36]. Furthermore, the weight loss rate of MADS-LDH between 452~800 °C was higher than that of CO₃-LDH due to the thermal decomposition of organic carbon constituted of the MADS anion present in the MADS-LDH interlayer [37]. The detailed T_{0.1} and T_{0.5} for MADS and LDHs are listed in Table 3, where ΔT represents the difference between MADS and LDHs at the temperature of T_{0.1} or T_{0.5}. Notably, the T_{0.1} and T_{0.5} values of MADS-LDH were at least 41 °C higher than those of MADS, indicating the superior thermal stability of MADS-LDH over MADS alone.

Table 3. Summary of TG analysis results (unit: °C).

Sample	T _{0.1}	ΔT _{0.1}	T _{0.5}	ΔT _{0.5}
MADS	58	—	156	—
CO ₃ -LDH	104	46	>800	>644
MADS-LDH	99	41	685	529

3.6. UV Absorption of CO₃-LDH, MADS-LDH and MADS

The UV-vis absorption spectra of CO₃-LDH, MADS-LDH, and MADS are presented in Figure 9. CO₃-LDH displayed moderate UV absorption in the wavelength range

of 200~228 nm and 300~400 nm, with low UV absorption in the range of 228~300 nm. In comparison with CO₃-LDH, MADS exhibited stronger absorption in the range of 228~300 nm. After intercalation, MADS-LDH showed a wider absorption band in the range of 200~400 nm and stronger UV absorption in the range of 228~320 nm. The absorbance of MADS-LDH reached a maximum of 0.835, which was about 28% higher than that of MADS. These results could be attributed to supramolecular interactions, such as hydrogen bonding, electrostatic and gravitational forces, and van der Waals forces, between the cations on the LDHs plate layer and the interlayer MADS anion [38]. The π - π conjugation interactions between the aromatic groups of the MADS-LDH interlayer MADS anion resulted in a lower excitation energy, leading to a red-shifted and broadened absorption band [39,40]. Therefore, the Zn₂Al-LDH not only inherits the strong UV absorbing capabilities of MADS but also broadens the absorption band through π - π conjugate interactions between the interlayer guest anions, resulting in a new material with superior UV shielding performance.

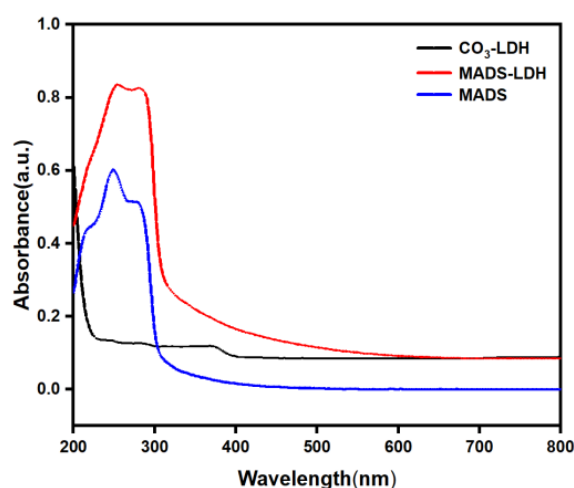


Figure 9. UV absorbance curves of CO₃-LDH, MADS-LDH and MADS.

3.7. Effect of LDHs on the Structure of PVC Film Composite Materials

The structural and dispersion effects of CO₃-LDH and MADS-LDH on PVC film composite materials were illustrated using X-ray diffraction (XRD) patterns. The XRD patterns of PVC, CO₃-LDH/PVC, and MADS-LDH/PVC film composite materials are presented in Figure 10. For the MADS-LDH/PVC film composite materials, the absence of characteristic diffraction peaks of MADS-LDH in the range of 2~10° on the test scale, as well as the increased half-peak width of the XRD diffraction peaks, indicated that the PVC macromolecular chains were intercalated within the pore channels of MADS-LDH [41]. This is related to the formation of a hydrophobic environment within the interlayer space of hydrotalcite by the alkyl chains on the interlayer MADS anion after intercalation [41,42], and the excellent compatibility of PVC with the alkyl chains on the MADS anion. During film preparation, hydrophobic solvated PVC molecules, which are soluble in 1,2-dichloroethane, preferred to enter the MADS-LDH interlayer [43], leading to the disappearance of the (003) characteristic diffraction peak of MADS-LDH. Conversely, the interlayer of CO₃-LDH constitutes a hydrophilic environment that is not conducive to the entry of hydrophobic PVC molecules into the interlayer. Consequently, all the characteristic X-ray diffraction peaks of CO₃-LDH were present in the XRD pattern of CO₃-LDH/PVC.

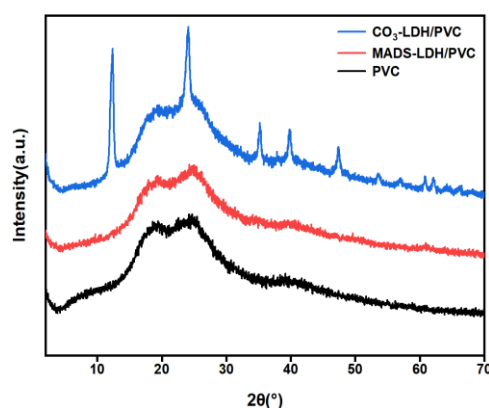


Figure 10. XRD patterns of PVC, CO₃-LDH/PVC, and MADS-LDH/PVC film composite materials.

3.8. Film Color Change of LDHs/PVC Film Composite Materials during Photoaging

Table 4 presents a comparison of the photostability of PVC film, CO₃-LDH/PVC, and MADS-LDH/PVC film composite materials. During UVB band irradiation aging, no significant color changes were observed in any of the films.

Table 4. Film color change process of PVC, CO₃-LDH/PVC, and MADS-LDH/PVC films during UVB, UVC, and UV ultraviolet light aging, respectively.

Sample \ Time	UVB				UVC			UV		
	0 h	48 h	96 h	144 h	48 h	96 h	144 h	48 h	96 h	144 h
PVC										
MADS-LDH/PVC										
CO ₃ -LDH/PVC										

However, under UVC band irradiation aging, PVC and CO₃-LDH/PVC film composite materials experienced significant color changes, turning orange-red after 96 h of aging and finally brown after 144 h. In contrast, the MADS-LDH/PVC film composite materials had a longer aging time before showing significant color changes and did not undergo an abrupt jump in color as observed in the other films.

During the aging process of UV band irradiation, the PVC film changed color rapidly. It turned brown after 48 h of aging, turns dark brown after aging to 96 h, and finally photoages to black after 144 h. Similarly, CO₃-LDH/PVC films underwent a similar change process during the aging process, but with relatively light aging. The color change during aging of CO₃-LDH/PVC film was more evident than that of MADS-LDH/PVC film. The color change process of MADS-LDH/PVC films when aged under UV band irradiation for 144 h was similar to the change process when aged under UVC band irradiation conditions. These findings suggest that the MADS-LDH/PVC films exhibit better photostability under UVC and UV band conditions.

The improved photostability of the MADS-LDH/PVC film composite materials can be further verified by the increase in carbonyl index values and relative degradation rates, as shown in Figure 11 and Table 5. Specifically, PVC film composite materials containing MADS-LDH exhibited good photostability.

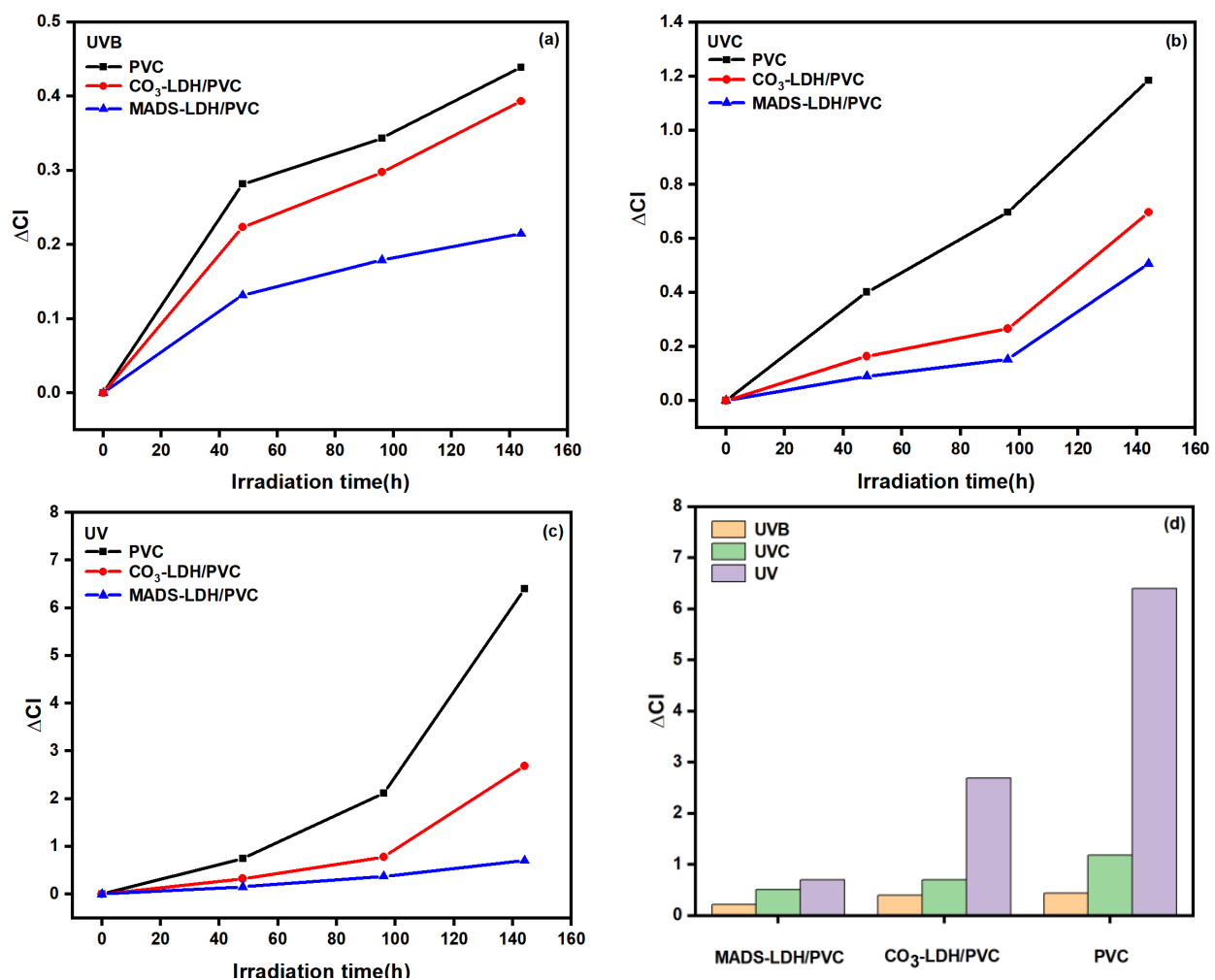


Figure 11. (a–c) The increase in carbonyl index (ΔCI) with aging time for PVC, CO₃-LDH/PVC, and MADS-LDH/PVC films during UVB (a), UVC (b), and UV (c) aging, respectively; (d) ΔCI of UVB, UVC and UV on PVC, CO₃-LDH/PVC, and MADS-LDH/PVC films after aging for 144 h, respectively.

Table 5. Carbonyl index (ΔCI) and relative degradation rate (RDR) of pristine PVC, CO₃-LDH/PVC, and MADS-LDH/PVC films after irradiation aging for 144 h.

Sample	UVB		UVC		UV	
	ΔCI	RDR	ΔCI	RDR	ΔCI	RDR
PVC	0.439	100%	1.185	100%	6.401	100%
CO ₃ -LDH/PVC	0.393	89.522%	0.697	58.819%	2.687	41.978%
MADS-LDH/PVC	0.215	48.975%	0.507	42.785%	0.705	11.014%

Moreover, by comparing the color changes during the aging process of the films, it could be inferred that the degree of influence of UVB, UVC, and UV band on the aging of MADS-LDH/PVC film composite materials was in the order of UV > UVC > UVB, which was consistent with the results obtained in Figures 11d and 12d below.

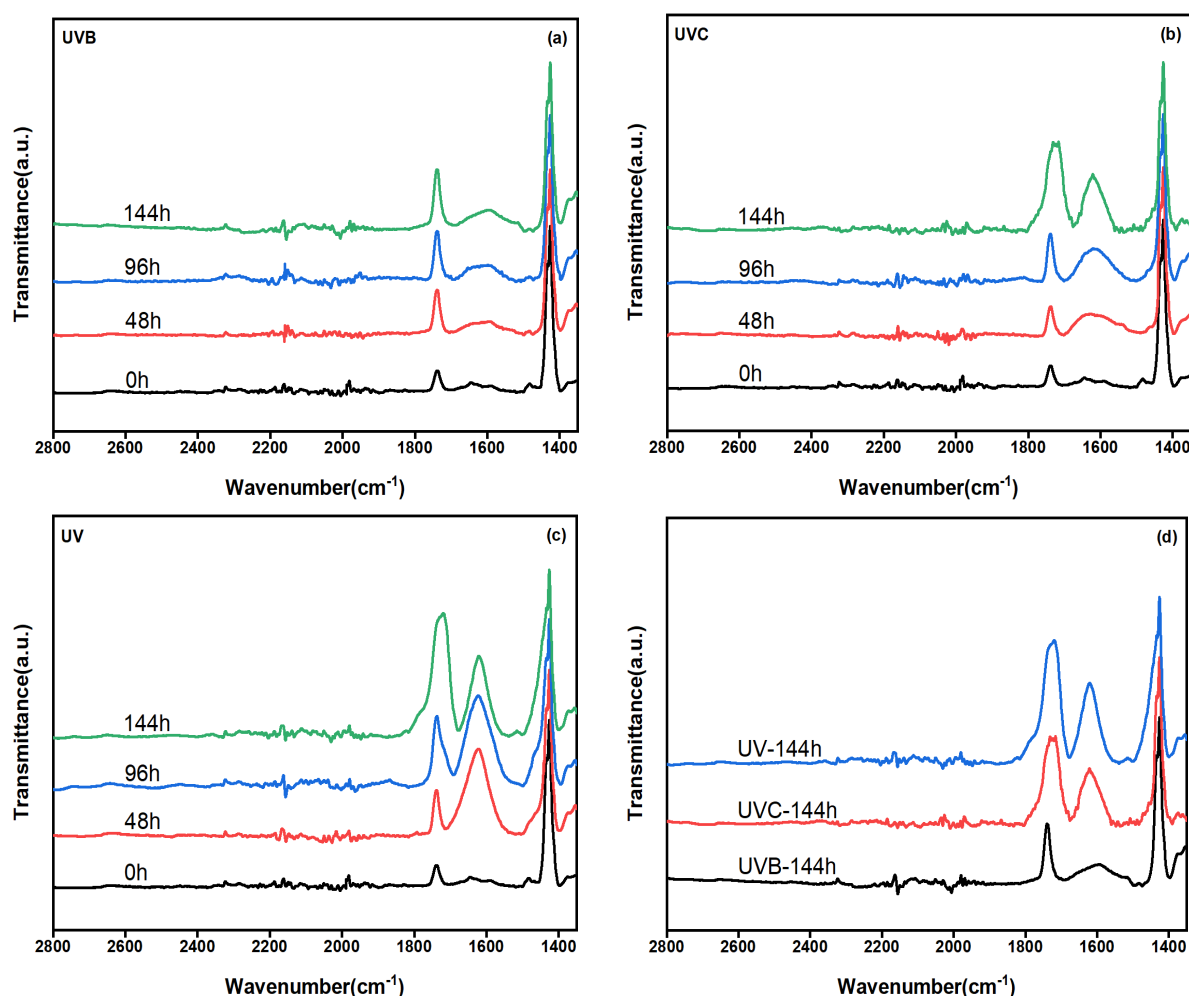


Figure 12. (a–c) FT-IR patterns of MADS-LDH/PVC films at different aging times under UVB, UVC, and UV photoaging conditions, respectively; (d) FT-IR patterns of UVB, UVC, and UV on MADS-LDH/PVC films after 144 h aging, respectively.

3.9. Light Stability of LDHs/PVC Film Composite Materials

To evaluate the UV-light aging resistance of MADS-LDH/PVC film composite materials, the surface chemical properties of pristine PVC, $\text{CO}_3\text{-LDH/PVC}$, and MADS-LDH/PVC film composite materials were analyzed and compared during UV photoaging. Previous studies have shown that carbonyl compounds are the primary molecules produced on the surface of PVC films during photo-oxidative aging [44]. PVC undergoes de-hydrogen chloride and photo-oxidative aging under UV-light, which results in the production of C=O compounds [45].

UV accelerated photoaging tests were conducted to assess the photostability of the pristine PVC and LDHs/PVC film composite materials. The degree of aging during photoaging was determined by analyzing the variation of ΔCI values with irradiation time [42,46]. When exposed to UV light radiation, PVC undergoes photoaging through oxidation reactions, which leads to the production of numerous carbonyl groups [44]. The ΔCI value represents the increase in the number of carbonyl groups induced by UV light [28]. Figure 11a–c display the curves of irradiation time vs. carbonyl index increase for pristine PVC, $\text{CO}_3\text{-LDH/PVC}$, and MADS-LDH/PVC film composite materials under UVB, UVC, and UV band ultraviolet light conditions, respectively. The increase in carbonyl index (ΔCI) during aging was calculated using the peak area method, with the absorption peak

area A_{1430} at 1430 cm^{-1} as the internal standard. This method provided a more intuitive way of evaluating the degree of photoaging. The calculation equations were as follows:

$$\Delta\text{CI} = \frac{(A_{1730,t} - A_{1730,0})}{A_{1430}} \quad (1)$$

The absorption peak areas at 1730 cm^{-1} at the aging times t and 0 were denoted as $A_{1730,t}$ and $A_{1730,0}$, respectively, to calculate the carbonyl index increase. Figure 11a–c shows the ΔCI values of both the pristine PVC and LDHs/PVC film composite materials increased with increasing photoaging time, indicating the occurrence of photooxidation reactions with different oxidation rates. The ΔCI value of the LDHs/PVC film composite materials was smaller during aging than that of the pristine PVC, suggesting that the LDH samples could reduce the formation of peroxides during PVC aging and improve its UV stability. Moreover, the ΔCI curves of the MADS-LDH films had the smallest values during the aging process, indicating a slower oxidation rate and better UV shielding properties compared to CO_3 -LDH.

The relative degradation rates (RDR) were calculated using the following equations, and the results are presented in Table 5. After 144 h of UVB, UVC, and UV band irradiation aging, the MADS-LDH/PVC films showed RDR values of 48.975%, 42.785%, and 11.014%, respectively, compared to the original PVC. Furthermore, analysis of Table 5 and Figure 11d indicated that the magnitude of the aging effect on all three films follows the order of $\text{UV} > \text{UVC} > \text{UVB}$.

$$\text{Relative degradation rate} = (\Delta\text{CI}_{\text{LDH/PVC}} / \Delta\text{CI}_{\text{PVC}}) \times 100\% \quad (2)$$

where $\Delta\text{CI}_{\text{PVC}}$ and $\Delta\text{CI}_{\text{LDH/PVC}}$ are the increase values of carbonyl index of the original PVC and LDHs/PVC film composite materials after irradiation aging process for 144 h, respectively.

Figure 12a–c present the FT-IR spectra of MADS-LDH/PVC film composite materials subjected to different photoaging times under UVB, UVC, and UV wavelength aging conditions. It is known that photoaging of pristine PVC under UVB irradiation produced a considerable number of carbonyl groups through oxidation reactions. The C-H anti-stretching vibrational absorption peak at 1430 cm^{-1} in the $\text{R-CH}_2\text{-R}'$ structure of the PVC molecular chain was accompanied by the peaks in the range of 1620 cm^{-1} and 1730 cm^{-1} , which were associated with the C=C stretching vibrational absorption peaks in the $\text{R-C=C-R}'$ polyene structure and C=O in the $\text{R-C=O-R}'$ carbonyl structure [47]. Both C=C and C=O stretching vibration absorption peaks in the sample were produced by the UV photoaging process. Therefore, the carbonyl group's absorption intensity at 1730 cm^{-1} was selected to represent the degree of photoaging. As shown in Figure 12a–c, the intensity of the carbonyl absorption peak at 1730 cm^{-1} increased to different degrees with increasing photoaging time, indicating different levels of photoaging degradation of the MADS-LDH/PVC film composite materials. Comparing with Figure 12d, it can be seen that the effect of UV, UVC, and UVB band irradiation conditions on the aging of MADS-LDH/PVC film composite materials followed the order of $\text{UV} > \text{UVC} > \text{UVB}$, which was consistent with the results obtained in Figure 11d above.

4. Conclusions

This study focused on the preparation and characterization of MADS-LDH and its potential to improve the photoaging resistance of PVC films. The mechanism of MADS-LDH inhibition of photoaging degradation of MADS-LDH/PVC film composite materials was also investigated. The results indicate that MADS-LDH effectively inhibits the production rate of carbonyl groups during photoaging, thereby improving the photoaging resistance of MADS-LDH/PVC film composite materials. Based on the experimental results obtained in this study, the following conclusions can be drawn:

- (1) The successful preparation of MADS-LDH was confirmed through XRD and FT-IR analysis, which presented a d_{003} peak position at 3.08° , a proportional relationship between planar spacing in $(d_{003}) = 2 (d_{006}) = 3 (d_{009})$, and a single set of Bragg reflections $(00l)$ ($l = 3, 6, 9$). Most of the characteristic absorption bands of MADS were detected in the FT-IR spectra of MADS-LDH.
- (2) The agglomeration of MADS-LDH nanosheet particles through stacking was observed using SEM and TEM. BET and TGA analysis indicated that the pore size of MADS-LDH is mesoporous with a homogeneous pore size distribution, and that the MADS anion intercalation created a hydrophobic environment within the layer, reducing the formation of interlayer crystalline water in MADS-LDH.
- (3) MADS-LDH/PVC film composite materials exhibited the least color change and the lowest degree of aging under both UVC and UV band irradiation compared to pristine PVC and CO_3 -LDH/PVC films. The color of PVC films changed significantly under both UVC and UV band irradiation, with similar changes in CO_3 -LDH/PVC films, but the degree of aging was relatively low.
- (4) The addition of MADS-LDH inhibited the generation of carbonyl groups in the MADS-LDH/PVC film composite materials during photoaging, resulting in lower values of both carbonyl index (ΔCI) and relative degradation rate (RDR) compared to pristine PVC and CO_3 -LDH/PVC films. The degree of influence of UVB, UVC, and UV bands on the photoaging of PVC film and LDHs/PVC film composite materials was found to be $\text{UV} > \text{UVC} > \text{UVB}$.

Author Contributions: Conceptualization, E.Z. and Y.L.; Methodology, E.Z. and X.C.; Validation, J.H. and X.L.; Data curation, H.Y. and Y.Z.; Writing—original draft preparation, E.Z.; writing—review and editing, E.Z.; Visualization, E.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This paper describes research activities mainly requested and supported by the Natural Science Foundation of China under grant numbers 22278086, supported by the Science and Technology Program of Guangzhou under grant numbers 202102021043, supported by the Demonstration Base for Joint Training of Postgraduates between Guangdong University of Technology and GCH Technology Co., Ltd., supported by the GCH Technology Co., Ltd., under grant numbers 607210383.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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