

## Synthesis and characterization of hydrotalcites: Potential thermal stabilizers for PVC

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Layered double hydroxides (LDH) are considered as a new emerging class of PVC stabilizers to replace toxic and environmentally hazardous class of heavy metals. A new series of Ca-Al-X ( $X=NO_3^-$ ,  $CO_3^{2-}$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $PO_4^{3-}$ ) hydrotalcites have been prepared by hydrothermal process. The hydrotalcite particles are nanosized and have been characterized by EDX, XRD, FTIR and TGA techniques. A comparative study has been carried out to evaluate the effect of anions on PVC stabilization mechanism. A clear anionic effect is observed when they are subjected to HCl evolution studies. Color stability and UV-Vis spectroscopic studies of stabilized and unstabilized polymeric sheets support the long-term stability behavior of LDHs. A mechanistic approach indicates the role of adsorption process along with ion-exchange. \

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Thermal stabilizers are needed in PVC processing to overcome its thermal instability, which is autocatalytic, and leads to discoloration, brittleness, insolubility and polymer sticking to equipment<sup>1-6</sup>. The lead-based stabilizers which react readily and provide effective stability are not desired due to physiological hazards when added to packaging materials, toys, bottle caps, pipes, etc.<sup>7</sup> The stabilizing effect of stearates of Pb, Ca, Zn in PVC has long been explained using Frye-Horst mechanism<sup>8-10</sup> and reversible blocking mechanism<sup>11-17</sup>. Lin *et al.*<sup>18</sup> have used Mg-Al- $CO_3$  LDH as thermal stabilizers and suggested that possible reason of stability is ion-exchange. Hydrotalcites have been used as antacids and antipepsin agent<sup>19</sup>, adsorbent<sup>20-22</sup>, catalyst and catalyst supports<sup>23-24</sup> and fillers<sup>25</sup>. But, studies on hydrotalcites as stabilizers need detailed exploration. Keeping that in mind, studies on Ca-Al-X have been carried out and the environment friendly stabilizers (hydrotalcites) have been synthesized, characterized and their suitability as primary stabilizers or co-stabilizers evaluated. The effect of various anions, viz.  $NO_3^-$ ,  $CO_3^{2-}$ ,  $Cl^-$ ,  $SO_4^{2-}$  and  $PO_4^{3-}$  on thermal stability has been evaluated. The hydrotalcites have been characterized by EDX, XRD, FTIR, and TGA techniques. The thermal stability of PVC sheets has been evaluated by oven-aging test and HCl evolution method. A possible mechanism of HCl scavenging using hydrotalcites is also suggested.

### Materials and Methods

Calcium nitrate tetrahydrate, calcium hydroxide, calcium carbonate, sodium carbonate, calcium sulfate dihydrate, calcium chloride, calcium phosphate dihydrate, aluminium phosphate, aluminium nitrate, aluminium hydroxide, aluminium chloride, aluminium sulfate, dioctyl phthalate were all of A.R. grade. PVC resin having *K* value 67 was procured from IPCL Baroda (India).

### Synthesis of Ca-Al-X series of hydrotalcites

Mixed salt solutions containing  $Ca^{2+}$  and  $Al^{3+}$  in Ca/Al molar ratios of 3:1 were taken. *pH* of the solution was raised to 8 using 25%  $NH_4OH$ . The thick white slurry was aged at 175°C and autogenous pressure in an autoclave to achieve small particle size and high surface area<sup>26</sup>. The precipitate was filtered, washed with deionized water and dried.

### Characterization of hydrotalcites

The atomic ratios ( $M^{II}/M^{III}$ ) were measured using X-ray microanalysis with an energy dispersive spectrometer (EDS). Infra red spectra were recorded using Perkin-Elmer FTIR spectrometer in the range 4000-400  $cm^{-1}$  using KBr pallets. XRD studies using powdered samples and Cu- $K\alpha$  radiation with a graphite diffracted beam monochromator ( $\lambda=1.5418 \text{ \AA}$ ) with Rigaku's D-300 X-ray diffractometer were carried out. The scan speed was: 2° per min. TGA analysis was

done under atmospheric conditions and 10°C/min heating rate.

#### Evaluation of thermal stabilizing efficiency (dehydrochlorination)

Thermal degradation studies were carried out by heating PVC and stabilizer mixture at 180±1°C. N<sub>2</sub> was used as carrier gas. HCl evolution was measured periodically using volumetric method.

#### Oven heat stability test (ASTM D 2115-92, reapproved 2003)

The PVC resin, plasticizer, stabilizer and other additives were accurately weighed and sheet was prepared by rolling machine. The sheets of dimension 1 cm × 1 cm × ~0.5 mm were placed in an oven at 180±1°C. Strips were examined visually after every 10 and 40 min.

#### Color intensity measurement and pattern of double bond formation

The polymeric sheets were heated at 180°C in oven at different time intervals, viz. 40, 100, 160 and 280 min. The sheets were accurately weighed (each 0.05 g) and dissolved in tetrahydrofuran solvent (5 mL). UV-spectra of resultant solutions were recorded.

## Results and Discussion

#### Structure of Ca-Al-X hydrotalcites

Metallic ratios of hydrotalcites were analyzed using EDX. The Ca:Al metal ratio was found in good agreement with the initially taken metallic ratio. The

observed value for Ca-Al-CO<sub>3</sub> was 3.2:1. In Ca-Al-SO<sub>4</sub>, it was 2.8:1, in Ca-Al-PO<sub>4</sub> it was 2.7:1 and in Ca-Al-NO<sub>3</sub> and Ca-Al-Cl it was 2.5:1 and 2.8:1, respectively.

The XRD patterns for the LDHs Ca-Al-CO<sub>3</sub> and Ca-Al-SO<sub>4</sub> exhibit features commonly shown by layered materials. There are narrow, symmetric, strong lines at low 2θ values and weaker, less symmetric lines<sup>27</sup> at high 2θ value (Fig. 1). The lattice parameters *a* and *c* were calculated assuming 3R packing of the layers<sup>28</sup> and from the positions of 110 and 003, 006 reflections. The crystallographic parameter *a* equals the average cation-cation distance in the brucite like layers, while parameter *c* is three times the distance from the centre of one layer to the next and is controlled mostly by the size (and orientation) of the interlayer anion and the electrostatic forces operating between the interlayer anion and the layers. Scherrer equation was used to estimate the crystalline size of the material<sup>29</sup>. Table 1 shows XRD parameters of the materials. SEM (Fig. 2) of the material shows high crystallinity. The particles of hydrotalcite Ca-Al-CO<sub>3</sub> clearly exhibit the hexagonal shape; however, big needle shape particles are also visible<sup>30</sup>. The IR-spectral data of hydrotalcites is given in Table 2. In Ca-Al-NO<sub>3</sub>, ν<sub>OH</sub> stretching vibration due to water molecule got split and appeared at 3301 and 3098 cm<sup>-1</sup>, respectively. The Ca-Al-CO<sub>3</sub> sample shows broad absorption at 3440 cm<sup>-1</sup> with two

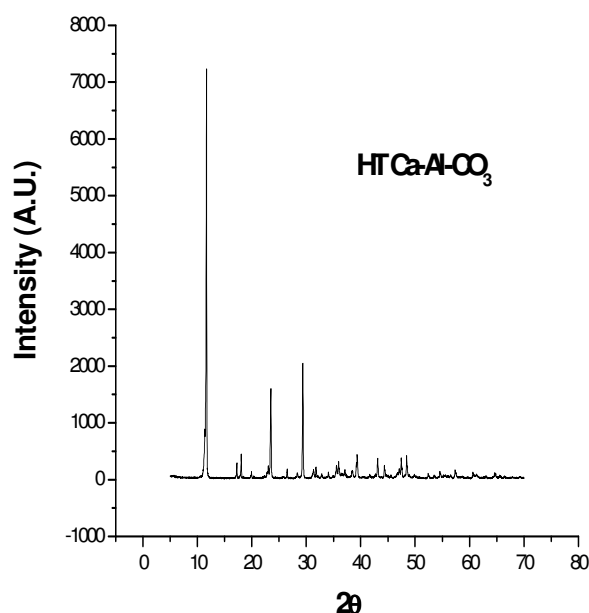


Fig. 1—XRD spectra of hydrotalcite Ca-Al-CO<sub>3</sub>.

Sample	<i>c</i> (Å)	<i>a</i> (Å)	Crystallite size ( <i>L</i> ) (nm)
Ca-Al-CO <sub>3</sub>	22.767	3.83	47.035
Ca-Al-Cl	18.408	2.91	25.57

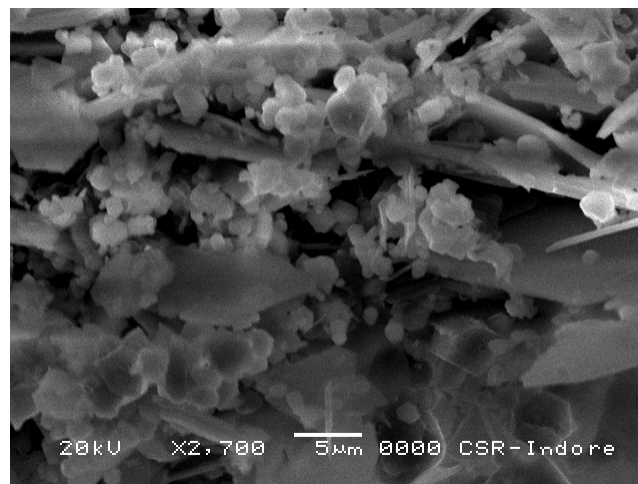


Fig. 2—SEM of hydrotalcite Ca-Al-CO<sub>3</sub>.

Table 2—Infrared data of Ca-Al-X hydrotalcites

Hydrotalcites	$\nu_{\text{OH}}$ ( $\text{cm}^{-1}$ )	$\delta_{\text{H}_2\text{O}}$ ( $\text{cm}^{-1}$ )	Anion			M-O & M-O-M*
			$\nu_3$	$\nu_2$	$\nu_4$	
Ca-Al-NO <sub>3</sub>	3301-3098	1635	1384			607 & 477
Ca-Al-CO <sub>3</sub>	3415-3363	1587	1352	823		679
Ca-Al-SO <sub>4</sub>	3302-3068	1632	1114	1157	595	673-485
Ca-Al-Cl	3045	1624		—		507-599
Ca-Al-PO <sub>4</sub>	3475	1639	1029			755-531

M-O and M-O-M\* = refer to Al-O and Ca-O-Ca lattice vibrations

shoulders at 3517 and 3062  $\text{cm}^{-1}$ , respectively. Samples of Ca-Al-SO<sub>4</sub>, Ca-Al-Cl and Ca-Al-PO<sub>4</sub> show  $\nu_{\text{OH}}$  stretching at 3068-3302  $\text{cm}^{-1}$ , 3045 and 3475  $\text{cm}^{-1}$ , respectively. The corresponding  $\delta_{\text{H}_2\text{O}}$  peak was observed<sup>31</sup> between 1587-1639  $\text{cm}^{-1}$ . Presence of intercalated anion was supported by FTIR bands at 1384, 1352, 1114 and 1115, 1029  $\text{cm}^{-1}$  for NO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, respectively. The regions below 700  $\text{cm}^{-1}$  show Al-O and Ca-O-Ca lattice vibrations<sup>32</sup>.

TGA analysis of Ca-Al-CO<sub>3</sub> shows weight loss in two steps. The initial loss was 9.746% and takes place up to 305°C. The second weight loss was 32.25% and was recorded up to 720°C. The second step shows inflection point, indicating that it is formed in two overlapping processes<sup>33</sup>. The first weight loss corresponds to elimination of water and the second one to loss of water and CO<sub>2</sub>. The temperature ranges at which these losses are recorded suggest that the first loss corresponds to elimination of water molecular from the interlayer, while the second step involves water loss from dehydroxylation of the layers. At 720°C essentially, all the carbonate is removed and significant lattice dehydroxylation takes place. The experimentally determined weight loss was 42%.

### Thermal stability studies

#### HCl evolution measurement

HCl evolution studies in presence of Ca-Al-X hydrotalcites were carried out and results are shown in Fig. 3. The Ca-Al-NO<sub>3</sub> shows induction period similar to that observed with blank PVC. The HCl evolution time was 60 min, which is more than the blank PVC but not significant. In contrast to this, Ca-Al-CO<sub>3</sub> gave superior results. The dehydrochlorination was substantially slow and 2 mmol HCl evolution took 349 min. When Ca-Al-SO<sub>4</sub> was used, HCl evolution time was 203 min. Ca-Al-PO<sub>4</sub> showed induction period 37 min, which is highest, and HCl evolution time was 254 min. In presence of Ca-Al-Cl (2 mmol), HCl was liberated in

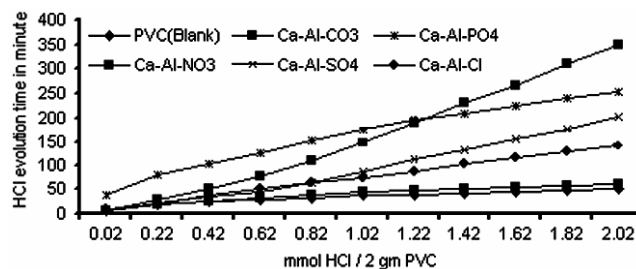


Fig. 3—Evolution of HCl (dehydrochlorination of PVC) at 180°C in presence of 2 phr hydrotalcites (Ca-Al-X series).

141 min. The observed thermal stability order follows the sequence Ca-Al-CO<sub>3</sub> > Ca-Al-PO<sub>4</sub> > Ca-Al-SO<sub>4</sub> > Ca-Al-Cl > Ca-Al-NO<sub>3</sub>. It clearly suggests that anions have significant effect on thermal stability regarding dehydrochlorination.

#### Oven-ageing test for color stability measurement

Sheets were subjected to static oven heat stability test. The results show that Sheet No. 2 (Ca-Al-CO<sub>3</sub>) remained white up to 30 min. The discoloration starts after 30 min and it becomes yellow in 40 min, and then turns brown in 60 min. It slowly turns darker and becomes black in 360 min. Sheet No. 3 containing 2 phr Ca-Al-SO<sub>4</sub> gave similar color stability data except that its blackening time was 280 min. The Sheet No. 4 and 5 (Ca-Al-Cl and Ca-Al-PO<sub>4</sub>, respectively) showed improved results when compared to Sheet No. 2 and 3. Sheet No. 4 and 5 remain white up to 40 min, turning brown in 50 min, and then black in 280 min. These results show that an improvement of 20 min in color stability was achieved when Ca-Al-Cl and Ca-Al-PO<sub>4</sub> were used. The blackening time for all the four sheets were almost similar. When these four sheets were compared with blank PVC sheet No. 1 (no stabilizer), a clear difference was observed in yellowing and browning time.

#### Polyene formation

UV-Vis spectra of blank PVC, dissolved in THF was recorded at 308 nm. It shows peaks referred to the presence of 3-conjugated double bond. The PVC sheet was heated at 180°C and spectra recorded after

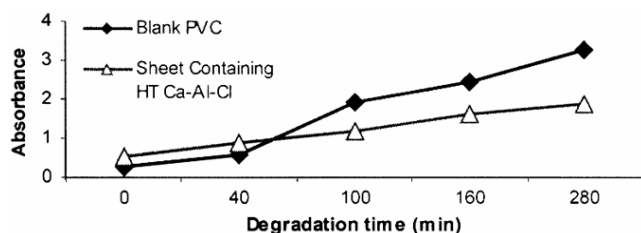


Fig. 4—Plot of absorbance versus degradation time (min) in presence of stabilizer system using UV-Vis spectrophotometer at  $\lambda_{\max}$  (308 nm).

40, 100, 160 and 280 min, respectively. The results show a slight increase in absorbance up to 40 min. After 100 min heating, absorbance at 308 nm increases rapidly. At degradation time 160 and 280 min, the absorbance increased rapidly (Fig. 4). Addition of Ca-Al-Cl hydrotalcite to PVC shows that short range polyene is formed at a faster pace compared to blank. But after 40 min of Ca-Al-Cl addition, increase in short range polyene formation is low and it acts as a long term stabilizer.

The spectra of blank PVC at 400 nm corresponds to 6-8 double bonds. It shows that up to 40 min, very less number of polyene ( $n=6-8$ ) are formed. After 40 min formation of average size polyene grows faster. The sheet is white up to 20 min, turns yellow in 40 min, brown in 50 min and black in 360 min.

Solution of PVC sheet having Ca-Al-Cl at 400 nm (Fig. 5) shows that absorption was higher. After 40 min, the average size of polyene formation ( $n=6-8$ ) was slow compared to blank. The increase in polyene formation was slow and steady during the degradation period. Long range polyene ( $n=10-12$ ) shows development of brown and black color. As the brown and black sheets were insoluble in THF, UV-Vis studies could not be made. This insolubility is attributed to crosslinking of polyene<sup>34</sup>.

#### Mechanism of HCl scavenging by hydrotalcites

HCl evolution data and color stability pattern show that anions in hydrotalcites play a significant role. Kalouskova *et al.*<sup>35</sup> have reported that  $\text{CO}_3^{2-}$  ion is exchanged by  $\text{Cl}^-$  ion thereby binding the  $\text{Cl}^-$  ion and restricting the availability of HCl which can catalyse dehydrochlorination. Costantino *et al.*<sup>36</sup> have reported that when Mg-Al- $\text{CO}_3$  is heated to 150°C and HCl gas flows over the hydrotalcite, the carbonate form is converted into the chlorides form. This is supported the reported hypothesis<sup>35</sup>. Kyowa Chemical Industry<sup>37</sup> in its products information has mentioned that  $\text{CO}_3^{2-}$  is easily replaced by  $\text{Cl}^-$  and these ions are

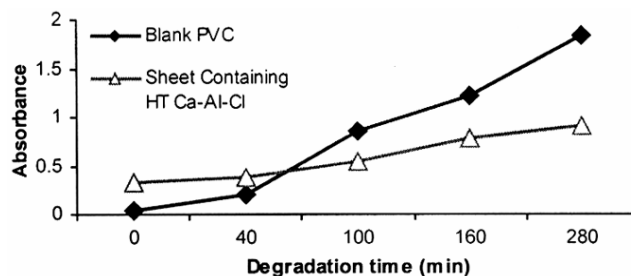


Fig. 5—Plot of absorbance versus degradation time (min) in presence of stabilizer system using UV-vis spectrophotometer at  $\lambda_{\max}$  (400 nm).

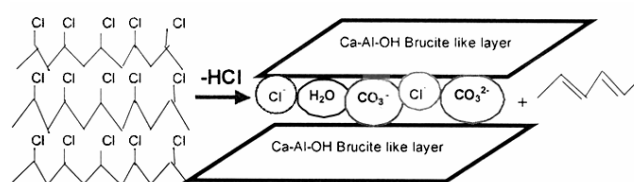
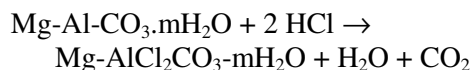


Fig. 6—Schematic representation of hydrotalcites behavior in PVC.

incorporated into the crystal structure. Thus, the reaction is:



The present observation contradicts the suggestion that ion exchange is the sole factor. Hydrotalcites Ca-Al- $\text{CO}_3$ , Ca-Al- $\text{SO}_4$  and Ca-Al-Cl show comparable stability behavior. The stability behavior of Ca-Al-Cl can not be explained by ion-exchange mechanism only. Zeolites are cation exchangers but when subjected to HCl evolution and color stability testing, it exhibited stability time 337 min. Zeolite can only exchange  $\text{Na}^+$  ion by  $\text{H}^+$  ions. Zeolites cannot exchange  $\text{Cl}^-$  ions, i.e. improved thermal stability of Zeolite can not be explained on the basis of ion-exchange. It can only be explained on the basis of adsorption and absorption. Besides this, hydrotalcite Ca-Al- $\text{CO}_3$  was placed at 180°C for 6 h and HCl gas was passed.  $\text{N}_2$  gas was flushed over the resultant material for 1 h and the contents were washed with distilled water and filtered. The test for  $\text{Ca}^{+2}$ ,  $\text{Al}^{3+}$  and free  $\text{CO}_3^{2-}$  ions were negative in the filtrate suggesting that the structure of hydrotalcites is stable under the experimental conditions. The thick precipitate for  $\text{Cl}^-$  ion on  $\text{AgNO}_3$  addition shows that hydrotalcites have absorbed large quantity of HCl, which is in unbound form (Fig. 6). The treated sample shows similar XRD and FTIR pattern as exhibited by parent hydrotalcites.

If some  $\text{Cl}^-$  ion enters into interlayers spaces, then  $d_{003}$  should have changed. But, the value of interlayer space remains unchanged (7.6 Å). Ookubo *et al.*<sup>38</sup> have studied Mg-Al-Cl hydrotalcite in which exchange by  $\text{PO}_4^{3-}$  ion has been done. The  $d_{003}$  space changes from 0.78 nm to 0.84 nm which depends on the concentration of  $\text{PO}_4^{3-}$  anion. Similar results have also been observed by other workers<sup>24, 39-41</sup> showing that interlayer space  $d_{003}$  changes with change of size of anion. The infrared studies show a very small decrease in peak intensity of  $\text{CO}_3^{2-}$  ions in Ca-Al- $\text{CO}_3$ . This may be due to loss of  $\text{CO}_3^{2-}$  ion from the sample as a result of prolonged heating or ion exchange of  $\text{CO}_3^{2-}$  from the interlayer, which makes no significant difference in interlayer spaces<sup>38</sup>. It shows that besides ion-exchange, adsorption is a predominant factor during stabilization mechanism.

### Conclusions

The nature of anions ( $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ) has predominant effect on thermal stability. By scavenging HCl, the thermal stability or autocatalytic degradation of PVC can be delayed. This efficiency is mainly dependent on the intercalated anion as well as adsorption capacity of the material surfaces.

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