



Synthesis and Characterization of Non-Toxic Thermal Stabilizers of PVC Based on Layered Double Hydroxides†

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Hydrotalcite-like compounds are expressed by the general formula $[M^{(2+)}_{1-x}M^{(3+)}_x(OH)_2]^{x+1}A^{n-}_{x/n} \cdot mH_2O$, where $M^{(2+)}$ and $M^{(3+)}$ are divalent and trivalent cations, respectively. $Mg_{1-x}Al_x(OH)_2CO_3 \cdot nH_2O$ structures, non-toxic thermal stabilizers of poly(vinyl chloride), were manufactured by various coprecipitation methods to optimize the manufacturing process of non-toxic thermal stabilizers of poly(vinyl chloride). These hydrotalcite-like compounds were characterized by field-emission-scanning electron microscopy, X-ray diffraction, thermal analysis and transmittance spectra. Samples were fabricated using different steps and a base reactant produced the most stable sample. The cell parameter c is related to the thickness of the brucite-like layer and the interlayer distance was 23.21 Å.

Keywords: Hydrotalcite-like compound, Thermal stabilizers, Poly(vinyl chloride), Brucite-like layer, Co-precipitation.

INTRODUCTION

Recently, layered double hydroxides (LDH) have received a great deal of attention because of their potential applications. Layered double hydroxides, also known as anionic clays or hydrotalcite-like compounds (HTlc), are naturally rare and are relatively simple and inexpensive to synthesize on the laboratory scale. Layered double hydroxides have been used as polymer stabilizers, anion exchangers, adsorbents, catalysts and anion scavengers¹⁻³.

Polyvinyl chloride (PVC) is an important thermoplastic resin with different applications². However, PVC is highly unstable upon exposure to heat or ultraviolet (UV) light; thus, researchers are investigating techniques to improve its thermal stability. Layered double hydroxides are well suited as non-toxic stabilizers, because they consist of magnesium, aluminum and zinc and thus, they are non-toxic. Layered double hydroxides have a high absorption capacity for HCl and are used as thermal stabilizers of PVC.

Hydrotalcite-like compounds consists of positively charged layers with anionic interlayers. The general formula of hydrotalcite-like compounds is $[M^{(2+)}_{1-x}M^{(3+)}_x(OH)_2]^{x+1}A^{n-}_{x/n} \cdot mH_2O$, where $M^{(2+)}$ is a divalent cation (Mg^{2+} , Ni^{2+} , Zn^{2+} , Co^{2+}), $M^{(3+)}$ is a trivalent cation (Al^{3+} , Fe^{3+} , Ga^{3+} , Cr^{3+}) and A is an anion with charge n (HO^- , CO_3^{2-} , NO_3^- , Cl^- , SO_4^{2-}). That is, hydrotalcite-

like compounds consist of a positively charged brucite-like layer $[Mg_{1-x}Al_x(OH)_2]^{x+1}$ and negatively charged interlayers $[A_{x/n}^{n-} \cdot mH_2O]^{x-}$. Magnesium and aluminium are randomly distributed among the octahedral positions⁴.

Hydrotalcite-like compounds can be synthesized by various techniques, such as hydrothermal treatment and synthesis^{5,6}, coprecipitation, urea hydrolysis⁷, sol-gel methods⁸ and microwave irradiation^{9,10}. Coprecipitation is the most commonly technique used to synthesize hydrotalcite-like compounds. This method provides flexibility in the layer charge density. Additionally, a wide variety of anionic species can be directly intercalated between the hydroxylated sheets.

In this study, we synthesized hydrotalcite powder as a non-toxic stabilizer of PVC using various coprecipitation combinations. The different characteristics are discussed based on four different process steps. The thermal stability of hydrotalcite-like compounds is important because the manufacturing temperature during a production of plastics, such as PVC, may reach 200 °C. In these experiments, various process combinations were used to improve the thermal stability of hydrotalcite-like compounds. To confirm the thermal behaviour of hydrotalcite-like compounds, we measured the thermogravimetry of different samples using a differential thermal analyzer. The microstructures were characterized by X-ray diffraction. Chemical bonds were analyzed using Fourier-transform infrared spectroscopy.

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EXPERIMENTAL

Hydrotalcite-like compounds were prepared by four different coprecipitation methods. Important factors that were considered include the nature of the anions, pH, temperature, aging and synthesis technique. Among these factors, pH control during precipitation led to different properties of the hydrotalcite-like compounds. In this study, all samples were synthesized using the same molar ratios. However, the process was conducted in several steps.

Sample 1: An acid reactant was prepared from a mixture of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.38 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.127 mol) in deionized water. A base reactant was prepared from a mixture of NaOH (1.2 mol) and Na_2CO_3 (0.2 mol) in deionized water. The two reactants were added to deionized water in a Pyrex reactor until the pH reached 10. After the reaction, the suspension was kept for 24 h at 90 °C with stirring. The hydrotalcite powder was collected by filtration and washed several times with deionized water until the pH was neutral. The powder was dried at 60 °C overnight.

Sample 2: An acid reactant was prepared from a mixture of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.38 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.127 mol) in deionized water. A base reactant was prepared from a mixture of NaOH (0.9 mol), KOH (90 %, 0.3 mol) and Na_2CO_3 (0.2 mol) in deionized water. The two reactants were added to deionized water in a Pyrex reactor until the pH reached 10. After the reaction, the suspension was kept for 24 h at 90 °C with stirring. The hydrotalcite powder was collected by filtration and washed several times with deionized water until the pH was neutral. The powder was dried at 60 °C overnight.

Sample 3: In a Pyrex reactor, a base reactant was prepared from a mixture of NaOH (1.2 mol) and Na_2CO_3 (0.2 mol) in deionized water at 25–35 °C. The pH was maintained at 10 by adding a mixture of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.38 mol), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.127 mol) and deionized water. After the reaction, the suspension was kept for 24 h at 90 °C with stirring. The hydrotalcite powder was collected by filtration and washed several times with deionized water until the pH was neutral. The powder was dried at 60 °C overnight.

Sample 4: In a Pyrex reactor, a base reactant was prepared from a mixture of MgSO_4 (0.38 mol) and $\text{Al}_2(\text{SO}_4)_3$ (0.127 mol) in deionized water at 25–35 °C. The pH was maintained at 10 by adding a mixture of NaOH (1.2 mol), Na_2CO_3 (0.2 mol) and deionized water. After the reaction, the suspension was kept for 24 h at 90 °C with stirring. The hydrotalcite powder was collected by filtration and washed several times with deionized water until the pH was neutral. The powder was dried at 60 °C overnight.

The morphologies of the powders were observed by field-emission-scanning electron microscopy. The structures were analyzed by X-ray diffraction. The thermal decomposition of layered double hydroxides is important, giving rise to mixed oxides of industrial interest for catalytic or other practical applications. Thermal analysis using thermogravimetric-differential thermal analysis techniques was used to determine mass-loss steps, measure the temperature of mass-loss steps and identify the mechanism of mass loss. Fourier-transform infrared spectroscopy measurements were performed in the absorption/transmission mode to investigate chemical bonding characteristics.

RESULTS AND DISCUSSION

The FE-SEM images (Fig. 1) show the morphologies of the synthesized hydrotalcite powders. The particles in sample 1 were hexagonal platelets and samples 2, 3 and 4 were porous-like particles. Thus, the shape of hydrotalcite-like compounds was adjusted according to the process combination.

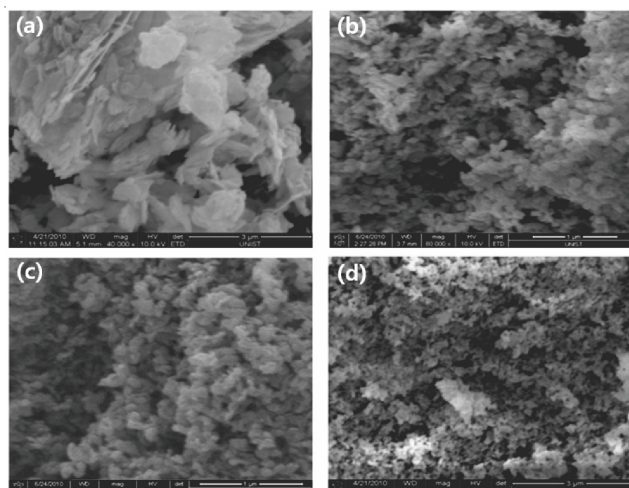


Fig. 1. SEM micrographs of (a) sample 1, (b) sample 2, (c) sample 3 and (d) sample 4

Fig. 2 shows the XRD patterns of coprecipitation-synthesized hydrotalcite powders. No other crystalline phases were detected in the XRD patterns. The cell parameters obtained from the (003) and (110) interplanar distances estimated from Fig. 2 are $a = 3.04 \text{ \AA}$, $c = 22.98 \text{ \AA}$ for sample 1, $a = 3.063 \text{ \AA}$, $c = 23.308 \text{ \AA}$ for sample 2, $a = 3.059 \text{ \AA}$, $c = 23.210 \text{ \AA}$ for sample 3 and $a = 3.06 \text{ \AA}$, $c = 23.3 \text{ \AA}$ for sample 4. The parameter a is the cation-cation distance within the brucite-like layer. The parameter c is related to the thickness of the brucite-like layer and the interlayer distance.

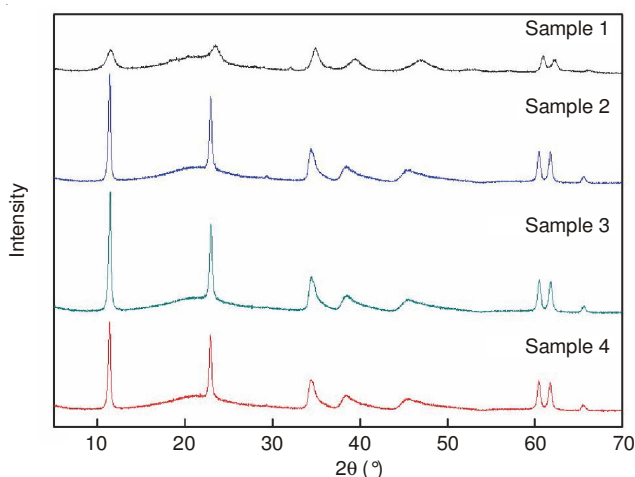


Fig. 2. XRD patterns of the samples

The $c/3$ value of sample 1 was $7.76 \text{ \AA}$, consistent with the value of $7.69 \text{ \AA}$ reported for the hydrotalcite-like compounds carbonate. This value confirms the crystalline structure of the samples and indicates a relatively well-ordered sheet arrangement, in agreement with that of a previous report¹⁰.

Fig. 3 shows the FT-IR spectra of the four samples. H_2O and CO_3^{2-} between the layers correspond to the bands in the $4000\text{--}1200\text{ cm}^{-1}$ region and the M-O stretching bands were observed in the $1200\text{--}600\text{ cm}^{-1}$ region. The bands in the $1200\text{--}600\text{ cm}^{-1}$ region were attributed to the lattice vibrations of oxygen ions in the interlayer, such as Mg-Al-O stretching and bending modes and Mg-O and Al-O stretching modes.

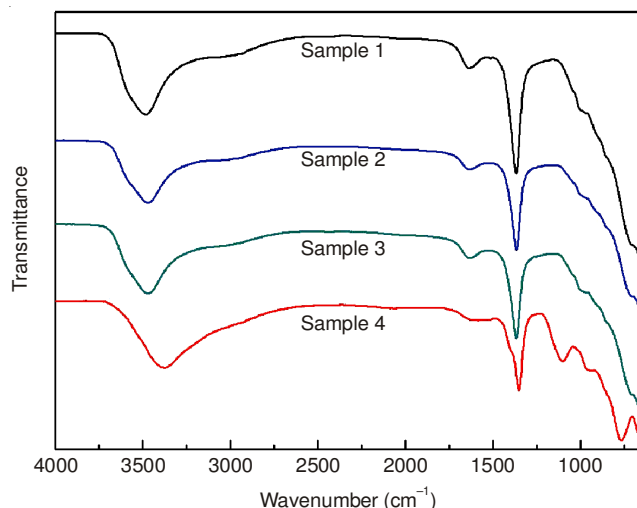


Fig. 3. FT-IR spectra for the samples

The broad band in the $3500\text{--}3300\text{ cm}^{-1}$ region was attributed to the OH stretching ($\nu(\text{OH})$) mode of water molecules in the interlayer. For this broad peak, a shoulder at 3000 cm^{-1} was attributed to $\nu(\text{OH})$, due to hydrogen bonding between water molecules and interlayer carbonate anions. The peak at $1635\text{--}1630\text{ cm}^{-1}$ shows the OH bending ($\delta(\text{H}_2\text{O})$) of water molecules. The ν_3 symmetric-stretching mode of carbonate in the interlayer was observed in the $1480\text{--}1300\text{ cm}^{-1}$ region.

Fig. 4 shows the TG-DTA curves of coprecipitation-synthesized hydrotalcite powders and the weight loss of each stage. Except for sample 4, there were three stages of weight loss, but the second and third stages overlapped. In the temperature range of $80\text{--}200\text{ }^\circ\text{C}$, the first stage, weight loss was due to dehydration of the interlayer. The second region ($300\text{--}350\text{ }^\circ\text{C}$), corresponds to weight loss due to dehydroxylation. This stage represents the process of decomposition of OH groups in the brucite layer. The range of $350\text{--}400\text{ }^\circ\text{C}$, the third stage, corresponds to weight loss due to de-carbonation reactions.

Conclusion

This study synthesized hydrotalcite-like compounds as non-toxic thermal stabilizers of PVC using various coprecipitation methods. No unexpected phases were detected for the four different hydrotalcite-like compounds powders. XRD results provided a and c values. FT-IR spectra were similar for all samples, except sample 4, which showed unique bands in the $1200\text{--}600\text{ cm}^{-1}$ region. Thermal stability is an important

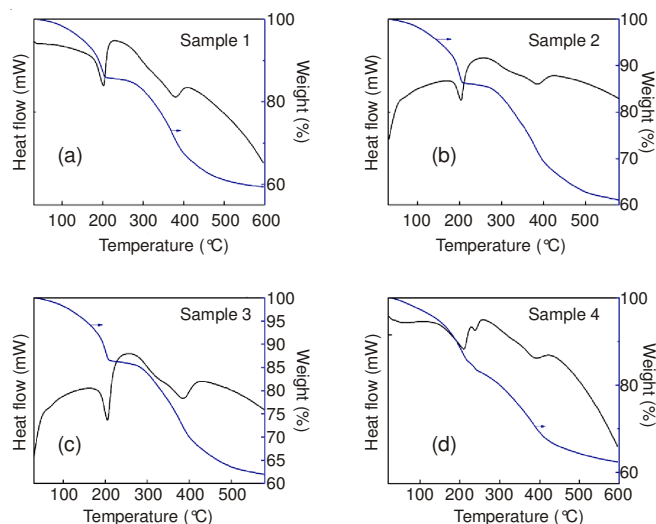


Fig. 4. TG-DTA curves of (a) sample 1, (b) sample 2, (c) sample 3 and (d) sample 4

property for thermal stabilizers of plastics such as PVC. TG-DTA results showed that the coprecipitation-synthesized hydrotalcite-like compounds powders were stable at $400\text{ }^\circ\text{C}$. This work introduced a synthetic method for stable hydrotalcite-like compounds powders by coprecipitation. These results may help in predicting possible stabilizers for high-temperature applications.

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REFERENCES

1. Y. Kuang, L. Zhao, S. Zhang, F. Zhang, M. Dong and S. Xu, *Materials*, **3**, 5220 (2010).
2. K.-H. Goh, T.-T. Lim and Z. Dong, *Water Res.*, **42**, 1343 (2008).
3. T. Kameda, T. Yoshioka, F. Yabuuchi, M. Uchida and A. Okuwaki, *J. Mater. Sci.*, **42**, 2194 (2007).
4. R. Allmann and B. Section, *Struct. Crystallogr. Crystal Chem.*, **24**, 972 (1968).
5. E.J. Park, S.D. Park, I.C. Bang, Y.-B. Park and H.W. Park, *Mater. Lett.*, **81**, 193 (2012).
6. H. Wang, H. Yi, P. Ning, X. Tang, L. Yu, D. He and S. Zhao, *Chem. Eng. J.*, **166**, 99 (2011).
7. H.-Y. Zeng, X. Deng, Y.-J. Wang and K.-B. Liao, *AIChE J.*, **55**, 1229 (2009).
8. J. Chandradass and M. Balasubramanian, *Mater. Manuf. Process.*, **23**, 158 (2008).
9. P. Benito, I. Guinea, F.M. Labajos and V. Rives, *J. Solid State Chem.*, **181**, 987 (2008).
10. G. Fetter, F. Hernández, A.M. Maubert, V.H. Lara and P. Bosch, *J. Porous Mater.*, **4**, 27 (1997).