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Cite this: DOI: 10.1039/cOxxOOOOOx

www.rsc.org/xxxxxx

ARTICLE TYPE

Green Preparation and Characterization of a Novel Heat Stabilizer for Poly (vinyl chloride) - Hydrocalumites

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Hydrocalumites are successfully prepared by using $Ca(OH)_2$, $Al(OH)_3$ and Na_2CO_3 with different reaction time and crystallization time. The as-prepared samples are characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The results show that the as-prepared sample with the reaction time and crystallization time both being 4 hour generally can be seen as pure hydrocalumites, and shows higher crystalline and has more regular crystals than the other samples. The different as-prepared samples were mixed with PVC resin. Thermal aging and Congo red of the resulting PVC composites were carried out in a thermal aging test box at195±1°C. The results show that all the as-prepared samples used as single thermal stabilizers could enhance both the long-term thermal stability and initial thermal stability of PVC. Especially, the as-prepared sample with the reaction time and crystallization time both being 4 hour has better thermal stability than the other samples. And Thermal aging tests of PVC with varying amounts of hydrocalumites shows that 4 phr are the optimum amount of hydrocalumites filler.

Introduction

Chlorine-containing polymers such as poly (vinyl chloride) (PVC) are widely used in many fields due to their advantages of the non-flammable nature, good performance and low price.[1] However, PVC resins have poor thermal stability, which leads to many problems including discoloration and deterioration of mechanical properties.[2,3] Thermal degradation of the PVC is the result of a process called "zipper dehydrochlorination", which generates polyenesequences in polymer chains that may produce an undesirable colour in the material.[4] Therefore, it is necessary to utilize thermal stabilizers for improving the thermal stability of PVC. Stabilizers can inhibit the degradation of removal of HCl due to their capacity for HCl-adsorption.[5] The main classes of thermal stabilizers used in currently are lead salts, rare earth compounds, metal soaps, and organo-tin compounds.[6] However, these stabilizers all have the disadvantages in terms of high cost, toxicity or environmental pollution. With the increasing of environmental awareness, attention is currently being focused on thermal stabilizers that are non-toxic, environmentally friendly and economical.[7]

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Layered double hydroxides (LDHs) or hydrotalcite-like materials, with a brucite-like layered structure are a family of synthetic anionic clays.[8] And its general formula is $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdot H_2O$, where M(II) is a divalent metal cation, M(III) is a trivalent metal cation, and A^{n-} is the interlayer anions, respectively. In recent years, LDHs has been serving as catalysts,[9] drug delivery materials,[10] battery active materials,[11-13] hydrogel[14] and chemically tailored functional material,[15] which has attracted great attention. In particular, LDHs may be a promising thermal stabilizer for PVC due to their alkalescency and layered structure.[7,16] Hydrocalumites belong to layered double hydroxides with its general formula being $[Ca_2Al(OH)_6]^+[A_{1/n}^{n-}]\cdot nH_2O$. And structurally hydrocalumites consist of stacked brucite-like ($Ca(OH)_2$) layers in which Ca^{2+} ions are partially substituted by Al^{3+} ions. The substitute on the layers necessitates the incorporation of anions, such as CO_3^{2-}, Cl^- and OH^-, between the interlayer to balance the resulting positive charge.[17,18] The water of crystallization is also generally found in the interlayer galleries. And the typical structure of hydrocalumites can be presented by Figure. 1. Obviously, hydrocalumites have some common characteristics with Mg-Al LDHs. Mg-Al LDHs have been used as PVC heat stabilizers for a long time and it also has been proved to be efficient.[7,19-24] Kyowa Chemical Industries of Japan have found that Mg-Al LDHs can enhance the thermal stability of PVC.[20] L. van der Ven has studied the stabilization mechanism of Mg-Al LDHs.[21] Liu has reported that

the PVC/LDH nanocomposites also can improve the thermal stability of PVC.[22-24] In recent years, hydrocalumites have drawn more and more attention for the advantages of low cost, environmentally friendly, low toxicity, convenient preparation and weatherability.[25] Especially, S-Fokken invented a kind of stabilizer composition including hydrocalumites, which has applied to halogenated polymers with the improvement of initial colour and colour maintenance.[26] Then, we can conclude that hydrocalumites have basic property, which make it possible to be a heat stabilizer for poly (vinyl chloride).

In this paper, hydrocalumites were successfully synthesized by using $Ca(OH)_2$, $Al(OH)_3$ and Na_2CO_3 with different reaction time and crystallization time. Especially, the by-products can be used directly in the industrial production of $Al(OH)_3$ stripping section, resulting to the zero discharge in the production process.[27] And hydrocalumites also were proposed as a novel heat stabilizer for PVC, and its thermal stability were studied in details.

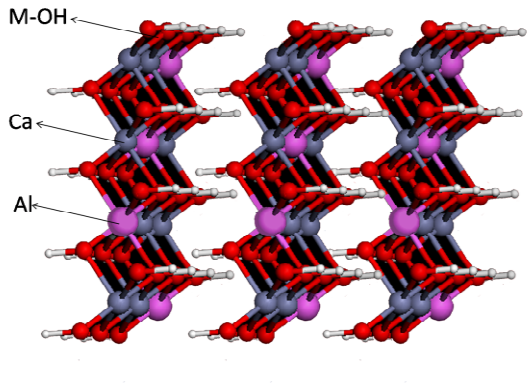


Fig. 1 the typical structure of hydrocalumites

Results and discussion

The effects of reaction time and crystallization time on the preparation of hydrocalumites

In this paper, the three different samples were prepared with different reaction time and crystallization time. In the process of samples' preparation, the mixing time of $Ca(OH)_2$ and $Al(OH)_3$ was named reaction time, and the crystallization time was the stirring time after adding the Na_2CO_3. The different times are shown in table 1. And Fig. 2 shows the powder XRD patterns of the as-prepared samples, pure hydrocalumites, pure calcium carbonate and pure tricalcium aluminate hexahydrate. It can be seen from the Fig. 2 that all the three samples show several diffraction pattern peaks at 2θ = 11.67º (002) and 23.49º (004), which are typical XRD patterns of hydrocalumites (JCPDS, File No. 41-0219). However, the XRD patterns of all the samples display the characteristic reflection (located at 29.40º) corresponding to calcium carbonate (JCPDS, File No. 24-0217). And the other peaks located at 17.27º, 31.82º, 39.22º and 44.4º can be assigned to the crystal faces of tricalcium aluminate hexahydrate (JCPDS, File No. 05-0586). For sample 2, its diffraction peaks corresponding to calcium carbonate are so low that it can be regarded as pure hydrocalumites. Especially, its diffraction peaks are sharp, narrow and symmetrical, with a low and stable baseline, indicating that the as-prepared sample 2 is well crystallized.[28] The chemical equation for the preparation of hydrocalumites can be represented as follows:

During the reaction process:[29]

$$3Ca(OH)_2+2Al(OH)_3+4H_2O\rightarrow Ca_3Al_2(OH)_{12} \quad (1)$$

During the crystallization process:

$$Ca(OH)_2+Ca_3Al_2(OH)_{12}+Na_2CO_3\rightarrow Ca_4Al_2(OH)_{12}CO_3+2NaOH \quad (2)$$

And the equation (3) is frequently accompanied by side-reaction.

$$Ca(OH)_2+Na_2CO_3\rightarrow CaCO_3+2NaOH \quad (3)$$

So there are fewer calcium carbonates in sample 2. And it can be seen from Fig. 2 that there are lots of impurities in sample 1. Comparing with the sample 2, the crystallization time of sample 1 is shorter, so the impurities in sample 1 may be associated with inadequate reaction of equation (2), resulting to some tricalcium aluminate hexahydrate and calcium carbonate in it. It also can be seen from Fig. 2 that there are small amounts of impurities in sample 3, and most of the impurities are calcium carbonate. As observed from Table 1, the reaction time of sample 3 is very short, resulting to the inadequate reaction of equation (1). And then the unreacted $Ca(OH)_2$ will contribute to the equation (3) leaving many calcium carbonate in sample 3.

Table 1 The different reaction and crystallization time for the preparation of hydrocalumites

	reaction time/h	crystallization time/h
Sample 1	4	2
Sample 2	4	4
Sample 3	2	4

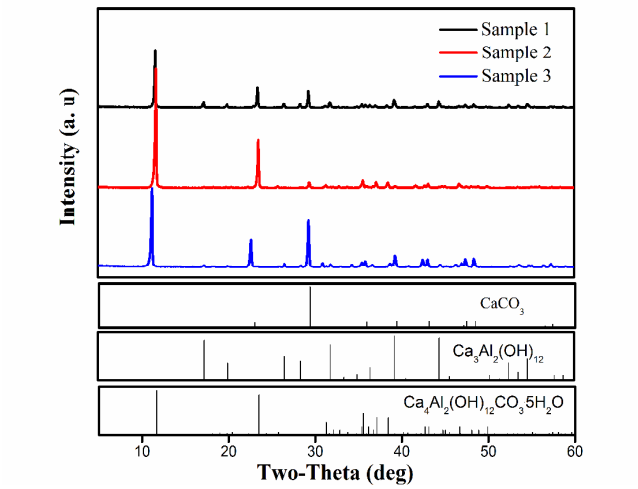


Fig. 2 XRD patterns of hydrocalumites prepared with different reaction time and crystallization time

As mentioned above, the overall chemical equation for preparation of hydrocalumites can be presented as follows:

$4Ca(OH)_2+2Al(OH)_3+Na_2CO_3 \rightarrow Ca_4Al_2(OH)_{12}CO_3+ 2NaOH$ (4)

That is to say, the by-product of this reaction is NaOH. However, NaOH can be directly used in the industrial production of $Al(OH)_3$ stripping section, resulting to the zero discharge in the production process. And compared with the lead stabilizer, the elements for the preparation of hydrocalumites are non-toxic.

Fig. 3 presents the FT-IR spectra of the as-prepared samples. For sample 2, there is a hydroxyl vibrational peak at 3540 cm^{-1}, which shifts to a lower wavenumber in comparison with the free hydroxyl group (3650 cm^{-1}). The reason is that the reaction among the interlaminar H_2O, CO_3^{2-} or –OH in hydrotalcite structure is happened through the association of hydrogenbond.[16] The prominent absorption bands (1562 cm^{-1} and 1364 cm^{-1}) are due to O-C-O asymmetric stretching. And a considerably lower shifted absorption peak at 1364^{-1}, as compared with CO_3^{2-} of $CaCO_3$ (1430 cm^{-1}), shows that there is an intercalation between CO_3^{2-} and interlayer H_2O through the strong hydrogen bonding.[5] The lower wavenumber bands at 400-800 cm^{-1} is due to Ca-O and Al-O. The spectra of sample 1 and 3 are similar to that of sample 2. However, hydroxyl vibrational peak of sample 1 presented at 3596, which shifts to a higher wavenumber compared with that of sample 2. This may be due to the presence of tricalcium aluminate hexahydrate in sample 1. And for sample 3, the peaks due to O-C-O asymmetric stretching are presented at 1340, which is the typical wavenumber for CO_3^{2-} in $CaCO_3$. This means that there are some calcium carbonates in sample 3. And the results are in accordance with the XRD patterns shown above.

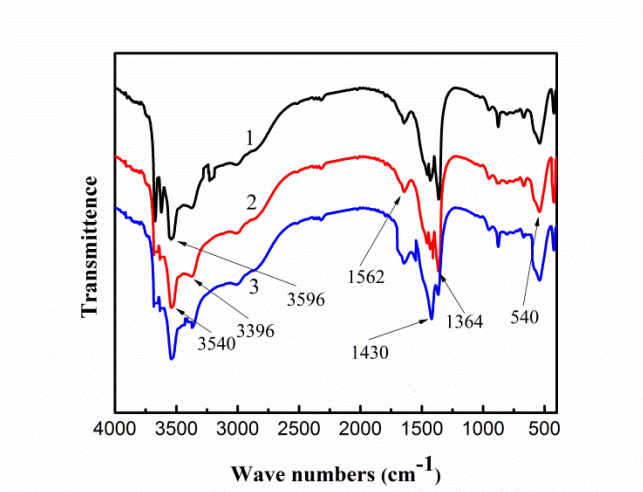


Fig.3 FT-IR spectra of hydrocalumites prepared with different reaction time and crystallization time

The SEM images of the as-prepared samples are shown in Fig. 4. It can be seen from Fig. 4 that all the as-prepared samples have a plate-like structure, which is the typical morphology of layered double hydroxides. Especially, the sample 2 has the hexagon layer structure, and shows higher crystalline and have more regular crystals than sample 1 and sample 3. It also can be seen that there are many finely ground particle in Fig 4 (a) and (c), which implies that there are many impurities in sample 1and 3. As mentioned above, there are some tricalcium aluminate hexahydrate and calcium carbonate in sample 1 due to the inadequate reaction of equation (3). And there are small amounts of calcium carbonate in sample 3 because of the inadequate reaction of equation (2). It also can be seen from the Fig. 4 that the particle size is assumed to be 0.5-2 um.

Effect of hydrocalumites prepared with different reaction time and crystallization time on the stability of PVC

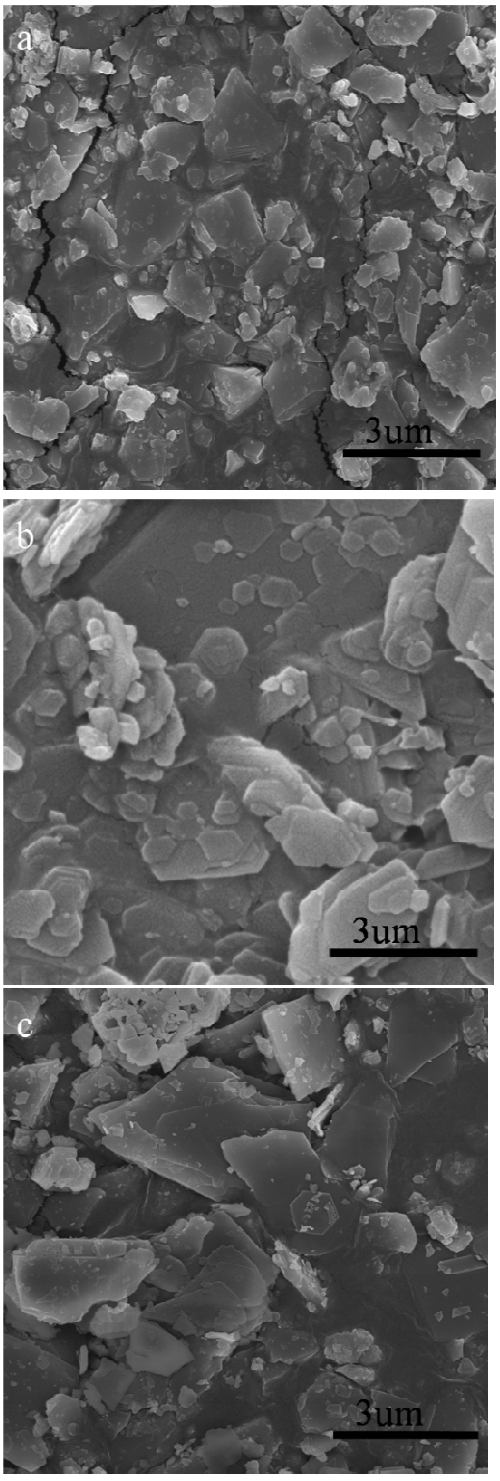
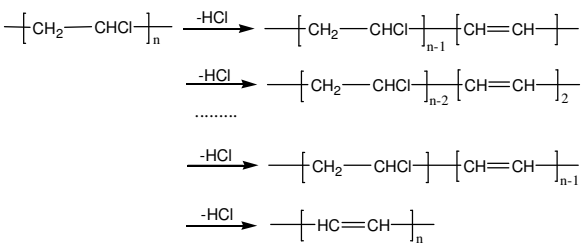


Fig.4 SEM images of (a) Sample 1, (b) Sample 2 and (c) Sample 3

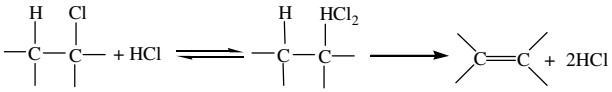
The effect of mixtures containing 10 g PVC powder and 5 g DOP

with (a) nothing, (b) 0.3 g sample 1, (c) 0.3 g sample 2 and (d) 0.3 g sample 3 on the thermal stability of PVC are illustrated in Fig. 5 by static thermal aging test. The thermal stability of PVC is defined by the time when the black decomposition products begin to appear.[7] It can be seen from the Fig. 5 (a) that pure PVC without any stabilizer began to color even during the mixing process and became completely black after only 20 min at 195 ± 1 °C. It is well known that PVC, under the influence of temperatures and energy radiation, suffers from the autocatalytic dehydrochlorination reaction and the HCl-catalytic reaction. These two processes may be expressed as follows:[16,30]

(1) PVC autocatalytic dehydrochlorination reaction:



(2) HCl catalytic reaction:



The thermal stability results for the PVC samples containing 0.3 g as-prepared samples are shown in Fig. 5 (b), (c) and (d), respectively. Compared to blank samples, their thermal stabilities are significantly enhanced, with the results of resisting initial coloring and promoting long-term stability. The colour of the strips became yellow for the first time appearing at 50 min, 70 min and 60 min, and then black specks appearing at 70min, 90min and 80min, respectively. The main reason is attributed to the presence of hydrocalumites. Hydrocalumites can work as the thermal stabilizer for PVC because of its reaction with HCl gas during thermal dehydrochlorination of PVC, then inhibiting the autocatalytic degradation of the polymer (HCl can work as a catalyst for the autocatalytic dehydrochlorination reaction of PVC). The reaction between hydrocalumites and HCl involves two steps, which were proposed by van der Ven.[21] Firstly, the counterions between the LDH-layers react with HCl gas from thermal dehydrochlorination of PVC, which make the Cl^- replace the CO_3^{2-} in the interlayer of LDH. That is to say, the first process does not destroy the structure of hydrocalumites.[31] Then, with further quantities of HCl gas produced, it will react with the hydroxyl groups in the layers, which will completely destroy the structure of hydrocalumites. And the Ca^{2+}, Al^{3+} contained in the hydrocalumites also will react with the HCl, and the finally products were the metal chlorides. This process can be presented by Fig. 5. And the overall reaction between hydrocalumites and HCl gas can be presented as follows:

$$Ca_4Al_2(OH)_{12}CO_3{\cdot}5H_2O+14HCl\rightarrow 4CaCl_2+2AlCl_3+CO_2+18H_2O \quad (5)$$

And the resulting products of equation (5) can not work as a catalyzer for the dehydrochlorination reaction of PVC. Then the two processes mentioned above inhibits the autocatalytic degradation of PVC, and lead to decreased early coloring and enhanced thermal stability. Thus, the thermal stability of PVC containing hydrocalumites becomes better.

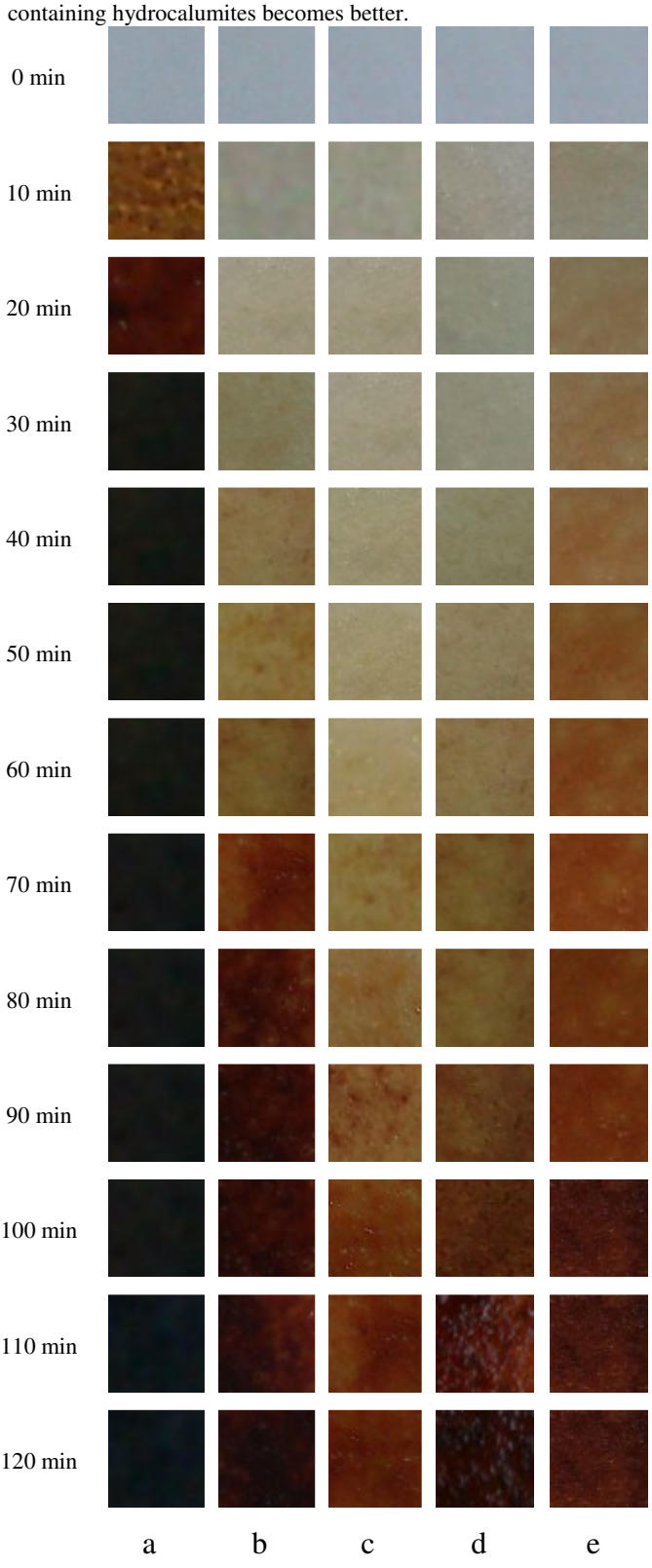


Fig.5 Effect of hydrocalumites prepared with different reaction time and crystallization time on the stability of PVC at 195±l °C.

(a) pure PVC; (b) sample 1; (c) sample 2; (d) sample 3; (e) Mg-Al-LDHs

Comparing with Mg-Al-LDHs (shown in Fig. 5e), the effects of hydrecalumites(shown in Fig. 5c) as a heat stabilizer is better. In periodic table, Ca and Mg both belong to the second main group. And Ca is in the fourth period, while Mg is in the third period. It is well known that in the second main group, metallic character will increase with the argument of period number. So the metallic character of Ca is better than that of Mg. Thus it is easier for Ca^{2+} to combine with Cl^- than that for Mg^{2+}. Then the thermal stability of PVC containing hydrecalumites is better than that with Mg-Al-LDHs. Especially, the content of element Ca is more than that of Mg in the crust. So hydrecalumites are more suitable for large-scale production than Mg-Al-LDHs.

As mentioned above, the black specks of the strips for sample 1, sample 2 and sample 3 firstly appear at 60min, 100min and 80min, respectively. Especially, their color changing processes of sample 2 were relatively slow, and the later color changed from yellow to brown, and didn't become all black. The reason may be as follows: As shown in the XRD patterns shown above, there are some impurities in the sample 1 and 3, and these impurities can not work as a heat stabilizer for PVC as well as hydrocalumites.[32] Thus the thermal stability of strips containing sample 2 is better than that of strips containing sample 1 and 3.

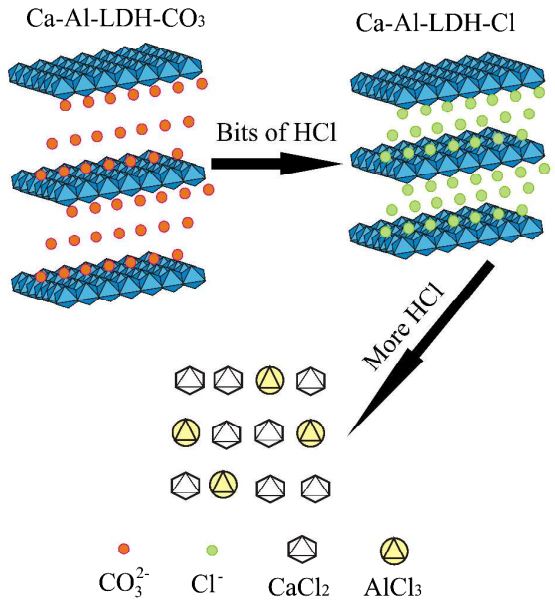


Fig. 6 Schematic illustration for the reaction between the hydrocalumites and HCl gas

In order to further investigate the thermal stability of the as-prepared samples, Congo red test was studied. The thermal stability time of pure PVC+DOP, PVC+DOP+sample 1, PVC + DOP+ sample 2 and PVC + DOP+ sample 3 are shown in Table 2. It can be seen from Table 2 that the thermal stability of pure PVC is very poor, and its thermal stability time is only 8 min. Compared with pure PVC, their thermal stabilities of PVC with hydrocalumites samples are significantly enhanced, with the thermal stability time of PVC with sample 1, sample 2 and sample 3 being 64 min, 86 min and 77 min, respectively. Especially, PVC with sample 2 presents the best thermal stability. And the results are in accordance with that of the static thermal aging tests shown above. The results show that hydrocalumites can contribute to the HCl adsorption during the PVC degradation, resulting in enhancement of the thermal stability of PVC.

Effect of varying the amount of hydrocalumites on the stability of PVC

In order to investigate thermal stability of the hydrocalumites, the effect of varying amount of hydrocalumites (sample 2) on the PVC was studied. DOP and varying amounts of hydrocalumite (in the range 2~5 phr) were mixed with PVC under the same conditions as above. The results of static thermal aging tests are shown in Figure S1. As shown in Figure S1. (a), (b) and (c), there is a marked increase in thermal stability of the PVC as the amount of hydrocalumite is increased from 2 to 4 phr (parts per hundred resins). Especially, when the amount of hydrocalumites in the PVC is equal to 4 phr, the colour of the strips became yellow for the first time appearing at 80 min, and then black specks appearing at 110 min. However, as higher quantities of hydrocalumites were added (from 4 to 5phr), there is only a very slight further increase in thermal stability suggesting that 4 phr is the optimum amount of hydrocalumite filler. For the addition of hydrocalumites at 2 phr and 3 phr, the amount of the heat stabilizer is so small that it can not effectivelyreact with HCl during thermal dehydrochlorination of PVC, and then it can not effectively inhibit the autocatalytic degradation of the polymer. And for the addition of hydrocalumites at 5 phr, the excessive heat stabilizer were added which may affect its compatibility and dispersion in PVC, then thermal stability only increase a little.

Table 2 Effect of hydrocalumites prepared with different reaction time and crystallization time on the stability of PVC at 195±1 ℃ (as determined by the Congo red method)

PVC composite	Thermal stable time of PVC composite / min
PVC	8
PVC+ sample 1	64
PVC+ sample 2	86
PVC+ sample 3	77

In order to further investigate the thermal stability of hydrocalumites with varying amount, Congo red test was studied. The results are shown in Table 3. It can be seen from Table 3 that the thermal stability time of PVC strips were 58 min, 86 min, 103 min and 107 min, respectively, and the results suggest that 4 phr is the optimum amount of hydrocalumite filler, which are in accordance with that of the static thermal aging tests.

Experimental section

Materials

PVC (SG5) having limiting viscosity number 107–118 ml/g and average polymerization degree of 1000–1100 were supplied by chemical plant of Zhuzhou, Hunan, China. $Ca(OH)_2$, Na_2CO_3 and

$Al(OH)_3$ were all of A.R. grade. Dioctylphthalate (DOP) was of C.P. grade. The deionized water was distilled twice to get rid of carbon dioxide (CO_2).

Table 3 Effect of varying the amount of hydrocalumites (sample 2) on the thermal stability of PVC (as determined by the Congo red method)

PVC composite	Amount of hydrocalumites / phr	Thermal stable time of PVC composite / min
PVC+ hydrocalumites	2	58
PVC+ hydrocalumites	3	86
PVC+ hydrocalumites	4	103
PVC+ hydrocalumites	5	107

Preparation of hydrocalumites

The as-prepared samples were synthesized as follows: $Ca(OH)_2$ and $Al(OH)_3$ (with Ca/Al molar ratios of 2:1) were added it, and all this process were carried out under vigorous stirring. Then, the solution of Na_2CO_3 (0.26g) was added into the above slurry. After stirring for a period of time, the resultant slurry was aged for 20 h at 60 °C. After filtered and washed with distilled water, the precipitate was dried and ground to fine power.

Characterization

X-ray diffraction (XRD) of samples was recorded by a D-500 (Siemens) power diffractometer (36 Kv, 30 mA) using Cu Kα radiation at a scanning rate of 2 θ = 8°min^{-1}. Fourier transform infrared (FT-IR) spectroscopy was conducted on a Nicolet Nexus-670 FT-IR spectrometer (as KBr discs, with wave number 400-4000 cm^{-1}, resolution 0.09 cm^{-1}, and the weight of measured sample 2 mg). The morphology of as-prepared Zn-Cu-Al-LDHs was observed using a scanning electron microscope (SEM, JSM-6360LV).

Thermal stability testing of PVC strips

Mixtures containing PVC powder, dioctylphthalate (DOP), and hydrocalumites were blended in a heated double-roller mixer for 5 min at 190°C. The resulting composites were molded at 100 °C to a film with a thickness of 1 mm and cut into 3 cm × 3 cm strips. These strips were placed in a thermal aging test box at 195±1°C and subjected to static thermal aging, which is according to the ISO standard. The strips were taken out of the box every 10 min and subjected to visual examination.

According to ISO standard 182/1-1990(E), PVC and stabilizers were mixed fully in the mortar. The resultant mixture was put into a tube with Congo red test paper located at 2 cm above the sample. The tube was heated with an oil bath at 195 °C for evaluating static thermal stability of PVC composites. The time when Congo red test paper began to turn to blue was defined as static stability time. Each sample was measured three times and the average time was obtained.

Conclusions

Hydrocalumites have been successfully synthesized by using $Ca(OH)_2$, $Al(OH)_3$ and Na_2CO_3 with zero discharge in the production process. The structure of hydrocalumites and thermal stability of PVC with hydrocalumites as the stabilizer are investigated. The results show that the hydrocalumites had a plate-like structure. And the PVC composites containing hydrocalumites prepared by different reaction time and crystallization time show a better thermal stability than pure PVC, with the improvement of long-term thermal stability and initial thermal stability of PVC. Especially, the sample 2 with the reaction time and crystallization time both being 4 hour has better thermal stability than the other samples. And when the amount of sample 2 in the PVC is equal to 4 phr, the colour of the strips became yellow for the first time appearing at 80 min, and then black specks appearing at 110min, while pure PVC without any stabilizer began to colour even during the mixing process and became completely black after only 20 min at 195±l °C. Based on these observations, the prepared hydrocalumites may be a promising heat stabilizer for PVC.

Acknowledgements

This work was supported by the Natural Science Foundation of China (No.21371180), Science and technology project of Changsha city (No.K1303015-11) and Specialized Research Fund for the Doctoral Program of Higher Education (No.20130162110018).

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