Bean Dreg–Hydrocalumite Composite as a Highly Efficient Thermal Stabilizer for Poly(vinyl chloride)

Deyi Luo, Bei Tang, Haokun Yuan, Chao Zhang,* and Xi Zhou*

ABSTRACT: Bean dreg (BD)—hydrocalumite composites were prepared by a hydrothermal method with BD, Ca(OH)2, Al(OH)3, and Na2CO3 as raw materials. The samples were characterized by powder X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy, and N2 physical adsorption—desorption. Their properties as a thermal stabilizer for poly(vinyl chloride) were tested using a torque rheometer and static thermal aging method. Compared with traditional hydrocalumite, the crystal size of the BD–hydrocalumite composite was relatively small, which made it exhibit good dispersion and better thermal stability for poly(vinyl chloride). In addition, the effects of preparation conditions on the properties of BD–hydrocalumite as a heat stabilizer were also investigated. Under the conditions of n[Ca(OH)2/Al(OH)3/Na2CO3] = 4.4:2:1, a BD dosage of 5%, a crystallization temperature of 90 °C, and 19 h, the prepared BD–hydrocalumite showed the best performance, and the dynamic thermal stability time of poly(vinyl chloride) reached 2149 s.

INTRODUCTION

Poly(vinyl chloride), abbreviated as PVC, is an important thermoplastic polymer, which is widely used in food packaging, medical equipment, plastic pipes, and other fields.1 PVC is easy to decompose at the processing temperature, resulting in the deepening of product color and the change of structure and properties. Therefore, a thermal stabilizer must be added during PVC processing to prevent or reduce its thermal degradation.2–4

Hydrocalumite is a layered double hydroxide composed of Ca2+ and Al3+ in the main laminate.5,6 It has a unique layered structure and exchangeable interlayer anions.7 Therefore, hydrocalumite has been widely used in industry as a thermal stabilizer, catalyst, and adsorbent.8–11 Hydrocalumite can react with HCl released by thermal degradation of PVC through interlayer anions or main laminate so as to significantly reduce the autocatalytic degradation rate of PVC by HCl.12–14 In recent years, the literature has reports mainly on the effects of preparation methods, intercalation ions, and surface modifiers on the properties of hydrocalumite as a thermal stabilizer for PVC.15–20 For example, Yang et al. investigated the effect of preparation methods on the performance of hydrocalumite as a thermal stabilizer for PVC.15,16 It was found that the thermal stability of hydrocalumite prepared by the hydrothermal crystallization method with sodium aluminate as an aluminum source is better than that prepared by the traditional coprecipitation method. Zhang et al. synthesized hydrocalumite by a clean method using Ca(OH)2, Al(OH)3, and Na2CO3 as raw materials and found that it shows efficient thermal stability for PVC.17 Yang et al. prepared nanosized hydrocalumite intercalated with HPO42− using Na2HPO3 instead of Na2CO3 as a raw material and found that its thermal stability to PVC is better than that of traditional hydrocalumite intercalated with CO32−.18 Zhou et al. found that the surface modifier has a significant impact on the particle size, morphology, and property of hydrocalumite as a thermal stabilizer for PVC.19,20 They also found that the property of
hydrocalumite prepared by the cleaning method is better than that of the coprecipitation method. However, there are few reports about hydrocalumite-based composites as heat stabilizers for PVC.

In the previous research, it was found that the crystal size, specific surface area, and adsorption performance of bean dreg (BD)–hydrocalumite composites were better than those of traditional hydrocalumite. In order to further improve the property of hydrocalumite as a thermal stabilizer of PVC, a BD–hydrocalumite composite was prepared by the hydrothermal method with BD, Ca(OH)\textsubscript{2}, Al(OH)\textsubscript{3}, and Na\textsubscript{2}CO\textsubscript{3} as raw materials and applied to the thermal stabilizer of PVC. It provides a feasible method for the development of a hydrotalcite-like composite as a thermal stabilizer for PVC.

## RESULTS AND DISCUSSION

### Material Characterization and Analysis

The structures of BD, hydrocalumite (LDH), and the BD–hydrocalumite composite (5% BD–LDH2) were characterized by powder X-ray diffraction (XRD). The results are shown in Figure 1. The prepared LDH had a typical hydrotalcite-like layered structure (Figure 2c,d). In addition, the size of LDH flakes was large and uneven, accompanied by certain agglomeration. As shown in Figure 2e,f, small and thin LDH flakes were evenly deposited on the surface of BD in 5% BD–LDH2. Compared with LDH, the size of LDH flakes in 5% BD–LDH2 was significantly smaller and more evenly distributed, which was consistent with the results of XRD (Figure 1). The reason might be that the polymerization degree of BD was reduced hydrolysis during the preparation of 5% BD–LDH2. Also, the LDH flakes were closely combined with BD and evenly deposited on the surface so as to inhibit the agglomeration of LDH. It was feasible to improve the dispersion of 5% BD–LDH2 in PVC so as to improve its thermal stability to PVC.

The functional groups of BD, LDH, and 5% BD–LDH2 were detected by Fourier transform infrared (FT-IR) spectroscopy, and the results are shown in Figure 3. There were stretching vibration valleys of \(-\text{OH}\) and \(-\text{C-H}\) at 3456 cm\textsuperscript{-1}, stretching vibration valleys of \(-\text{CH}_3\) and \(-\text{CH}_2\) at 2930 and 2860 cm\textsuperscript{-1}, respectively, characteristic absorption valleys of the hemiacetal group at 1740 and 1640 cm\textsuperscript{-1}, and characteristic absorption valleys of \(-\text{C-O}\) in the spectrum of BD. Also, the spectra of LDH and 5% BD–LDH2 were roughly similar. The same infrared absorption bands appeared at 3670 and 3530 cm\textsuperscript{-1} corresponding to Ca\textsuperscript{2+} and Al\textsuperscript{3+} bonded \(-\text{OH}\) of the LDH laminate, indicating that the addition of BD does not affect the formation of LDH. Compared with the spectrum of LDH, BD-related valleys were also found in the spectrum of 5% BD–LDH2, indicating that BD was successfully introduced into 5% BD–LDH2.

The specific surface area (\(S_{\text{BET}}\)), pore size, and pore volume of LDH and 5% BD–LDH2 were measured by N\textsubscript{2} physical adsorption–desorption. As shown in Table 1, the \(S_{\text{BET}}\) values of LDH and 5% BD–LDH2 were 6.626 and 15.013 m\textsuperscript{2}·g\textsuperscript{-1}, respectively, and the \(S_{\text{BET}}\) of 5% BD–LDH2 was greatly weakened, which might be due to the reduction particle size or crystallinity of the LDH sheet in 5% BD–LDH2.

The characteristic diffraction peaks of hydrocalumite appeared at 11.6, 23.5, 31.3, 35.4, 38.5, and 61.2° in the spectrum of LDH and 5% BD–LDH2. The diffraction peaks of 5% BD–LDH2 were similar to those of LDH. The peaks at 29.4, 35.9, 46.7, and 49.9° indicated that there was a small amount of CaCO\textsubscript{3} in LDH and 5% BD–LDH2. However, the crystal surface of cellulose was not obvious in the spectrum of 5% BD–LDH2, which was mainly due to the low content and uniform dispersion of BD. Compared with LDH, the characteristic diffraction peak intensity of the LDH phase in 5% BD–LDH2 was greatly weakened, which might be due to the reduction particle size or crystallinity of the LDH sheet in 5% BD–LDH2.

In order to explore the surface morphology of the sample, BD, LDH, and 5% BD–LDH2 were characterized by scanning electron microscopy (SEM), as shown in Figure 2. The morphology of BD was massive and flaky, with a smooth surface and obvious pores and folds (Figure 2a,b). The
respectively. The results showed that the $S_{BET}$ of 5% BD–LDH2 was more than twice that of LDH. The reason might be that the particle size of 5% BD–LDH2 was significantly smaller than that of LDH (Figure 2). In addition, the pore volume of 5% BD–LDH2 was also higher than that of LDH with a similar pore size.

### Thermal Stability Evaluation of the Composite for PVC
Under the conditions of $n[\text{Ca(OH)}_2/\text{Al(OH)}_3/\text{Na}_2\text{CO}_3] = 4.4:2:1$, a crystallization temperature of 90 °C, and 19 h, BD–hydrocalumite composites were prepared by changing the amount of BD. Their effects on the thermal stability of PVC were evaluated using a torque rheometer. As shown in Figure 4, the error bar represents the standard deviation of the three experimental results. The dynamic thermal stability time of PVC was 1823 s using LDH as the thermal stabilizer, which was similar to the results reported in the previous literature.15,17–19 When BD–hydrocalumite was used as the heat stabilizer instead of LDH, the dynamic thermal stability time of PVC was significantly prolonged, up to 2092 s. The results showed that the thermal stability of BD–LDH composite for PVC is better than that of traditional LDH. According to the SEM characterization result (Figure 2), adding an appropriate amount of BD to the reaction solution for preparing LDH can reduce the size of LDH flakes and prevent agglomeration, which is conducive to improve its dispersion and thermal stability to PVC.20

As shown in Figure 4, the amount of BD had a significant impact on the performance of the BD–hydrocalumite composite as a PVC thermal stabilizer. When the dosage of BD increased from 2.5% (based on the mass of LDH) to 5%, the dynamic thermal stability time of BD–hydrocalumite for PVC increased from 2037 to 2092 s. However, the dynamic thermal stability time decreased upon further increasing the dosage of BD to 10%. The above results showed that the addition of an appropriate amount of BD was conducive to improve the thermal stability of the composite to PVC. However, the excessive addition of BD would reduce the content of LDH in the composite and affect its ability to absorb HCl, resulting in the decline of the thermal stability of the composite to PVC.

In addition to the torque rheometer test method, the static thermal aging method was also an important method to evaluate the performance of the thermal stabilizer for PVC. Therefore, the static thermal stability of LDH, 2.5% BD–LDH2, 5% BD–LDH2, 7.5% BD–LDH2, and 10% BD–LDH2 to PVC was tested by a static thermal aging method. As shown in Figure 5, PVC sheet began to turn yellow at 10 min and turned brown at 90 min when LDH was used as the thermal stabilizer. When the BD–hydrocalumite composite was used as the thermal stabilizer instead of hydrocalumite, the coloring time of PVC sheet was prolonged. The results also showed that the thermal stability of the BD–hydrocalumite composite for PVC was better than that of traditional LDH, which was consistent with the evaluation results of dynamic thermal stability (Figure 4).15 Among the investigated BD–hydrocalumite composites, 5% BD–LDH2 showed the best performance as a thermal stabilizer for PVC, which was also consistent with the results obtained from the torque rheometer (Figure 4).
Effect of the Ca/Al Molar Ratio on the Property of Composites. According to the literature, the molar ratio of Ca/Al had a significant effect on the properties of LDH-based PVC heat stabilizers. Therefore, the effect of the Ca/Al molar ratio on the property of BD–hydrocalumite as a PVC heat stabilizer was investigated under the conditions of $n[\text{Al(OH)}_2/\text{Na}_2\text{CO}_3] = 2:1$, 5% BD dosage, 90 °C, and 19 h. As shown in Figure 6, the dynamic thermal stability time of BD–hydrocalumite to PVC increased from 2017 to 2118 s upon increasing the Ca/Al molar ratio from 1.6:1 to 2.2:1. However, the dynamic thermal stability time decreases to 2082 s with further increase of the Ca/Al molar ratio to 2.4:1. According to the literature, the laminate structure, layer spacing, and intercalation ions could be adjusted by controlling the proportion of metal ions in the laminate of hydrotalcite-like materials so as to affect its performance as a PVC thermal stabilizer.

Effect of Na$_2$CO$_3$ Dosage on the Property of Composites. According to the literature, the alkalinity of the reaction solution had an important influence on the preparation and structure of hydrotalcite-like materials. Therefore, the effect of Na$_2$CO$_3$ dosage on the property of BD–hydrocalumite as a PVC thermal stabilizer was investigated under the conditions of $n[\text{Ca(OH)}_2/\text{Al(OH)}_3] = 2.2:1$, 90 °C, and 19 h, and the results are shown in Figure 7. When the dosage of Ca(OH)$_2$ and Al(OH)$_3$ was 0.088 and 0.04 mol, respectively, the dynamic thermal stability time of the PVC mixture increased from 2045 to 2149 s with the increase of the Na$_2$CO$_3$ dosage from 0.018 to 0.02 mol. However, the dynamic thermal stability time of the PVC mixture decreased with further increase of Na$_2$CO$_3$ dosage to 0.022 mol. Therefore, the optimal proportion of raw materials was $n[\text{Ca(OH)}_2/\text{Al(OH)}_3/\text{Na}_2\text{CO}_3] = 4.4:2:1$ in the process of preparation of BD–hydrocalumite.

Effect of Crystallization Temperature on the Property of Composites. Under the conditions of $n[\text{Ca(OH)}_2/\text{Al(OH)}_3/\text{Na}_2\text{CO}_3] = 4.4:2:1$, 5% BD dosage, and 90 °C, the effects of crystallization temperature on the property of BD–hydrocalumite as a PVC thermal stabilizer were investigated. As shown in Figure 8, the dynamic thermal stability time of BD–hydrocalumite to PVC was extended from 1935 to 2145 s with increase of crystallization temperature from 70 to 90 °C. However, the dynamic thermal stability time decreased to 2082 s with further increase of crystallization temperature to 110 °C. According to the literature, the crystallization temperature affected the dissolution of raw materials, the diffusion of metal ions in the reaction solution, and the formation and growth of crystal nuclei. Thus, the crystallization temperature had a significant impact on the particle size of the product. Therefore, crystallization temperature was also one of the key factors affecting the property of hydrotalcite-like materials.

Effect of Crystallization Time on the Property of Composites. Under the conditions of $n[\text{Ca(OH)}_2/\text{Al(OH)}_3/\text{Na}_2\text{CO}_3] = 4.4:2:1$, 5% BD dosage, and 90 °C, the effects of crystallization time on the property of BD–hydrocalumite were also investigated. As shown in Figure 9, the dynamic thermal stability time of BD–hydrocalumite to PVC was extended from 2028 to 2149 s upon prolonging the crystallization time from 15 to 19 h. However, the thermal stability of BD–hydrocalumite to PVC decreased upon further...
prolonging the crystallization time to 23 h. The reason might be that too short crystallization time causes the crystal nucleus of BD–hydrocalumite to grow incompletely, resulting in its poor thermal stability to PVC. Appropriately prolonging the crystallization time is conducive to improving its performance. However, too long crystallization time will lead to the aggravation of product agglomeration, which is not conducive to the dispersion of BD–hydrocalumite in PVC. Therefore, the preferred crystallization time was 19 h for the preparation of BD–hydrocalumite.

**CONCLUSIONS**

Compared with the traditional hydrocalumite, the BD–hydrocalumite composite showed better thermal stability for PVC. The reason might be that the introduction of BD could effectively reduce the size and agglomeration of hydrocalumite flakes in the preparation, which was conducive to the dispersion of BD–hydrocalumite in PVC so as to improve its thermal stability to PVC. The Ca/Al molar ratio, BD dosage, Na₂CO₃ dosage, crystallization temperature, and time had a significant impact on the performance of BD–hydrocalumite as a thermal stabilizer of PVC. When \[ \frac{[Ca-(OH)₂]_x[Al(OH)₃]_y[Na₂CO₃]}{Ca(OH)₂[Al(OH)₃]Na₂CO₃} = 4.4:2:1, 5\% BD dosage, 90 °C, \] and 19 h, the prepared BD–hydrocalumite showed the best thermal stability for PVC, and the dynamic thermal stability time could reach 2149 s. The above research results provide a feasible method for the development of a hydrotalcite-like composite as a thermal stabilizer for PVC.

**EXPERIMENTAL SECTION**

**Preparation of Thermal Stabilizers.** Pretreatment of BD was carried out as follows. Fresh BD was washed with distilled water until the filtrate was clarified. After filtration, the BD was dried at 80 °C for 20 h, crushed, and passed through a 200 mesh sample sieve to obtain the product, marked as BD.

Typical preparation of the BD–hydrocalumite composite was as follows. Ca(OH)₂ (6.23 g, 0.08 mol), Al(OH)₃ (3.12 g, 0.04 mol), Na₂CO₃ (2.12 g, 0.02 mol), and BD (0.57 g) were added into a three-neck flask containing 150 mL of distilled water. The mixture was sheared at high speed to prepare a slurry. Then, the slurry was reacted at 80 °C for 30 min. After adding 0.91 g of stearic acid, the slurry was allowed to react for 1 h. The slurry was poured into a hydrothermal reactor and crystallized at 90 °C for 19 h. At last, it was filtered, washed, and dried. The solid was ground through a 200 mesh sample sieve to obtain the BD–hydrocalumite composite, marked as xBD–LDHy, where x is the mass percentage of BD to hydrocalumite and y is the molar ratio of Ca/Al in the raw material.

The preparation of hydrocalumite was similar to the preparation procedure of BD–hydrocalumite in the absence of BD, marked as LDH.

**Characterization of Thermal Stabilizers.** The surface morphology of thermal stabilizers was determined by SEM (Zeiss sigma 300, Germany) at an accelerating voltage of 3 kV. The crystal structure of thermal stabilizers was analyzed by XRD (DX-2700BH, China) using Cu Kα ray (λ = 0.154056 nm) in continuous scanning mode. The scanning range of 2θ was 10°–80°. The functional groups of thermal stabilizers were characterized by FT-IR spectroscopy (Nicolet iS5, USA) in the range of 400–4000 cm⁻¹. The physical structure of thermal stabilizers was examined by the N₂ adsorption–desorption method (Autosorb-iQ, USA). The specific surface area (S BET) was calculated by the BET equation, and the pore size and volume were calculated by the BJH equation.

**Evaluation of Thermal Stability.** The dynamic thermal stability of PVC mixture was tested using a torque rheometer (RM-200A, China). The three temperature zones of the torque rheometer were set at 190 °C, and the rotor speed was set at 35 rpm. The formula of the PVC mixture is as follows: 46.30 g of PVC (SG-5), 8.60 g of CaCO₃, 3.40 g of chlorinated polyethylene, 1.30 g of TiO₂, 0.68 g of acrylate copolymer, 1.17 g of xBD–LDHy, and 0.52 g of other additives.

The static thermal stability of the PVC sheet was tested using a thermal aging drying oven at 185 °C. The test compound formula is as follows: 50 g of PVC (SG-5), 20 g of dioctyl phthalate, 15 g of CaCO₃, 1.17 g of xBD–LDHy, and 0.57 g of other additives.

**AUTHOR INFORMATION**

**Corresponding Authors**

Chao Zhang — Department of Food and Chemical Engineering, Shaoyang University, Shaoyang 422000, China; Email: zcsysu0701@163.com

Xi Zhou — Department of Food and Chemical Engineering, Shaoyang University, Shaoyang 422000, China; orcid.org/0000-0002-6736-7160; Email: z_zhouxi@163.com

**Authors**

Deyi Luo — Department of Food and Chemical Engineering, Shaoyang University, Shaoyang 422000, China

Bei Tang — Hunan Xiongchuang New Material Co., LTD, Shaoyang 422000, China

Haokun Yuan — Department of Preschool Education, Xiangzhong Normal College for Preschool Education, Shaoyang 422000, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c01835

**Notes**

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