

Article

Characteristics of Low-Temperature Polyvinyl Chloride Carbonization by Catalytic CuAl Layered Double Hydroxide

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Received: 3 December 2019; Accepted: 13 January 2020; Published: 17 January 2020



Abstract: A good way to make carbon materials was presented in low-temperature polyvinyl chloride (PVC) carbonization by catalysis. The process of low-temperature PVC carbonization by CuAl-layered double hydroxide (CuAl-LDH) was investigated by thermogravimetric analysis (TGA) and tubular furnace. The results show that CuAl-LDH accounting for 5% of PVC mass enabled acceleration of the dehydrochlorination in PVC as soon as possible and maximized the yield of the PVC carbonized product. The vacuum with 0.08 MPa, 20 °C/min heating rate and 90 min carbonized maintenance time were optimal for PVC carbonization. Moreover, the best morphology and yield of the carbonized product was provided at a carbonization temperature of 300 °C.

Keywords: catalytic PVC pyrolysis; PVC carbonization; CuAl layered double hydroxide (CuAl-LDH)

1. Introduction

Polyvinylchloride (PVC) is a general-purpose resin, ranked second to polyolefins amongst thermoplastics in total world production volume [1]. Due to its properties such as excellent acid and alkali resistance, wear resistance, flame resistance, insulation, excellent processing performance, cost-effectiveness and good compatibility with plasticisers, PVC can greatly improve the mechanical properties of most materials. With the rapid increase in the use of plastics, plastic waste accounts for a large proportion of municipal solid waste and as such, has gained more attention regarding the inefficient methods for its disposal [2–4].

Amongst all types of plastics, PVC is one of the most important but also a potentially hazardous polymer material in the environment [5,6]. Current disposal methods include landfill, incineration, chemical recovery, etc. Traditional landfill accumulation and other treatment methods are non-biodegradable approaches. Incineration disposal has a large amount of treatment, good reduction and can recover heat energy, but it also leads to serious environmental pollution. When PVC is incinerated, it generates a considerable amount of smoke as well as potentially harmful volatile organic compounds [7–9], such as HCl. PVC contains chlorine as high as 56.7 wt % [10,11] and when burnt, releases a class of highly toxic substances such as dioxins. Additionally, PVC can generate chlorinated hydrocarbons during pyrolysis, which act as precursors for toxic emissions of substances such as polychlorinated dibenzo-p-dioxine and dibenzofurane [12,13]. The usual approach for chemical recycling of PVC is the cracking/pyrolysis method, which includes hydrocracking, thermal cracking and catalytic cracking [14,15]. Feed-stock recycling pyrolysis is capable of converting mixed, unwashed plastic waste into fuels, monomers or other valuable materials [16].

Qiao et al. indicated that the pyrolysis and carbonization of two forms of waste PVCs were examined to understand the carbonization process of waste PVC and thus develop mesoporous structures in carbonized products [17]. This is also a new research direction for the reuse of waste PVC materials. In its initial phase, the thermal degradation of PVC is primarily a process of sequential dehydrochlorination that forms conjugated polyene sequences. Chlorine in PVC leaves pyrolysis units mainly as hydrogen chloride [18,19], and HCl is released in large amounts at a relatively lower temperature (≤ 300 °C) [20].

Limitations in the solid waste combustion or energization processes (pyrolysis or gasification) are due to the chlorine compounds in PVC and to the corrosive effect of the generated acid gas (HCl) on the inner wall of the equipment; as a result, the difficulty in the subsequent purification treatment is increased. Therefore, the presence of a chlorine source causes potential danger in the generation of highly toxic compound dioxins [21,22].

The prior removal of chlorine from PVC in the form of hydrogen chloride at a relatively lower temperature is vital for inhibiting the generation of hazardous dioxins followed by the stabilization of the dechlorinated polyene fractions to be converted into char with elevated temperatures. Hydrotalcite is a non-toxic, environmentally friendly compound which can be commercially produced by the co-precipitation method. The use of hydrotalcite, a PVC thermal stabilizer, was initially proposed and tested by Kyowa Chemical Industries, Japan [23]. The stabilization mechanism was further studied by van der Ven et al. who reported that the process involves the following steps: the interlayer counter ions initially react with HCl and secondly, the layers react with HCl to form metal chlorides with loss of the layered structure [24].

Pike et al. showed that copper compounds greatly suppress benzene production during PVC pyrolysis [25]. Copper-containing layered double hydroxides (LDHs) with extremely high catalytic activities of copper ions show excellent catalytic performance for volatile organic compound (VOC) oxidation and organic dye degradation, as well as phenol hydroxylation as described by Fan et al [26,27].

Yang et al. showed that the CuAl-layered double hydroxide (CuAl-LDH) additive has a strong charring effect on PVC/CuAl-LDH nanocomposites. This result demonstrates that the CuAl-LDH in the PVC matrix has further favored the oxidative dehydrogenation–crosslinking–charring process and increased the char yield [28].

Chen et al. indicated that CuAl-LDH exhibited extraordinary catalysis in the pyrolysis and combustion of PVC. The addition of CuAl-LDH significantly decreased the release of aromatics and increased the yield of solid char [29].

In this study, the characteristics of low-temperature (about 300 °C) PVC carbonization by catalytic CuAl-LDH was investigated. It was found that many factors affected PVC pyrolysis and carbonization. Different contents of CuAl-LDH, pyrolysis atmosphere, carbonization temperature, the heating rate and carbonization maintenance time on the yield of carbonized PVC product was tested by thermogravimetric analysis (TGA) and tubular furnace. The morphology and composition of the carbonized products were examined by scanning electron microscopy (SEM) and elemental analysis.

2. Experimental

2.1. Materials

PVC resin was kindly provided by Shanghai Chlor-Alkali Chemical Industry Stock Co., Ltd. (Shanghai, China). Plasticizer (Tri-Octyl Tri-Meta-Benzoate, abbreviating TOTM) was supplied by Aladdin Chemical Co., Ltd. (Shanghai, China). The preparation procedure and structural characterization of CuAl-LDH have been reported in [28].

2.2. Preparation of Sample

PVC/CuAl-LDH were directly prepared via melt blending with the mixture of the desired amount of CuAl-LDH and 100 g PVC. The formulations were mixed on a two-roll mill at 105–110 °C for 30 min,

then the resulting mixtures were cooled to room temperature for testing. Table 1 shows the mixing mass ratio of PVC formulations.

Table 1. Sample compositions. PVC = polyvinyl chloride; LDH = layered double hydroxide.

Sample	PVC (g)	TOTM (g)	CuAl-LDH (g)
PVC	100	25	0
PVC/CuAl-LDH-4%	100	25	4
PVC/CuAl-LDH-5%	100	25	5
PVC/CuAl-LDH-6%	100	25	6
PVC/CuAl-LDH-7%	100	25	7

2.3. Methods of Characterization and Instruments

Thermogravimetric analysis was performed using a thermogravimetric analyzer (TGA, SII-TGA/DTA 6300, SII Nano Technology Inc. Northridge, CA, USA). The heating rate was 20 °C/min from 50 °C to 600 °C under a nitrogen atmosphere.

The pyrolysis experiment was tested using a tubular furnace (SG-GS1400, Shanghai Jiejie Electric Furnace Co., Ltd. Shanghai, China). The temperature, heating rate and maintenance time were regulated by a computer (LenovoB5040, Beijing Lenovo Co., Ltd. Beijing, China). The varying atmosphere was provided by TGA and a vacuum pump (SHB-LL1, Zhengzhou Changcheng Branch Industry and Trade Co., Ltd. Zhengzhou, China). The experimental apparatus is shown in

The microstructure of the carbonized product was observed by scanning electron microscopy (SEM, Hitachi s-3400n, Hitachi, Japan), and their magnifications were 10,000 times and 20,000 times respectively. The elemental analysis of the carbonized product was carried out with an element analyzer (Vario EL III). Figure 1.

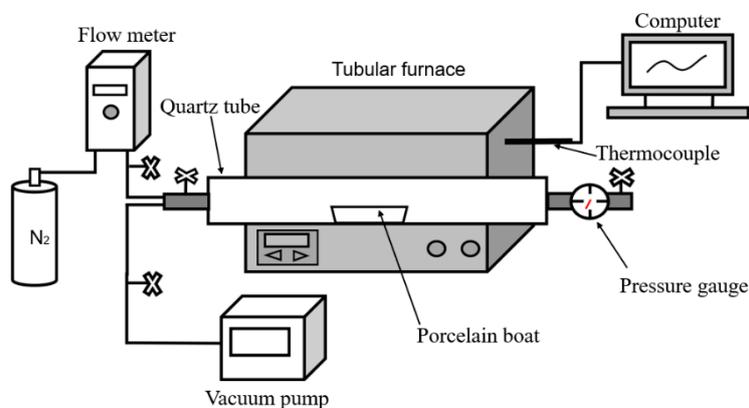


Figure 1. Diagram of apparatus of pyrolysis.

3. Results and Discussion

3.1. Thermogravimetric Analysis of Catalytic Pyrolysis of PVC

The pyrolysis process of PVC and its composites were investigated by TGA in the temperature range of 50 °C to 600 °C. The DTG and TG curves are presented in Figure 2a,b. The pyrolysis trend of PVC/CuAl-LDH-4% is similar to PVC, but they present with two different mass loss stages. The first region ranges from 50 °C to 400 °C, and the second ranges between 400 °C and 600 °C. The first stage is attributed to the dehydrochlorination of PVC and volatilization of the plasticizer, and the second is due to the further degradation of the molecular chains after dichlorination [29].

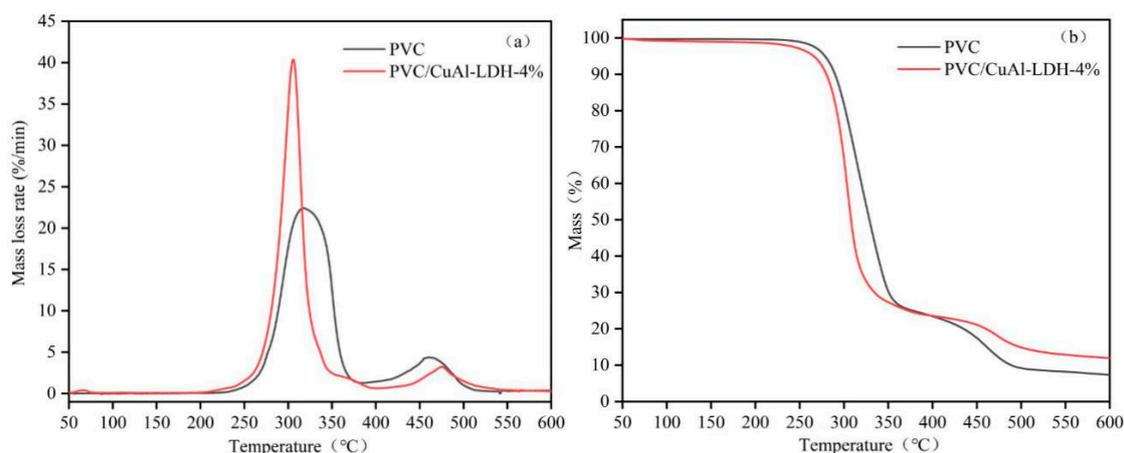


Figure 2. DTG and TG curves for the degradation of PVC and its composite: (a) the curve of Derivative Thermogravimetry; (b) the curve of Thermogravimetry.

From the DTG curves shown in Figure 2a, at the first stage, the temperature at the maximum mass loss rate of PVC/CuAl-LDH-4% appearing at 305 °C is lower than that of PVC resins. Meanwhile, the degradation temperature at the mass loss of the first stage spans a narrower temperature range from 241 °C to 352 °C. This is because the released hydrogen chloride is absorbed by CuAl-LDH to form a lot of Lewis acid sites that can combine with electrons and hydrogen radicals, which would give rise to the further dehydrochlorination of PVC. This indicates that the CuAl-LDH can significantly accelerate the degradation of PVC and reduce the pyrolysis temperature.

According to the TG curves shown in Figure 2b, from the beginning of the second stage to the end of thermal degradation, PVC/CuAl-LDH-4% always displays higher residue compared to that of PVC. This may be attributed to the fact that a number of the Lewis acid sites formed during the first stage would combine firstly with hydrogen radicals, impeding the reaction of hydrogen radicals and the conjugated alkene, and decreasing the release of low molecule hydrocarbons. These results represent that CuAl-LDH not only inhibits the molecular chain fracture, but also increases the residue yield [9,30].

3.2. Thermogravimetric Analysis of Different Contents of CuAl-LDH on the Carbonization of PVC

The pyrolysis process of PVC and its composites were investigated by TG in the temperature range between 50–600 °C under nitrogen atmosphere. From Figure 3, the TG curves of PVC/CuAl-LDH are similar to that of PVC. It is clearly observed that the degradation of PVC is accelerated after the addition of CuAl-LDH. According to the TG curves, the onset degradation temperature (T_{onset}), the temperature of the maximum mass loss rate of the first stage (T_{max1}) and the yield of residue at the end temperature of 600 °C (W_{end}) can be determined. The determined values are given in Table 2.

From Figure 3, the onset degradation temperature of PVC/CuAl-LDH-5% appearing at 238 °C and the temperature at the maximum mass loss rate of PVC/CuAl-LDH-5% appearing at 300 °C were both the lowest temperatures compared to those of other PVC composites. This indicates that the addition of CuAl-LDH-5% can most effectively stimulate the dehydrochlorination of PVC and significantly accelerate the degradation of PVC.

Additionally, from Table 2, at the maximum temperature of 600 °C, the yield of residue of PVC/CuAl-LDH-5% (20.48%) was more than three times that of PVC without CuAl-LDH. It may be concluded that the addition of CuAl-LDH promotes charring during the pyrolysis process, and the charring amounts of PVC/CuAl-LDH-5% were larger than that of PVC and its composites. Thus, CuAl-LDH accounts for 5% of PVC mass, which is the best choice for PVC carbonization.

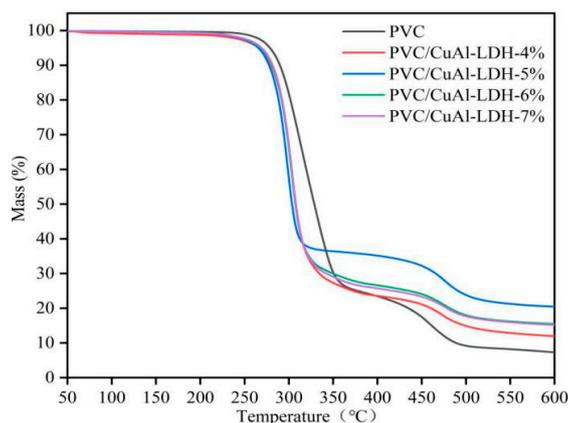


Figure 3. TG curves for the pyrolysis of pure PVC and its composites.

Table 2. Dynamic TGA results for the pyrolysis of PVC and its composites.

Name	Symbols/Units	Mass Ratio of CuAl-LDH (%)				
		0	4	5	6	7
Onset degradation temperature	T_{onset} (°C)	252	241	238	239	241
Temperature of the maximum mass loss rate in the first stage	T_{max1} (°C)	317	305	300	304	305
Yield of residue at end temperature	W_{end} (%)	6.35	11.38	20.48	15.04	14.71

3.3. Effect of Varying Pyrolysis Atmosphere on the Carbonization of PVC Composites

The carbonized product of PVC/CuAl-LDH-5% was achieved using a tubular furnace. The temperature of carbonization was 300 °C, the heating rate was 20 °C/min and the maintenance time of carbonization was 30 min. We examined this process under three atmospheres: nitrogen, vacuum and air. The morphology of the carbonized products are shown in Figure 4. The surface of Figure 4a,b shows black lustre before grinding which turns into dry and black solid particles after grinding. Thus, whether ground or not, Figure 4c shows a light gray powder all along. There is no doubt that the carbon element of PVC/CuAl-LDH-5% would combine with oxygen in the air to form carbon dioxide, which would be released quickly. The carbon content of the product decreases sharply, so the morphology of the carbonized product is hardly seen. Moreover, at the end of pyrolysis, these products have a light green powder appearance due to the presence of copper ions.

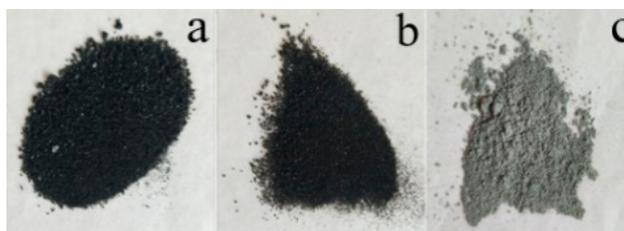


Figure 4. The morphology of the carbonized product under different pyrolysis atmospheres: (a) nitrogen; (b) vacuum; (c) air.

From Figure 5, the yield of the carbonized product was 33.5%, 33.3%, 1.4% in nitrogen, vacuum and air, respectively. The yield of carbonized product is virtually identical under nitrogen and vacuum atmospheres. However, it is difficult to realize the nitrogen condition as it needs more auxiliary equipment which indirectly increases the energy consumption. However, the vacuum condition would be easily realized with less energy consumption. Considering the above, the best choice of pyrolysis atmosphere on the yield of the carbonized PVC product is the vacuum with 0.08 MPa.

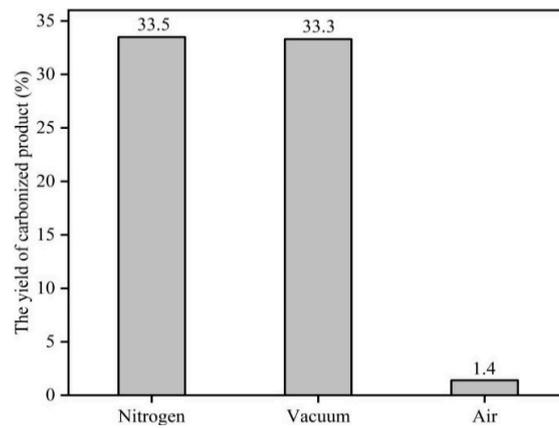


Figure 5. The yield of carbonized product under three different pyrolysis atmospheres.

3.4. Effect of Carbonization Temperature on the Carbonization of PVC Composites

The carbonized product of PVC/CuAl-LDH-5% was obtained using a tubular furnace with different pyrolysis conditions in a vacuum. The vacuum was set at 0.08 MPa, and the carbonization temperature, heating rate and carbonization maintenance time ranged from 250 °C to 600 °C, 10–40 °C/min and 10–120 min respectively. The morphology of the carbonized product is shown in Figure 6.

The temperature at the red region was between 250 °C and 280 °C. The carbonized products in this range were irregular blocks, black lustre and soft texture; impossible to be ground. The product in the blue and green regions were irregular blocks and black lustre before being ground which then turned into black solid particles after grinding. The temperature of the blue region was 290 °C and the carbonized product had hard texture before grinding. After grinding, the surface of the solid particles was moist; furthermore, an oily substance was found in the grinder. The temperature of the green region was between 300 °C and 600 °C. The carbonized product was crispy before grinding, and the solid particles were dry, and there was no oily substance in the grinder after grinding.

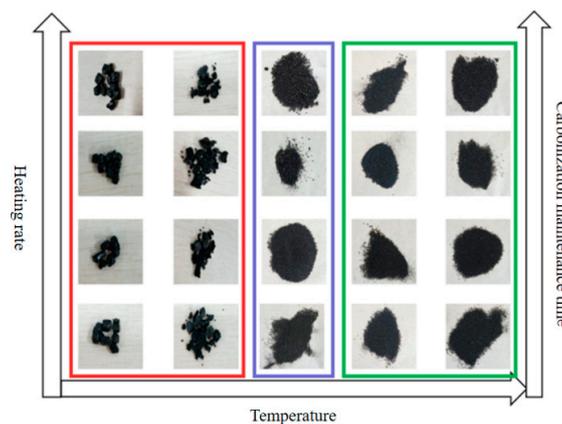


Figure 6. The morphology of the carbonized product.

Moreover, whether carbonized at low or high temperatures, the morphology of the carbonized product was not influenced by the heating rate or the maintenance time of carbonization. At the carbonization temperature of 300 °C, the morphology of the carbonized product changes drastically, but not after 300 °C. This result illustrates that the temperature of carbonization is the primary interfering factor for the morphology of carbonized product compared to the heating rate and the maintenance time of carbonization. Thus, 300 °C is a significant temperature value for the change in carbonized product morphology.

The yield of the PVC/CuAl-LDH-5% carbonized product was gained by using a tubular furnace with different carbonization temperatures. The pyrolysis conditions were: under vacuum (0.08 MPa), heating rate of 20 °C/min and carbonization maintenance time of 30 min. The curves for the yield of the carbonized products are shown in Figure 7. It can be seen that the yield of the carbonized product declines rapidly before 300 °C, but from 300 °C to 600 °C, its yield declines slowly and reaches 33.3% at 300 °C, which is the highest yield compared to those of other temperatures. Based on the earlier results, the temperature at the maximum mass loss rate of PVC/CuAl-LDH-5% is exactly 300 °C and hydrogen chloride was released rapidly at 300 °C; for this reason, the yield of the carbonized product changes drastically at 300 °C.

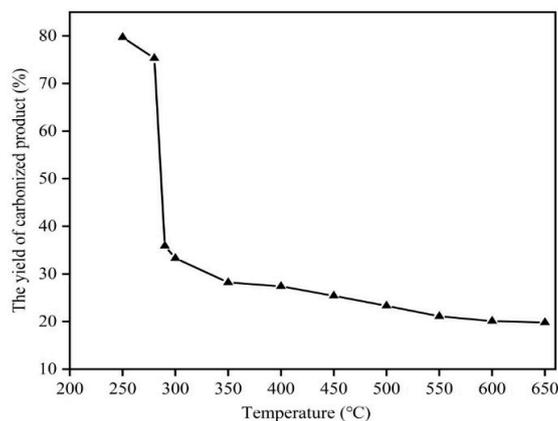


Figure 7. The curves for the yield of carbonized product different carbonization temperatures.

However, after 600 °C, the yield of the carbonized product remains constant. It can be concluded that the pyrolysis of PVC/CuAl-LDH-5% was basically completed in a tubular furnace at 600 °C. According to the temperature needed for a change in carbonized product morphology and the yield of carbonized product generated, 300 °C is tentatively selected as the carbonization temperature.

3.5. Effect of Heating Rate on the Carbonization of PVC Composites

PVC/CuAl-LDH-5% was investigated by TG at different heating rates in the temperature range between 50–600 °C under nitrogen atmosphere. The TG curve is presented in Figure 8. It can be seen that the pyrolysis trend of PVC/CuAl-LDH-5% at different heating rates are similar to each other. At the termination pyrolysis temperature, the yield of the PVC/CuAl-LDH-5% carbonized product is virtually identical at all different heating rates. These results suggested that the yield of the carbonized product is unaffected by heating rate in TG.

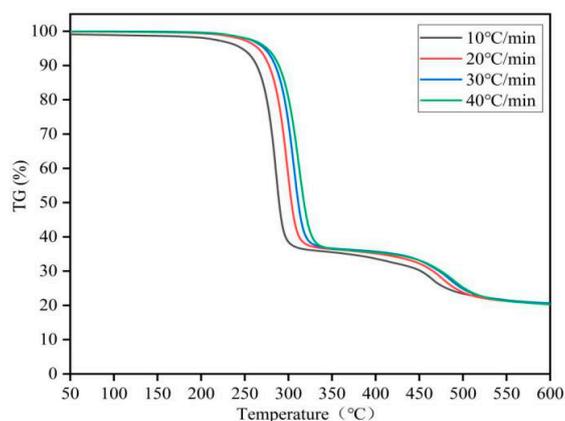


Figure 8. TG curves for the pyrolysis of PVC/CuAl-LDH-5% at different heating rates.

The carbonized product of PVC/CuAl-LDH-5% was obtained by the use of a tubular furnace at different heating rates. The pyrolysis conditions were: under vacuum (0.08 MPa), carbonization temperature of 300 °C, heating rate of 10–40 °C/min and carbonization maintenance time of 30 min. The yield of carbonized product is shown in Table 3. It can be seen that the yield of carbonized product with the 20 °C/min of heating rate is the highest compared to those of others, which reaches 33.3%. We propose that the yield of carbonized product is affected by the heating rate in a tubular furnace.

Though there are contradictions in the conclusions between the yield of the carbonized products at different heating rates from TGA and the tubular furnace, it is worth considering utilizing the conclusion of the tubular furnace. Thus, the 20 °C/min heating rate is one of the optimum experimental conditions of PVC carbonization.

Table 3. The yield of the carbonized product at different heating rates.

Heating Rate (°C/min)	10	20	30	40
Yield of carbonized product (%)	31.5	33.3	31.3	30.5

3.6. Effect of Carbonization Maintenance Time on the Carbonization of PVC Composites

The PVC/CuAl-LDH-5% carbonized product was gained by tubular furnace under different carbonization maintenance times. The carbonization conditions were: under vacuum (0.08 MPa), carbonization temperature of 300 °C, heating rate of 20 °C/min and carbonization maintenance time ranging from 10–150 min. The curves for the yield of the carbonized product with different carbonization maintenance times is shown in Figure 9. Obviously, as the maintenance time of carbonization increases, the yield of the carbonized product gradually reduces. The carbonization temperature of 300 °C was used, which is the temperature at the maximum mass loss rate of PVC/CuAl-LDH-5% at the first stage of degradation. The fact that the plasticizer is volatilized at the release of hydrogen chloride (HCL) explains the carbonization process. Before 90 min, the yield of the carbonized product is maintained at approximately 28% after its initial reduction.

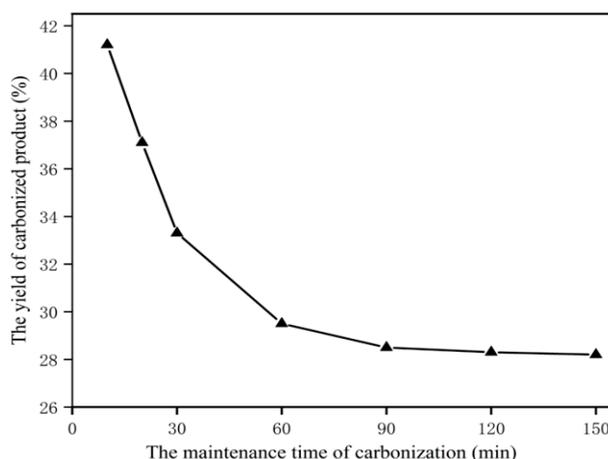


Figure 9. The curve for the yield of carbonized product with different carbonization maintenance times.

3.7. Analysis of the Carbonized Product of PVC/CuAl-LDH-5% by Elemental Analysis

The elements in the carbonized product were measured using an element analyzer. The carbonized product of PVC/CuAl-LDH-5% was obtained by tubular furnace. The carbonization conditions were: under vacuum (0.08 MPa), carbonization temperature of 300 °C, heating rate of 20 °C/min and carbonization maintenance time of 90 min. The carbonized product acid-washing process involved adding a 3:1 volume of aqua regia to the carbonized product and soaking it at 25 °C for 24 h. As listed in Table 4, the carbon content of the acid-washed PVC/CuAl-LDH-5% carbonized product reaches

66.91%. The results show that it has the potential to be a source of carbon material due to the high carbon content.

Table 4. Element analysis of the carbonized product.

Sample	C (%)	H (%)	N (%)
PVC/CuAl-LDH-5%	66.91	5.16	0.95

3.8. Analysis of the Carbonized Product of PVC/CuAl-LDH-5% by SEM

The microstructure of the carbonized product was observed by SEM. The carbonized product of PVC/CuAl-LDH-5% was treated with aqua regia after the tubular furnace tests. Detailed images are shown in Figure 10.

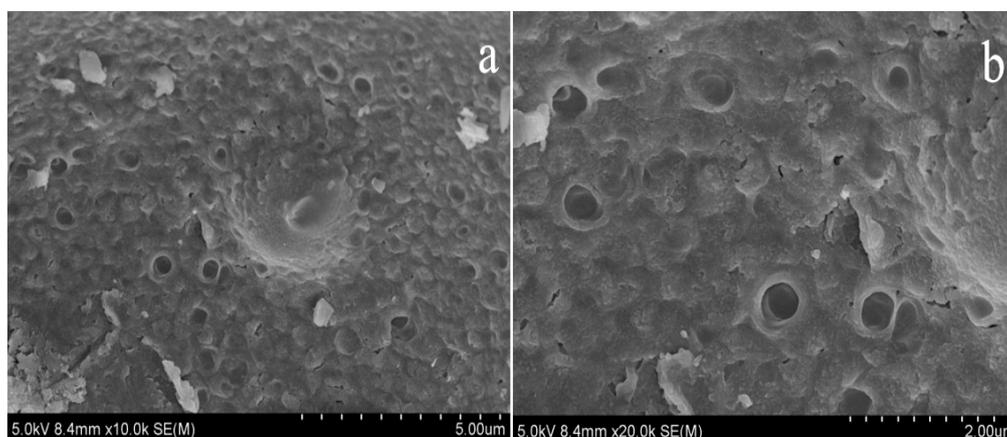


Figure 10. Images of the acid-washed carbonized product of PVC/CuAl-LDH-5%: (a) the surface of carbonized product; (b) the amplifying surface of carbonized product.

It can be seen from Figure 10a that the carbonized product has a rough and porous surface. Moreover, cavities at the surface were found which were derived from the dissolution of the solid particles by the acid. These solid particles are dispersed uniformly on the carbonized product surface, which bond to each other together to form larger aggregates that contribute to the improvement of the material's adsorption properties. Thus, the structure of the carbonized product was improved by these cavities. However, in Figure 10b, these cavities were blocked by something. This may be attributed to the fact that the carbonized product was generated at a low temperature at the same time the tar was produced as well, and the cavities were filled with the tar. To be exact, these are the precursors of the porous carbon material.

4. Conclusions

This paper proposes a method for preparing carbon materials by the use of low-temperature catalytic pyrolysis of PVC. The carbonization process is affected by many factors such as the catalyst, carbonization atmosphere, carbonization temperature, heating rate and carbonization maintenance time. This experimental research has reached the following conclusions:

- (1) CuAl-LDH acts as a catalyst for pyrolysis, and at the right carbonization temperature (about 300 °C), the carbon material can be prepared by the use of low-temperature carbonization of PVC.
- (2) For a double-stage process for the low-temperature catalytic pyrolysis and carbonization of PVC, CuAl-LDH not only reduces the pyrolysis temperature and accelerates the dehydrochlorination of PVC in the pyrolysis stage, but also impedes the release of hydrocarbons in the carbonization stage.
- (3) For the process of low-temperature carbonization of PVC by CuAl-LDH catalysis, CuAl-LDH accounts for 5% of PVC mass when under vacuum atmosphere (vacuum degree ≤ 0.08 MPa) at a

carbonization temperature of ≥ 300 °C, heating rate of ≥ 20 °C/min and carbonization maintenance time of 90 min.

- (4) The carbonized product is prepared by low-temperature carbonization of PVC, which displays a cellular structure on the surface and has high carbon content (66.91%) and hydrogen content (5.16%).

Author Contributions: W.L. and S.Z. conceived and designed the experiments; N.F. and Z.T. contributed analysis tools; E.P. performed the experiments, analyzed the data and wrote the paper. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by Shanghai University of Engineering Science Program, Program of Graduate Research Innovation Project (No. 0231E309031901249).

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

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