

Behavior and products of mechano-chemical dechlorination of polyvinyl chloride and poly (vinylidene chloride)

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Abstract

The mechano-chemical (MC) dechlorination of polyvinyl chloride (PVC) and polyvinylidene chloride (PVDC) was performed by mechanical milling PVC/PVDC powder with zinc powder in a planetary ball mill, and the products of dechlorination were characterized by Infrared spectra (IR), X-ray diffraction (XRD), Raman spectroscopy, gas chromatography–mass spectrometry (GC–MS), and ¹³C solid-state nuclear magnetic resonance (NMR). The experimental results show that PVC/PVDC can be easily dechlorinated by milling with zinc powder, and formed various kinds of inorganic and organic products. Inorganic compounds included Zn₂OCl₂·2H₂O, Zn₅(OH)₈Cl₂·H₂O etc., and organic products involved diamond-like carbon, carbyne fragment, polyacetylene etc. Organic products formed following the paths of dechlorination, dehydrochlorination, crosslink, and oxidation. The mechano-chemical dechlorination process of PVC/PVDC may be an effective approach for carbyne synthesizing in the appropriate condition.

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1. Introduction

Polyvinyl chloride (PVC) is a kind of universal synthetic resin, and widely used in industry, agriculture, architecture, utility, and commodity etc. Polyvinylidene chloride (PVDC) is mainly used for package of meal, tea, and medicines etc. because of its excellent moisture blocking and air blocking performance even in high temperature.

At present, the waste of PVC/PVDC is mainly disposed by combustion or reclamation. The combustion has been carried out for many years, but it generates harmful substances such as dioxins and HCl gas. The reclamation needs a huge land area, which is not always available. Therefore, the new methods are needed urgently for dealing with PVC/PVDC wastes safely and economically.

Since Rowlands and his cooperators have applied mechano-chemical (MC) process to dechlorination of DDT by milling with CaO in the early 1990s [1], mechano-chemical dechlori-

nation has attracted more and more attentions due to its simple and safe operation [2–4]. For example, Saeki et al. have investigated the dechlorination of PVC by milling with CaO, and found that the Cl is almost completely removed from PVC [5–6].

In our earlier work, we have investigated the dechlorination of PVC by milling with zinc powder, and obtained a good result [7]. The present work is mainly about the dechlorinated products of PVC/PVDC characterizing, with the main purpose to provide information for the structure of dechlorinated products and the mechanism of the dechlorination.

2. Experimental

2.1. Materials

The PVC powder used in this experiment is the food grade resin (produced by Zhuzhou Chemical Co., Ltd., Hunan, China), with the initial particle size -100 mesh, and polymerization degree was about 1100. The PVDC powder is produced by Juhua Group corporation (Zhejiang, China), with the initial particle size -100 mesh, and the polymerization degree was about 210.

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The zinc powder is produced by Umicore Hunan Fuhong Zinc Chemicals Co., Ltd (Hunan, China), with the initial particle size -500 mesh.

2.2. Procedure

A planetary ball mill (QM3SP-2, Nanjing university instrument plant, Zhejiang, China) was used for the mechanical milling treatment of the PVC/PVDC with zinc powder. The mill was equipped with two pairs of stainless steel vials. The volume of each vial was approximately 500 cm³. One kilogram stainless steel balls (diameter at 10 mm 400 g, 6 mm 600 g) and 30 g mixture of PVC/PVDC and zinc powder were charged into each vial, and then the vials were sealed with rubber O-rings. The rotational speed was fixed at 550 rpm. The mixture was milled for different periods of time, and then it was carefully removed from the vial.

One gram-milled mixture was dispersed in 3 ml 65% nitrate acid and 197 ml distilled water for 2 h to leach the inorganic chlorides and remained zinc powder, then the suspension was filtered. After filtration, the concentration of chloride ions in filtrate was measured according to GB 11896-1989, and the dechlorination ratio was calculated from the ratio of Cl in filtrate to the initial Cl in PVC/PVDC. A second 1 g ground mixture was agitated in 50 ml acetone with a magnetic stirrer for 30 min to extract the organic chemicals into the solution, and then filtrated, the acetone extracts were used to gas chromatography–mass spectrometry (GC–MS) analysis.

2.3. Characterization

The milled mixture and leaching residue were measured by X-ray diffraction (XRD), Infrared ray (IR) technology, Raman spectrometer, ¹³C solid state nuclear magnetic resonance (NMR). The acetone extracts were characterized by gas chromatography–mass spectrometry.

XRD analysis was performed on Rigaku D/max-2550 (Cu K α , $\lambda = 0.154056$ nm), IR spectrum were obtained using a Nicolet NEXUS 470 FT-IR spectrophotometer. Raman spectrometer was conducted on Laboram-010, with an exciting wavelength at 632.8 nm. ¹³C solid state NMR spectrum was recorded with a Varian infinity Plus 300 at a resonance frequency of 70 MHz, adopting the cross polarization magic angle spinning technique (CP MAS). GC–MS was carried on the Shimadzu QP-2010.

3. Results

3.1. Dechlorination extent

Figs. 1 and 2 shows the dechlorination rate of PVC/PVDC as the function of milling time under different molar ratios of Zn to Cl in PVC/PVDC. The dechlorination ratio increases as the MC treatment progresses and the dechlorination ratio is improved as the molar ratio increases. In Fig. 1, in all molar ratio examined (from 2–9:1), the dechlorination ratio is more than 96% within 3 h, and when molar ratio is greater than 2, the dechlorination ratio almost reaches to 100% within 3 h. In Fig. 2, when molar

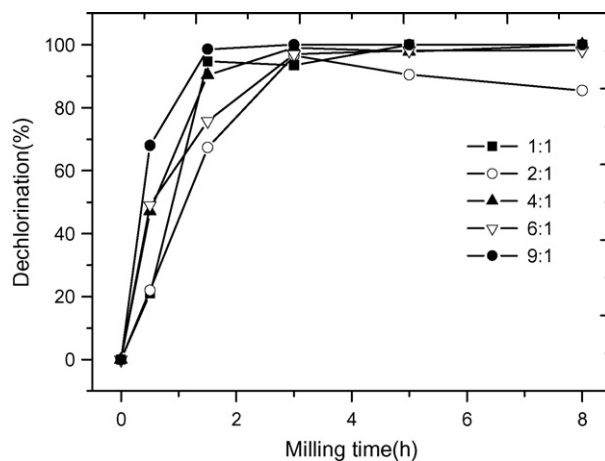


Fig. 1. Dechlorination extent of PVDC as a function of milling time.

ratio is 9:1, 6:1, 4:1, the milling time when extent of dechlorination reached to 100% is 1.5, 3, and 5 h, respectively, and when molar ratio is 2:1, after 8 h milled, the dechlorination extent of PVC is only 92%.

From Figs. 1 and 2, it can also be found that the dechlorination of PVDC is faster than that of PVC, this may because that the structure of PVDC is different that of PVC. Two Cl atoms bond to the same C atom in PVDC structure, which causes it to be more unstable than PVC, and the Cl atom can be more easily removed from the polymer.

3.2. Inorganic products

Fig. 3 shows the XRD patterns of the mixtures of PVDC/Zn milled for different time. In the initial mixture, the peaks of Zn₅(OH)₈Cl₂·H₂O appears in the pattern of 0.5 h milled mixture, then become stronger and stronger, until strongest in the pattern of the 3 h milled mixture, and disappears in the pattern of 8 h milled mixture. The peaks of Zn₂OCl₂·2H₂O appear in the pattern of the PVDC/Zn mixture milled for 1.5 h, and then become stronger and stronger in the patterns of the samples after milled from 3 to 8 h.

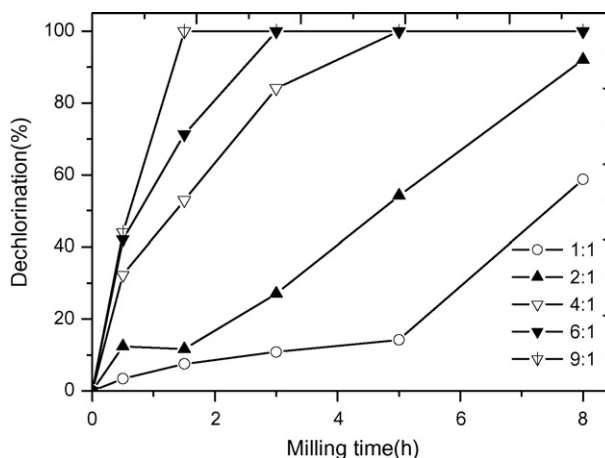


Fig. 2. Dechlorination extent of PVC as a function of milling time.

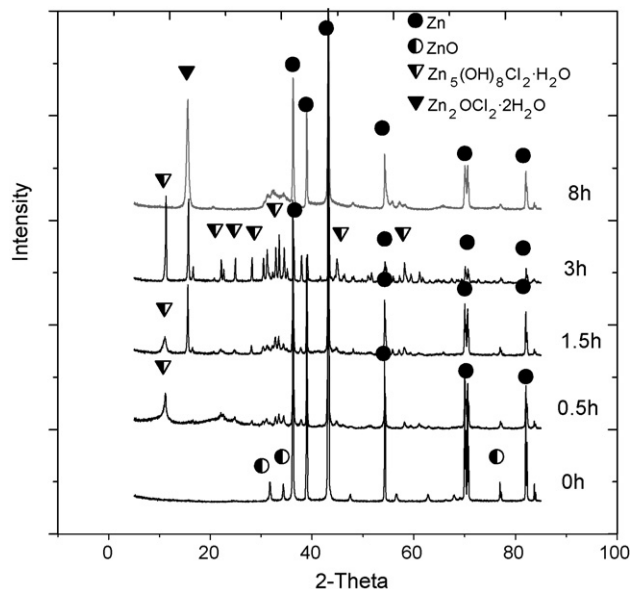


Fig. 3. XRD patterns of the PVDC/Zn mixture milled for different times (Zn/Cl molar ratio 2:1).

Fig. 4 shows the XRD patterns of the milled mixtures of PVC/Zn, in which the pattern of PVDC/Zn mixture milled in the same condition is shown to conveniently compare the structure of inorganic product in these two systems. The main inorganic product is $Zn_2OCl_2 \cdot 2H_2O$ too, as that in PVDC system.

It can be clearly seen that, after milling, the compounds of $Zn_2OCl_2 \cdot 2H_2O$ and $Zn_5(OH)_8Cl_2 \cdot H_2O$ was formed, by the reaction of Zn and Cl removed from PVC/PVDC.

3.3. Organic products

Fig. 5 shows the IR spectra of the milled mixture of PVDC/Zn, the leaching residue and original PVDC. It is evident that the spectrum of the milled mixture is different from that of original PVDC. The absorption bands of C–Cl stretch

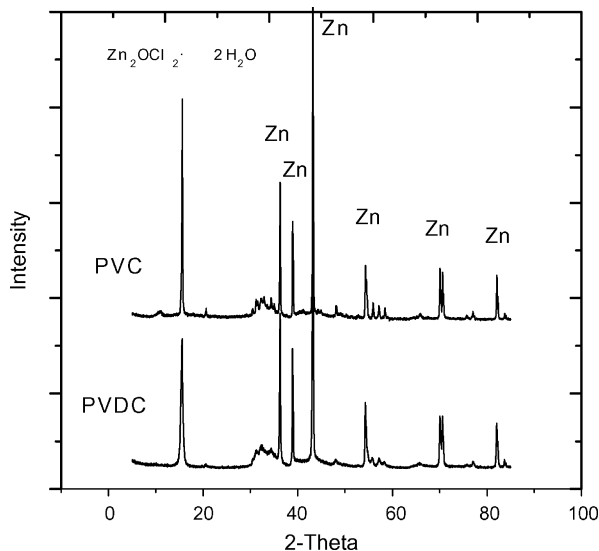


Fig. 4. XRD patterns of PVC/PVDC and Zn mixture milled for 8 h, respectively (Zn/Cl molar ratio 2:1).

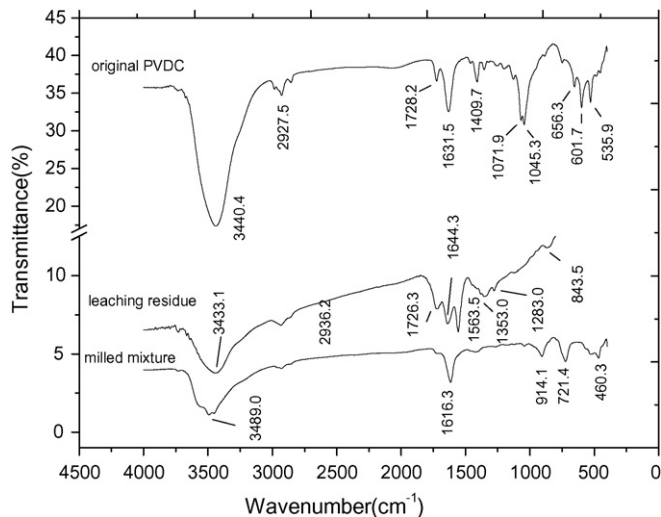


Fig. 5. IR spectra of PVDC, PVDC/Zn milled mixture and its leaching residue (Zn/Cl molar ratio 2:1, milling time 3 h).

vibration at 535.9 , 601.7 , and 656.3 cm^{-1} , and C–C at 1043 and 1087 cm^{-1} in PVDC cannot be discerned. A very strong absorption band appears at 1616.3 cm^{-1} , which is assigned to C=C stretch vibration absorption, resulted from the conjugative or cumulated C=C bonds of the dechlorinated product of PVDC. The mediate absorption bands appear at 914.1 , 721.4 , and 460.3 cm^{-1} attribute to O–H, Cl–Zn, and Zn–O in $Zn_5(OH)_8Cl_2 \cdot H_2O$ and Zn–O in $Zn_2OCl_2 \cdot 2H_2O$, respectively.

It can also be found that the spectrum of the leaching residue is different from that of the mixture and original PVDC. In the spectrum of the leaching residue, absorption bands of inorganic products such as 460.3 , 721.4 , and 914.1 cm^{-1} disappeared. A new C=O stretching vibration band appear at 1726.3 cm^{-1} , C–O–C stretching vibration appear at 1283.0 cm^{-1} , and bending vibration of =C–H appear at 843.5 cm^{-1} , while C=C conjugative double bond absorption band shift to a lower wave number at 1563.5 cm^{-1} and a higher wave number at 1644.3 cm^{-1} .

Fig. 6 shows the IR spectra of the milled mixture of PVC/Zn, the leaching residue and the original PVC. From

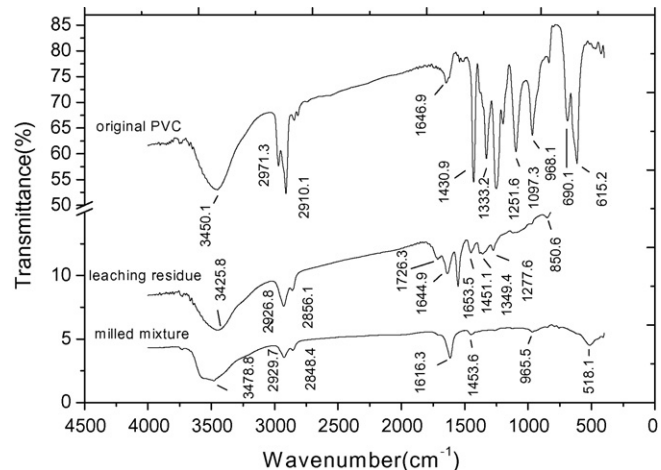


Fig. 6. IR spectra of PVC, PVC/Zn milled mixture and its leaching residue (Zn/Cl molar ratio 2:1, milling time 8 h).

the spectra, it can be seen that the spectrum of the mixture, the leaching residue, and original PVC is very different from each other. Firstly, in the spectrum of the mixture, absorption bands of C–Cl stretch vibration at 615.2, 690.1 cm^{-1} , and C–H at 1251.6 cm^{-1} in original PVC cannot be discerned, and very strong absorption bands of CH_2 – at 1430.9, 2910.1 cm^{-1} in original PVC become very weak. A new strong absorption band appears at 1616.3 cm^{-1} which can be assigned to C=C stretch vibration absorption, resulted from the conjugative or cumulated C=C bonds of the dechlorinated product of PVC. The mediate absorption bands appear at 965.5 and 518.1 cm^{-1} attribute to O–H, Cl–Zn/Zn–O in $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ and Zn–O in $\text{Zn}_2\text{OCl}_2 \cdot 2\text{H}_2\text{O}$, respectively. Also, the absorption bands of inorganic products such as O–H, Zn–O bands at 965.5 and 518.1 cm^{-1} in the spectrum of the milled mixture disappear in the spectrum of the leaching residue. The new C=O stretching vibration band appears at 1726.3 cm^{-1} , C–O–C stretching vibration appears at 1277.6 cm^{-1} , and bending vibration of =C–H appears at 850.6 cm^{-1} , while C=C conjugative double bond absorption bands shift to a lower wave number at 1563.5 cm^{-1} and a higher wave number at 1644.9 cm^{-1} . Additional band at 3425.8 cm^{-1} can be assigned to H_2O .

Comparing Fig. 6 with Fig. 5, we can find that the strong C=C absorption band at 1616.3 cm^{-1} appears either in Figs. 5 and 6, this suggests that the dechlorinated products of PVDC and PVC contain many C=C structure. Furthermore, the absorption band at 2929.7 cm^{-1} , which attributes to C–H stretch vibration absorption in Fig. 6 is stronger than that in Fig. 5, shows that there exists more $-\text{CH}_2-$ in the dechlorinated product of PVC than that of PVDC.

Fig. 7 shows the GC–MS spectra of the acetone extracts from PVC/Zn milled mixture. In the spectra, the peaks assign to diacetone alcohol, dodecanoic acid, tetradecanoic acid, diisobutyl ester, and *n*-hexadecanoic acid in turn according to increasing retention time. The main products in acetone extracts are series of fatty acids, additionally, a little cricoid compound is also found. The fatty acids may be resulted from the oxidation of PVC/PVDC during the process of dechlorination, while the formation of cricoid compound shows that a little PVC/PVDC chain is cyclized in the dechlorination process.

Fig. 8 shows the Raman spectrum of 3 h milled mixture of PVDC/Zn. There are three strong bands in the spectrum, the line at 3065.9 cm^{-1} is due to =C–H stretching vibration, 1560.8 cm^{-1} can be attributed to C=C stretching vibration, and 1366.5 cm^{-1} is due to C–H or C–C single bond. In addition, several weak bands can be found in the spectrum, 2709.7 and 2612.8 cm^{-1} can be assigned to C–H single bond, 2413 cm^{-1} and 2000.5 cm^{-1} may be due to C≡C triple bond and C=C cumulated double bond, respectively [8–10], while 844.3 cm^{-1} may be due to C–H bond in =C–H structure, respectively.

Fig. 9 shows the Raman spectra for the residue of 3 h-milled mixture of PVDC/Zn (Zn/Cl molar ratio 2:1). There are three broad bands, two strong bands and one weak band. The strong band at 1354.1 cm^{-1} is due to C–C or C–H single bond and 1566.8 cm^{-1} is due to C=C double bond, and the weak band at 900.1 cm^{-1} is due to =C–H bending vibration.

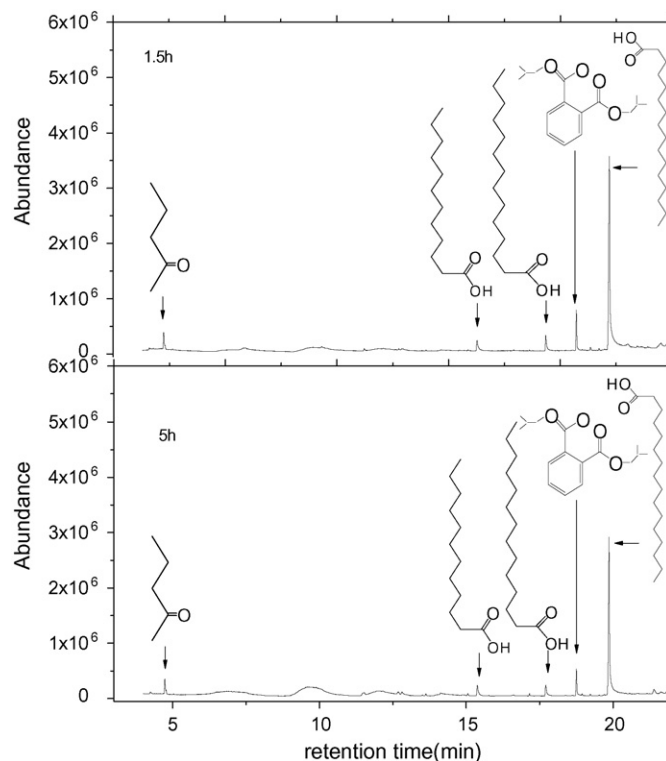


Fig. 7. GC–MS spectra of the acetone extracts from PVC/Zn mixture milled for different time (Zn/Cl molar ratio 4:1).

Fig. 10 shows the IR spectra of the PVDC/Zn mixture after 5 h milled and the leaching residue (Zn/Cl molar ratio is 1:1). It can be found that the IR spectrum of the mixture exhibits the same feature as that of the milled mixture of Zn/Cl 2:1. But the spectrum of the leaching residue is different from that of Zn/Cl 2:1. There is only one absorption bands at 1384.4 cm^{-1} which is attributed to C–C, besides the absorption bands of H_2O at 1638.7 and 3443.2 cm^{-1} .

The solid state ^{13}C NMR spectra of 5 h milled PVDC/Zn mixture and the leaching residue (Zn/Cl molar ratio 1:1) is shown in Fig. 11. It can be observed that there are two more resonance

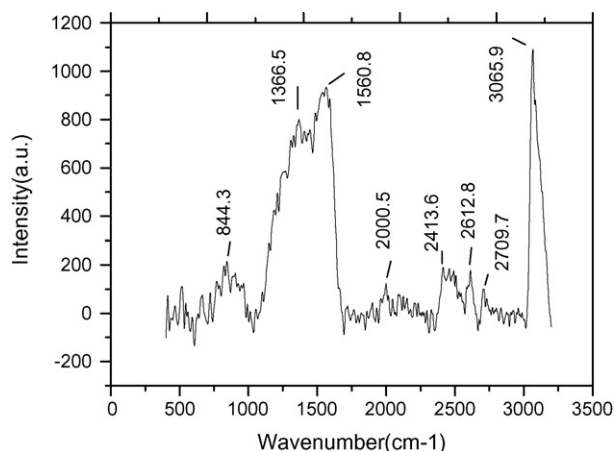


Fig. 8. Raman spectrum of PVDC/Zn mixture after 3 h milled (Zn/Cl molar ratio 2:1).

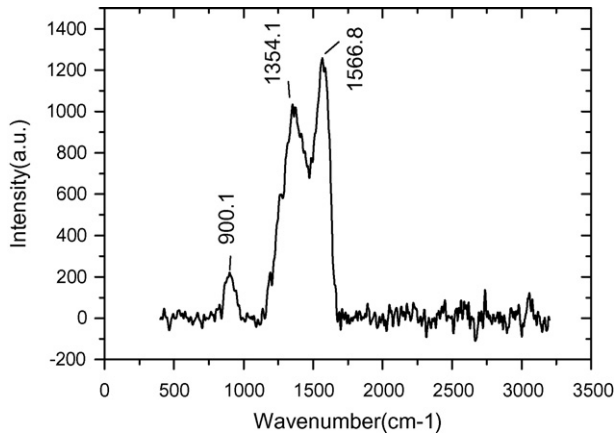


Fig. 9. Raman spectrum of the leaching residue for milled PVDC/Zn mixture (Zn/Cl molar ratio 2:1, milling time 3 h).

lines in the spectrum of the milled mixture than that of the leaching residue, one is at 152.3 ppm, attributed to C=C comulene double bond [11], the other is at 218.1 ppm, attributed to C=O. The strong peak at 131.1 ppm, is due to C=C; while the peak at 31.2 ppm is due to C–C.

Fig. 12 shows the Raman spectrum of the residue of 5 h milled PVDC/Zn mixture (Zn/Cl molar ratio 1:1). From the spectrum, it can be observed that a strong luminescent background. There are only two peaks in the spectrum, one is at 1359.5 cm⁻¹, and the other is at 1582.5 cm⁻¹. This resembles that of diamond-like carbon, which is also called hydrogenated amorphous carbon.

It can be deduced that the mechano-chemical dechlorinated products of PVC/PVDC include diamond-like carbon, carbyne fragment, polyacetylene in the milled mixture, while diamond-like carbon and polyacetylene in the leaching residue. But when Zn/Cl molar ration reaches to 1:1, dechlorinated products are mainly diamond-like carbon and a little carbyne debris in milled mixture, while only diamond-like carbon remained in the leaching residue.

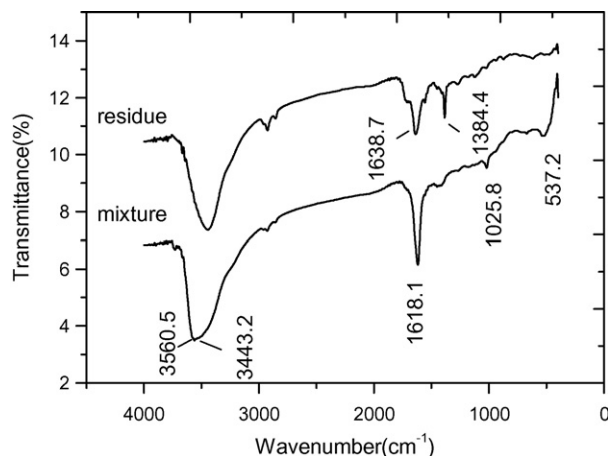


Fig. 10. IR spectra of the milled PVDC/Zn mixture and its residue (Zn/Cl molar ratio 1:1, milling time 5 h).

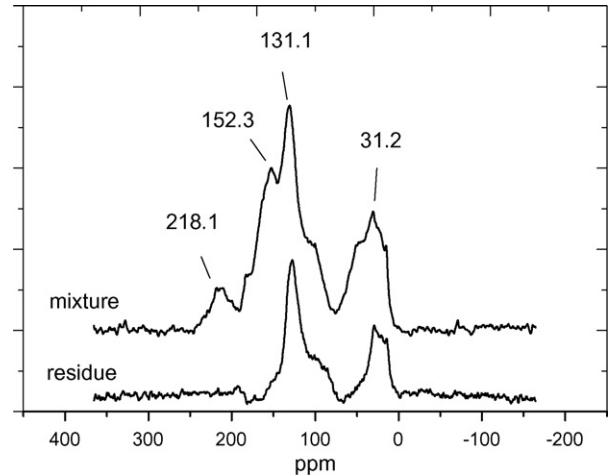


Fig. 11. Solid-state ¹³C NMR spectra of the milled PVDC/Zn mixture and its residue (Zn/Cl molar ratio 1:1, milling time 5 h).

4. Discussions

4.1. The mechano-chemical dechlorination reaction path

Although the mechanism of dechlorination of PVC/PVDC is not well understood, many researchers believe that the free radical theory is reasonable, and Volker Birke et al. has detected free radicals in the milled samples [4,12,13]. In the milling process, metal can easily form free radical under the effect of impact, compressive, and shear forces caused by the milling ball [12]. Therefore, we believe the mechanism of dechlorination of PVC/PVDC with zinc powder as reductive agent should be in accordance with the free radical theory.

From the products analysis (Sections 3.2 and 3.3), it is found that during the mechano-chemical process, Cl atom is split off from the main chain of PVC/PVDC, at the same time, and a part of H break away from the chain, and the backbone of PVC/PVDC was partly scissored [14]. The possible dechlorination paths of PVC/PVDC are displayed in Fig. 13 (only PVDC is shown). During the milling process, PVC/PVDC can be

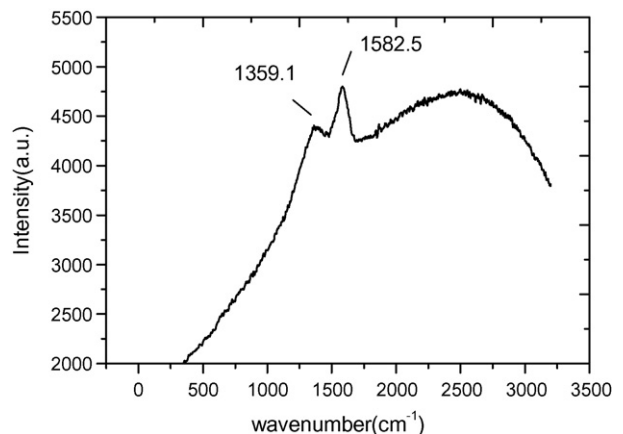


Fig. 12. Raman spectrum of the residue for milled PVDC/Zn mixture (Zn/Cl molar ratio 1:1, milling time 5 h).

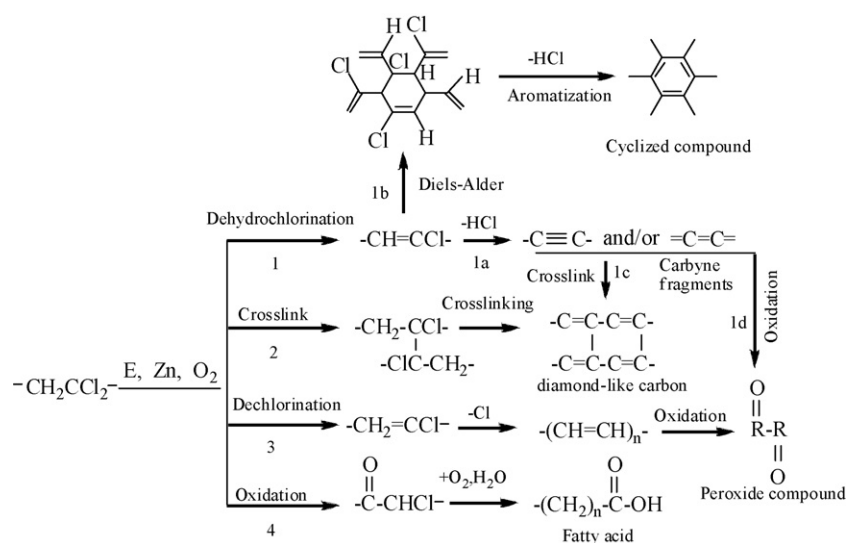


Fig. 13. The mechano-chemical dechlorination path of PVDC.

dechlorinated following the paths of dechlorination, crosslink, dehydrochlorination and oxidation. Diamond-like carbon is the main dechlorinated product of PVC/PVDC, formed by the path of PVC/PVDC chain crosslinking (Path 2) or carbyne fragments crosslinking (Path 1c). The formation of cyclized compounds is through the Diels–Alder action (Path 1b) [12], and the fatty acid and ester are through oxidation reaction [15]. Through the path of dehydrochlorination, carbyne fragment, and polyacetylene formed, part or all of which is further oxidized into peroxide compound [16–18].

4.2. The formation of carbene

Chemical or electrochemical reduction dechlorination of PVC/PVDC is the effective method to obtain carbene carbon [8–11,19–23]. But it must be performed in toxic liquid environment and special strong reductive agents, such as alkali metal amalgam. Moreover, the dechlorination cannot be completed. Since the mechanism of these methods is that the Cl and H are split off from the backbone of PVC/PVDC in the assist of reductive agent, zinc powder is an effective reductive agent for dechlorination of chlorinated ethylene in aqueous solution, and its reactivity can be greatly strengthened by the milling, so we can expect that chemical or electrochemical process can be performed by mechano-chemical process, using zinc powder as reductive agent.

In fact, it can be clearly found that the carbene fragments have formed during the dechlorination process of PVC/PVDC by milling with zinc powder, for examples, in the PVDC/Zn mixture after 3 h milled with Zn/Cl molar ration 2:1 (Fig. 6) and after 5 h milled with Zn/Cl molar ration 1:1 (Fig. 11), although the carbene is not much and pure enough to be separated effectively. Because the carbene fragment is unstable, when washed by diluted nitric acid, part or all of which crosslinks into diamond-like carbon or is oxidized into peroxide compounds and fatty acid etc. [10,15,17], without the protection of remained zinc

powder, $\text{Zn}_2\text{OCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$. Therefore, only diamond-like carbon remains in the residue.

It has been discussed in the above section (Section 4.1), carbene can form through the path of dehydrochlorination (Path 1a), crosslink into diamond-like carbon (Path 1c) and be oxidized into peroxide compounds (Path 1d). Therefore, if the mechano-chemical process is performed in the appropriate condition, such as low milling temperature, the reductive atmosphere, and keeping PVC/PVDC separated from each other, the mechano-chemical dechlorination process of PVC/PVDC may be an effective process for carbene preparing.

5. Conclusions

The Cl atom can be effectively removed from PVC/PVDC by mechanical milling with zinc powder. The dechlorination ratio is improved as the Zn/Cl molar ratio increases, and the dechlorination rate of PVDC is faster than that of PVC.

Zn reacts with Cl split from PVC/PVDC to form $\text{Zn}_2\text{OCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ compounds. The mechano-chemical dechlorinated products of PVC/PVDC include diamond-like carbon, carbene fragment, polyacetylene in the milled mixture, while diamond-like carbon and polyacetylene in the leaching residue. When Zn/Cl molar ration is 1:1, the dechlorinated products are mainly diamond-like carbon and a little carbene fragment in milled mixture, while only diamond-like carbon remained in the residue.

PVC/PVDC can be dechlorinated following the paths of dechlorination, crosslink, dehydrochlorination, and oxidation. Through the path of dehydrochlorination, carbene fragment, and polyacetylene have been formed. If the mechano-chemical process is performed in the appropriate condition, the mechano-chemical dechlorination process of PVC/PVDC may be an effective approach for carbene synthesizing.

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