Study on Characterization of Pyrolysis and Hydrolysis Products of Poly(vinyl chloride) Waste

Jun Lu,[1] Shibai Ma,[1] Jinsheng Gao,[1] Jair C. C. Freitas,[2] Tito J. Bonagamba[3]

[1]*Department of Chemical Engineering for Energy Resources, East China University of Science and Technology, Shanghai 200237, China*
[2]*Departamento de Física, Universidade Federal do Espírito Santo, 29060-900 Vitória, ES, Brazil*
[3]*Instituto de Física de São Carlos, Universidade de São Paulo, P. O. Box 369, 13560-970, São Carlos, SP, Brazil*

ABSTRACT: Poly(vinyl chloride) PVC pyrolysis and hydrolysis are conducted in a fixed bed reactor and in an autoclave, respectively, under different operating conditions such as the temperature and time. The product distribution is studied. For the PVC pyrolysis process, the main gas product is HCl (55% at 340°C), there is 9% hydrocarbon gas (C_1–C_5), the liquid product fraction is about 5% (at 340°C), and the solid residue fraction is about 31% (at 340°C). For the hydrolysis process, the main gas product is HCl (55.8% at 240°C) and the solid residue is about 49.6% (at 240°C). The pyrolysis liquid product is analyzed by using gas chromatography with magic-angle spinning. Aromatic hydrocarbons are the main class (90%), of which the major part is benzene (33%). The residue produced through pyrolysis and hydrolysis is investigated by high-resolution solid-state ^{13}C-NMR. These details revealed by the high-field NMR spectra provide important information about the chemical changes in the PVC pyrolysis and hydrolysis process. The mechanism of PVC hydrolysis dechlorination is also discussed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3252–3259, 2003

Key words: poly(vinyl chloride); pyrolysis; hydrolysis; NMR

INTRODUCTION

The disposal of waste plastics has been recognized as a major environmental problem. The conventional solution of landfilling is becoming too expensive and direct incineration is undesirable because of increased greenhouse gas emission, primarily CO_2 and other toxic pollutants.[1,2] Recycling should be the best alternative to landfilling because it is the most environmentally friendly method. Unfortunately, the diversity of the nature of wastes makes it difficult to find a universal treatment approach for them. Another possibility is pyrolysis, which is especially appropriate for thermoset composites that cannot be remolded. In the pyrolysis process, the organic part of the material is decomposed to low molecular weight products (liquids or gases), which are useful as fuel or a chemical source; whereas the inorganic components, such as fiberglass and $CaCO_3$, remain unmodified and therefore can be recycled into other composites or any other plastic materials.[3] In the chemical recycling of waste plastics, poly(vinyl chloride) (PVC) materials cause various problems. At higher decomposition tempera-tures, the main chain decomposition of the PVC proceeds to yield a char and aromatic compounds, leading to the formation of undesirable materials.[4]

Supercritical water has been used for the decomposition of plastics to recover low molecular weight products.[5] Studies of the dechlorination of PVC in water under high pressure and high temperature conditions have been reported.[6,7] However, such hydrolysis processes are almost always carried out in an organic solvent, such as methanol and THF. This causes the problem of recycling of the organic solvent and generates a secondary pollution.

In previous work,[8,9] low temperature pyrolysis and pressurized hydrolysis of PVC were reported. The present article is concerned with the identification and quantitative determination of the pyrolysis and hydrolysis products of PVC.

EXPERIMENTAL

The commercial PVC (38.4% C, 4.8% H, 56.8% Cl) used in this study was additive free and supplied by Shanghai Chlorine and Soda Factory in a powder (M_w = 38,000) form; the ground particle size is 0.12–0.14 mm. The pyrolysis experiments were performed by heating a vessel containing approximately 5 g of the PVC sample in a quartz tube inside a furnace in a stream of nitrogen (40 mL/min).[8] The furnace was heated at 25°C/min to the desired temperature. This temperature was held for dif-

TABLE I
Mass Balance of PVC Pyrolysis at 180–340°C (wt %)

Products	Pyrolysis Temperature (°C)					
	180	200	220	260	280	340
Liquid	—	0.41	3.91	3.32	2.88	3.43
Gas	0.97	11.69	48.53	57.77	61.55	66.09
Solid residue	98.9	85.74	48.66	36.94	35.61	31.58
Total	99.87	97.84	101.1	98.03	100.04	101.1

ferent residence times, and thereafter the sample was cooled under nitrogen and weighed. The hydrogen chloride evolved from the pyrolysis of PVC was trapped in a flask containing an aqueous solution of NaOH. The products were classified into three groups: liquid products, which are condensable at ice-water temperature; gaseous products; and residue, which refers to both carbonaceous species and waxy compounds. The hydrogen chloride trapped in the NaOH solution was analyzed by chemical titration, and the amount of chlorine in the liquid products and residue was analyzed by Schoniger's[10] method.

The PVC hydrolysis reaction was carried out in a 1000-mL stainless autoclave equipped with a stirrer.[9] The PVC (5 g) and 200 mL of 2–10 wt % NaOH solution were placed in the reactor, and the autoclave was heated from room temperature to the desired temperature at a heating rate of 20°C/min and held for the reaction time with continuous stirring. The reaction temperatures were 120–260°C, the reaction time was 0.5–4 h, and the initial pressure was 3.0 MPa. After the desired reaction time, the reactor was then cooled to room temperature, the reaction mixture was filtered, and the residue was washed thoroughly with distilled water to eliminate all traces of alkali. Then, the residue was dried well and stored under a vacuum at 80°C. The amount of HCl evolved was established after various residence times by titration and the amount of chlorine in the residue was analyzed by Schoniger's[10] method. The extent of dechlorination (% conversion) was calculated from the ratio of HCl evolved to the amount available in the polymer. The HCl yield (%) was found as

$$(w_{Cl,t}/w_{Cl,0}) \times 100$$

and the residue yield (%) as

$$(w_t/w_0) \times 100$$

where $w_{Cl,t}$ is the quantity of Cl^- in the filtered solution; $w_{Cl,0}$ is the quantity of Cl in the PVC sample; and w_0 and w_t are the quantities of the sample before and after the reaction, respectively.

The gases collected in the experiments were analyzed off-line. Hydrocarbons including methane, ethane, ethene, propane, propene, butane, and butene were analyzed using gas chromatography (GC; GC-9A, Shimazdu). The liquid product of the PVC pyrolysis was analyzed by GC mass spectrometry (GC–MS) instrument (Shimazdu). The functional groups of the residue were analyzed by Fourier transform IR (FTIR), and the FTIR transmission spectra were obtained on a Nicolet 5SXC spectrometer by casting onto KBr disks. Sixty-four scans were coadded at 4 cm^{-1} resolution, and the residue's surface was observed by using scanning electron microscopy (SEM). The residue of PVC dechlorination was scanned by with CDS-2000 Bio-Rad FTS-165 pyrolysis FTIR combination instruments at an interval of 120 s.

NMR measurements

The ^{13}C-NMR spectra were recorded using a Varian INOVA 400 spectrometer operating at 100.5 MHz (magnetic field = 9.4 T). The experiments were realized with cross-polarization (CP), dipolar decoupling (DD), and magic-angle spinning (MAS) using silicon nitride rotors spinning at a frequency of about 5.0–6.0 kHz. These measurements were performed with a proton $\pi/2$ pulse of 4.6 μs, a contact time of 1 ms, and a recycle delay of 3.0 s. About 2000 transients were recorded and an exponential broadening of 50 Hz was applied to the free induction decays before Fourier transform. Some measurements were performed with interrupted decoupling (ID) for comparison.[11] In these measurements a 30–50 μs interval, during which the decoupling field was turned off, was introduced before the acquisition. The MAS speeds used in all the experiments were not high enough to completely eliminate the spinning side bands in the CP and DD spectra of the carbonized samples. However, the existence of such side bands do not preclude the qualitative analysis presented here, because in most cases they are readily distinguishable and can be easily deconvoluted from the "true" NMR lines. In addition, a sufficiently broad spectral width (50 kHz) was used in all measurements in order to avoid the folding of high order spinning side bands. The chemical shifts (ppm) were externally referred to tetramethylsilane, using adamantane for setting the reference frequency.
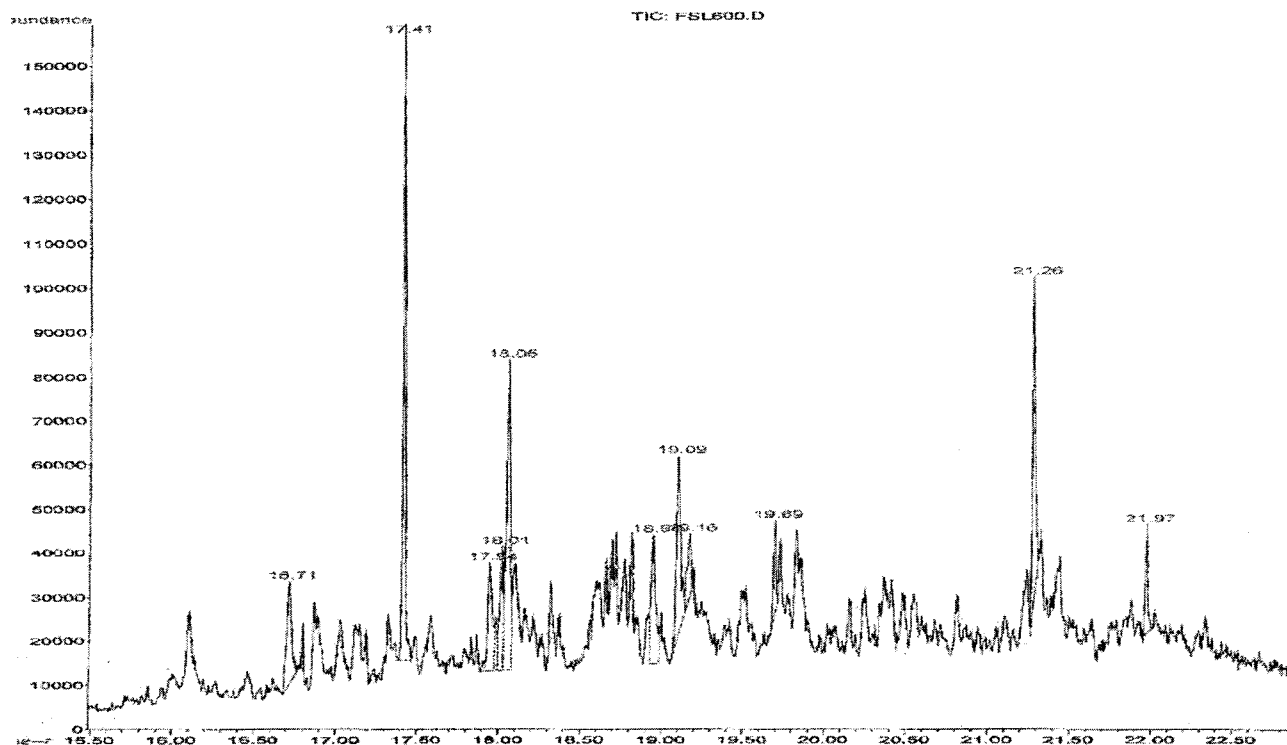
Figure 1 The magnified total ion chromatogram of the oil derived from the pyrolysis of PVC.

RESULTS AND DISCUSSION

Analysis of pyrolysis products

Table I presents the material balance of the products obtained through the pyrolysis up to 340°C. The yields of liquid and gas products increase and the solid residues decrease with the increasing of the pyrolysis temperature. Apart from HCl, the gas products comprise CH_4 (5.7%), C_2H_4 (1.5%), C_2H_6 (1.8%), C_3H_6 (0.3%), and C_3H_8 (0.7%).

The pyrolysis of PVC is initiated by a dechlorination reaction resulting in the formation of hydrogen chloride. The elimination of the chlorine atom from the structure results in the formation of a double bond in addition to hydrogen chloride. Further double bonds are formed as more hydrogen chloride is evolved from the resultant chain. Eventually the chain undergoes cyclization to yield aromatic and alkyl-aromatic compounds. The total ion chromatogram of the oil derived from the pyrolysis of PVC is presented in Figure 1 and the compositions of the liquid fractions collected during the pyrolysis of PVC are presented in Table II. From Figure 1 and Table II it can be seen that benzene was identified as the main fraction of PVC pyrolysis oils (32.55%); naphthalene and other polycyclic aromatic hydrocarbons were also identified.

The elemental analysis and H/C atomic ratios of the pyrolysis residues are presented in Table III. The chlorine content decreases markedly after the reaction and the carbon content of the residue is more than the original polymer; consequently, it has a lower H/C atomic ratio (0.82), which indicates that the organic matter left at >240°C is more unsaturation than the original PVC (Table IV). About 90% of the chlorine contained in PVC became gaseous HCl. The C—Cl bond in the PVC structure has a lower bond energy than other bonds, and upon heating it has a tendency to break first.

TABLE II
Composition of Liquid Fraction Collected During Pyrolysis of PVC

Compounds	wt %
Benzene	32.55
Toluene	21.77
Naphthalene	12.97
Phenanthrene	22.26
Others	10.45
Total	100

TABLE III
Elemental Analysis of PVC and Its Pyrolysis Residues

	C (%)	H (%)	CI (%)	Total (%)	H/C
Raw material	38.4	4.8	56.8	100.0	1.50
Solid residue					
240°C	79.55	5.3	12.45	97.3	0.80
260°C	83.34	5.8	9.56	98.7	0.83
340°C	91.2	6.2	4.13	101.53	0.82

TABLE IV
Reactor Pressures at Different Temperature.

T (°C)	Pressure (MPa)
140	4.5
160	5.0
180	5.5
200	7.0
220	9.0
240	10.0
260	12.0

TABLE VI
Elemental Analysis of PVC Hydrolysis Residues
(2%NaOH, 2 h)

	PVC	160°C	180°C	200°C	240°C	260°C
C	38.4	38.36	45.69	63.11	72.92	73.13
H	4.8	3.63	4.10	4.53	5.29	5.36
CI	56.74	49.88	35.86	16.90	4.25	3.71
H/C	1.5	1.13	1.08	0.86	0.87	0.88
O (diff)	—	8.13	14.35	14.46	17.54	17.80

Table V presents the material balance of the products obtained through the pyrolysis up to 240°C. As can be seen, apart from HCl as the major product (55.8%), another major product is the solid residue (49.58%).

Hydrolysis dechlorination of PVC in the solution phase in the presence of bases was evidenced by a change in the color of the reaction mixture. When the mass loss due to dechlorination reaches 0.1%, the color of PVC starts to change. Depending on the number of conjugated double bonds formed, which are attributable to elimination of HCl, it becomes yellow, orange, red, brown, or black. The extent of dechlorination can be determined by elemental analysis of the PVC residues (Table VI).

Although the content of Cl decreases with the reaction temperature increase, the content of H is not decreased accordingly because of side reactions. The typical side reaction during chlorine elimination is the substitution reaction. In the case of PVC hydrolysis, the replacement of the chlorine atom by the base should be considered. A strong nucleophilic solvent such as water and a low base concentration support this side reaction.

The elemental analysis results also prove the incorporation of oxygen into the molecules.

Table VI shows that the content of oxygen can reach to about 8–17%. With the increasing reaction temperature, the content of C and O in the residue increase, the ratio of H/C decreases gradually, and the degree of unsaturation increases. It can be concluded that the hydrolysis reaction of PVC includes the cracking of the C—Cl bond and substitution of Cl with hydroxyl. Between 240 and 260°C, there may be small reactions (both dechlorination and substitution with OH^-) as

was evidenced by the relatively small changes in the elemental composition. About 3 wt % Cl remained in the hydrolysis residue; we thought that some Cl atoms inside the PVC particles did not take part in the reaction because of its unapproachability.

Comparison of PVC pyrolysis and hydrolysis process

Figure 2 shows the conversion of the chlorine of PVC in pyrolysis and hydrolysis process. It can be seen that at 240°C, the chlorine conversion can reach 95% in hydrolysis process and the chlorine conversion can only reach 80% in the pyrolysis process. Under the same reaction temperature conditions, the PVC hydrolysis process had a higher dechlorination efficiency than the pyrolysis process.

FTIR and SEM analysis of pyrolysis and hydrolysis products

Figure 3(a) shows the functional-group compositional analysis of PVC pyrolysis residue as analyzed by FTIR spectrometry. From Figure 3(b) it can be seen that in the residue exist aliphatic groups of CH (2957 and 2927 cm^{-1}), CH$_3$ (1375 cm^{-1}), and CH$_2$ (1450 cm^{-1}). The C=C absorbance peak at 1625 cm^{-1} confirms that

TABLE V
Mass Balance of PVC Hydrolysis Product
(8%NaOH, 2 h)

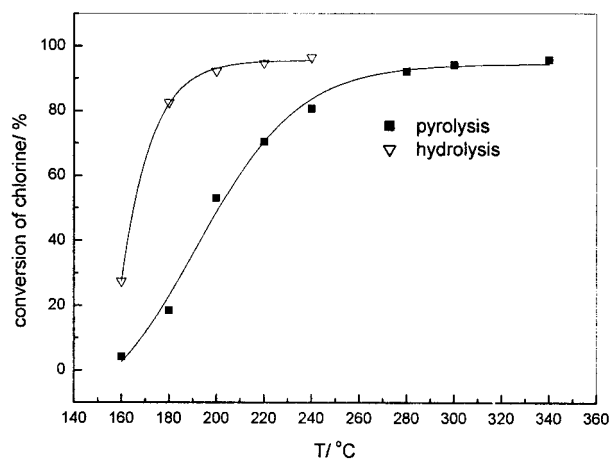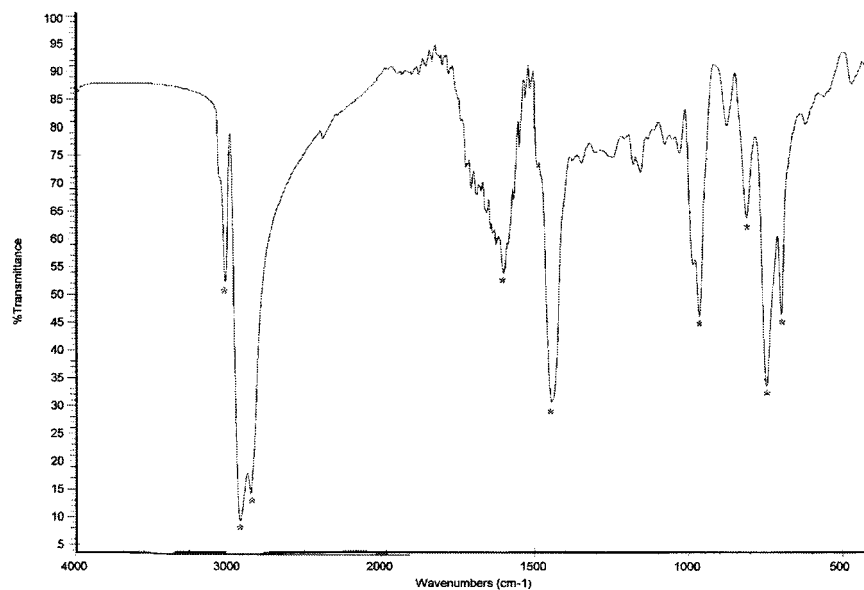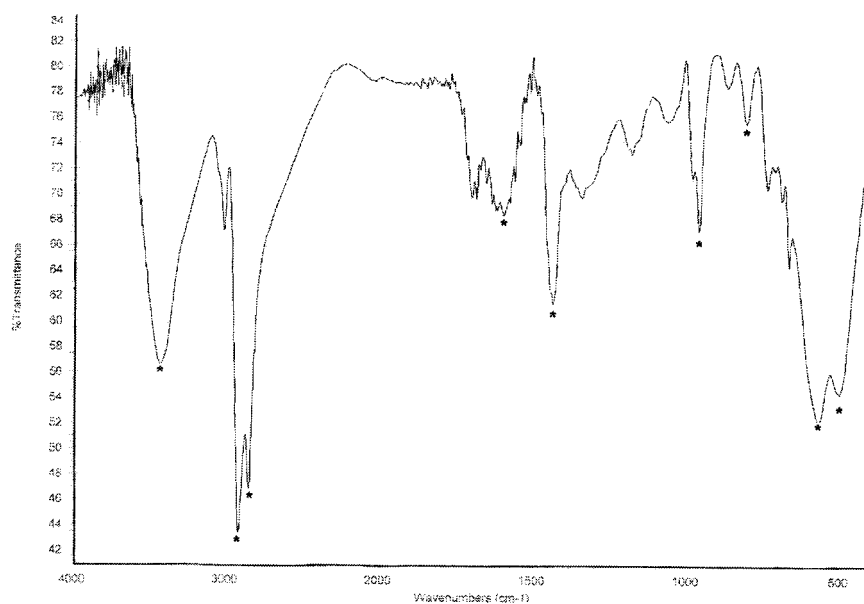| Temp. (°C)	HCl Yield (wt %)	Residue Yield (wt %)	Total (%)
180	46.18	54.36	100.54
200	53.90	50.21	104.11
240	55.80	49.58	105.38

**Figure 2** The conversion of the chlorine of PVC in various processes.

(a)

(b)

Figure 3 Fourier transform IR spectra of (a) the pyrolysis residue of PVC and (b) the hydrolysis residue of PVC.

alkene groups are present. The presence of peaks in the region from 1350 to 1500 cm^{-1}, which are due to the deformation vibrations of C—H bonds, confirm the presence of aliphatic groups. The peak located at 980 cm^{-1} represents CH stretching and deformation vibrations of alkene structures. The bands between 600 and 700 cm^{-1} can be attributed to C—Cl stretching vibrations. The spectra of the PVC pyrolysis residue shows that there are additional peaks in the region between 675–900 and 3000–3050 cm^{-1}. The presence of these peaks indicates the presence of aromatic structures.

Comparatively, in the spectrum of the PVC hydrolysis residue [Fig. 3(b)], the peaks at 3050 cm^{-1} indi-

cate the presence of =C—H stretching vibrations, which confirms the alkenes or aromatics. It is obvious that the main route of hydrolysis of PVC was dehydrochlorination in high temperature water at high pressure as in that of PVC in an N_2 atmosphere. The peaks at 3300 cm^{-1} show the presence of —OH, which confirms a side reaction such as the substitution of the —OH group that occurred in the PVC hydrolysis dechlorination reaction. The peaks between 1650 and 1850 cm^{-1} indicate the presence of stretching vibrations of C=O.

The SEM photographs in Figure 4 show a sectional view of the pyrolysis residue of PVC [Fig. 4(a)] and a
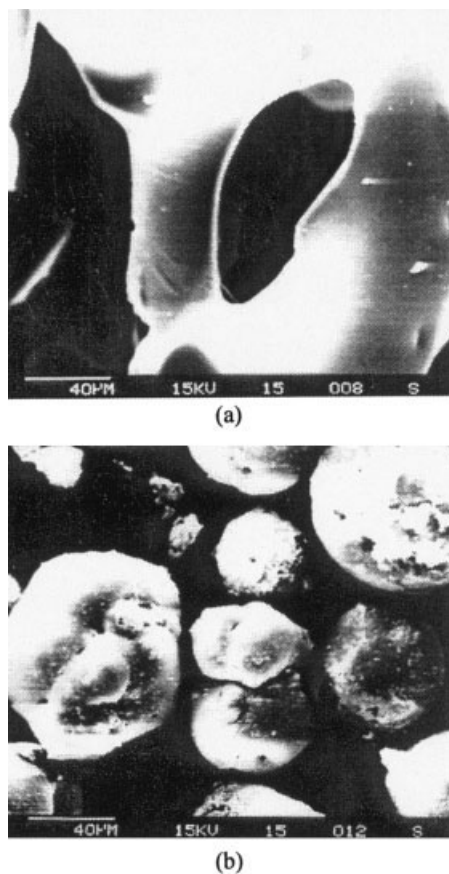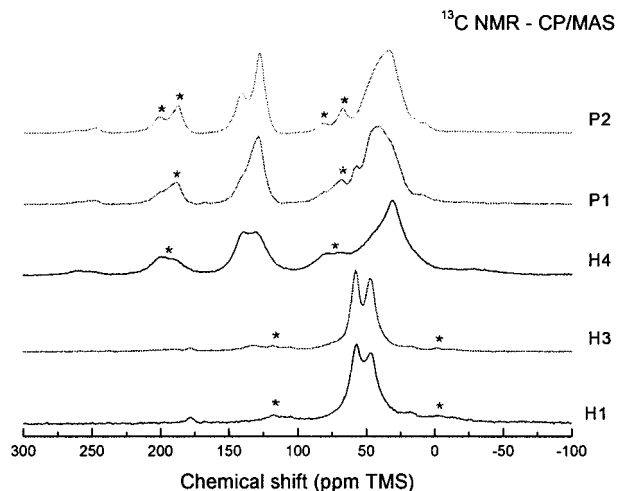
Figure 4 SEM photographs of (a) the residue of PVC pyrolysis at 300°C and (b) the residue of PVC hydrolysis at 240°C.

Figure 5 The ^{13}C/CP–MAS NMR spectra of the analyzed samples; (*) spinning side bands.

sectional view of the residue of granular PVC with a 95% degree of dehydrochlorination and treated in 4% NaOH at 240°C for 2 h [Fig. 4(a)]. Pores about 100 μm in size were observed inside the PVC pyrolysis residue. However, in the PVC hydrolysis residue, only 2–4 μm pores can be found. This may be due to the swelling effect of the hydrolysis residue and substitution of Cl with the —OH group on the polymer chain.

^{13}C-NMR analysis of pyrolysis and hydrolysis residues

The following conditions were used: H1, hydrolysis, 180°C for 2 h; H3, 200°C for 2 h; H4, 240°C for 2 h; P1, 280°C for 2 h; and P2, 340°C for 2 h. The spectra corresponding to samples H1 and H3 display the two peaks typical of the PVC structure: the peak at around 58 ppm is assigned to CHCl groups, whereas the one at 47 ppm is associated with CH$_2$ groups.[12,13,14] Both spectra also present spinning side bands (which are artifacts from the MAS process, appearing as satellite lines separated from the true NMR lines by the amount of Hertz equal to the spinning frequency[15]), which are identified in Figure 5. When examined on

an expanded scale (Figs. 6, 7), one can also observe the presence of other signals of lower intensity in the ^{13}C-NMR spectra of H1 and H3. In the spectrum of H1 one detects the presence of signals at 178 ppm for carboxyl groups and 17 ppm for methyl groups. In order to show that these are real NMR signals and not artifacts, we recorded an NMR spectrum for sample H1 with a different value for the spinning frequency. In Figure 6 the spectra acquired with spinning frequencies of 6.0 and 5.0 kHz (which correspond to 60 and 50 ppm, respectively) are compared. As can be clearly seen, the spinning side bands are shifted but the peaks at 178 and 17 ppm remain at the same chemical shift. For sample H3, Figure 7 shows that, in addition to the same peaks at 178 and 17 ppm, there is a broad and reasonably intense signal at 132 ppm that is associated with aromatic carbons, which indicates some degree of aromatization in this sample.
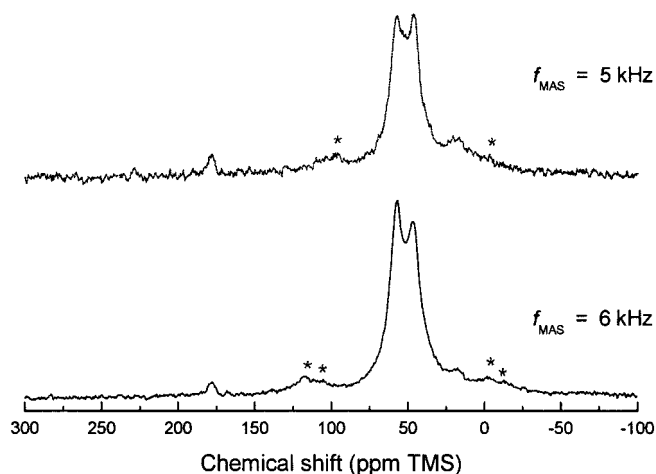
Figure 6 The ^{13}C/CP–MAS NMR spectra of sample H1 at two different MAS speeds.
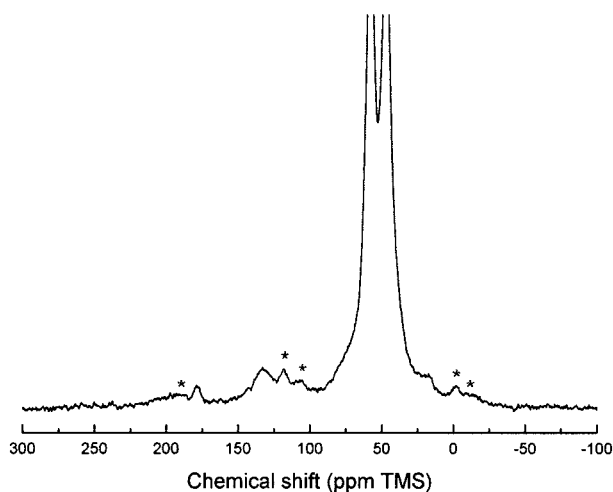
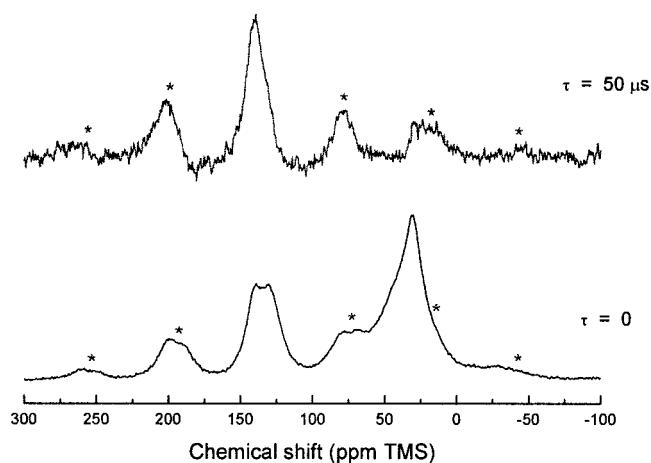**Figure 7** The ^{13}C/CP–MAS NMR spectra of sample H3.

For samples H4, P1, and P2, the spectra displayed in Figure 5 show that the original polymeric structure has been almost completely destroyed. Only for sample P1 can we observe a detectable signal at 57 ppm that is associated with the chlorinated carbons that are probably remaining from the vinyl chloride monomer. All these samples present two broad and intense bands in the 110–160 and 10–60 ppm regions, which are associated with aromatic lamellae and aliphatic chains, respectively. There are strong spinning side bands associated with the aromatic signals, which extend over a large chemical shift range and overlap with the aliphatic peaks, as is typical of aromatic structures.[14,15]

If we compare these results with those achieved for carbonized PVC samples,[14] we can note the similarity between the ^{13}C-NMR spectra of samples H4, P1, and P2 and the spectra achieved for samples with heat treatment temperatures in the range of 250–400°C. The splitting of the aromatic bands in two well-defined peaks, shown with clearness in the P2 sample but also visible in the H4 and P1 samples, is indicative of the presence of alkyl-substituted aromatic carbons. These are responsible for the peak at a higher chemical shift (140 ppm), whereas hydrogenated and internal aromatic carbons give rise to the most intense signal at a lower chemical shift. The exact position of this peak changes from sample to sample: 131.0, 128.5, and 127.4 ppm for H4, P1, and P2 samples, respectively. This slight monotonic decrease may suggest the occurrence of a progressive growth of the aromatic lamellae, leading to an increase in the diamagnetic susceptibility associated with these planes and consequently to a deshielding of the carbon nuclei.[16]

In order to distinguish the contribution from hydrogenated and nonhydrogenated groups in the ^{13}C-NMR spectra, some experiments were conducted with ID, varying the time (τ_D) during which the decoupling

field is turned off. With this procedure, the signals originating from more hydrogenated carbons have their intensity reduced faster than the ones from less hydrogenated groups, because of the strong dipolar interaction between ^{13}C and ^{1}H nuclei.[11] The comparison of normal CP spectra and ID/CP spectra is shown in Figures 6–8 for samples H4, P1, and P2, respectively. In all cases it the strong reduction in intensity of the aliphatic band is evident, which is expected as a consequence of the high degree of hydrogenation of the groups responsible for those resonances (mainly CH_3, CH_2, and CH groups). On the other hand, the aromatic signals display a slower reduction in intensity on increasing τ_D. However, the relative intensity of the two aromatic peaks is significantly changed in the ID spectra. In the H4 and P1 samples, where the peaks are poorly resolved in the normal CP spectra of Figure 5, the increase in τ_D leads to a shift of the center of gravity of the aromatic band toward the higher chemical shift side (Figs. 8, 9). This is caused by the progressive reduction of the signals originating from hydrogenated aromatic carbons, which appear at around 130–127 ppm, whereas the resonance due to alkyl-substituted aromatic carbons (around 140 ppm) is preserved because of the smaller dipolar interaction with protons. Figure 10 shows this effect in detail for the P2 sample. For a τ_D value of 30 μs, the relative intensity within the doublet is already inverted and the aliphatic band is present with reduced intensity; with a τ_D of 50 μs, there is only a shoulder at 132 ppm due to hydrogenated and/or interior aromatic carbons and a weak signal at 53 ppm due to aliphatic carbons (with a lower degree of hydrogenation). Naturally, the overall signal to noise ratio of this spectrum is severely reduced because of the pause introduced in the decoupling process.

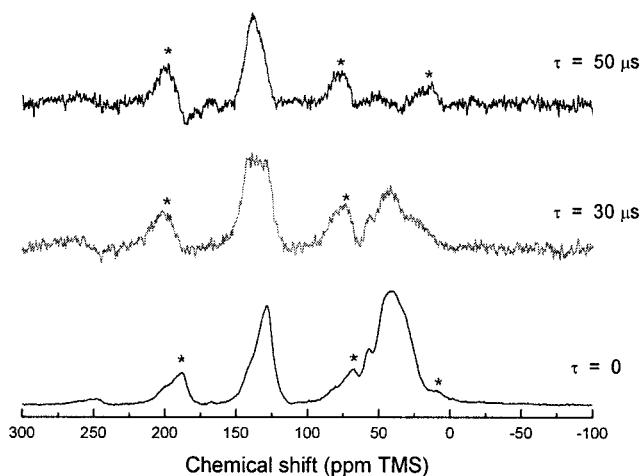The mechanism of the PVC hydrolysis dechlorination is shown schematically as

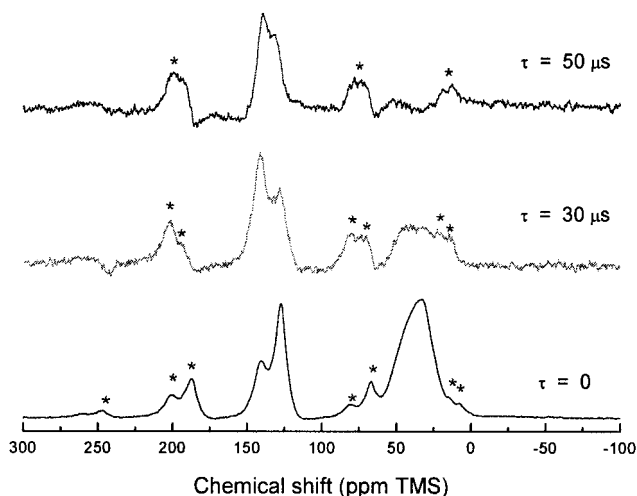**Figure 8** The ^{13}C/CP–MAS and ID/CP–MAS NMR spectra of sample H4.
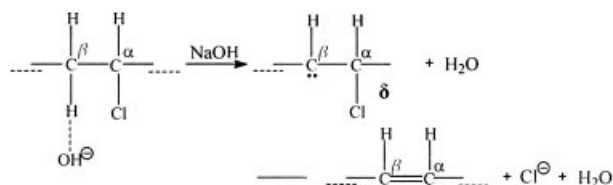
The OH$^-$ ion approaches the hydrogen atom of the β-carbon and forms H$^+$—OH$^-$ bonding. After the removal of the H$^+$ ion, a noncovalent odd pair of electrons takes the place of the hydrogen. The chlorine atom of the β-carbon become δ^- because of the "I effect," and the elimination of the Cl$^-$ ion takes place immediately and a double bond forms between the two carbons.

CONCLUSIONS

For the PVC pyrolysis process, the main gas products are HCl (55% at 340°C) and 9% hydrocarbon gas (C$_1$–C$_5$), the liquid product is about 5% (340°C), and the solid residue is about 31% (340°C). The pyrolysis liquid product was analyzed using GC–MS. We found that aromatic hydrocarbons are the main class (90%), of which the major part is benzene (33%). For the hydrolysis process, the main gas product is HCl (55.8% at 240°C) and the solid residue is about 49.6% (340°C). It can be seen from the elemental analysis and FTIR spectra of the PVC hydrolysis residue that side reactions such as a hydroxide radical substitution reaction occurred in the reaction. High-resolution solid-state ^{13}C-NMR was used to study the PVC pyrolysis and hydrolysis products. The high-field CP measure-

Figure 10 The ^{13}C/CP–MAS and ID/CP–MAS NMR spectra of sample P2.

ments revealed the details about the chemical changes during the stages of the PVC pyrolysis and hydrolysis processes. In the spectrum of PVC hydrolysis products, we detect the presence carboxyl groups and methyl groups. There are strong spinning side bands associated with the aromatic signals, which extend over a large chemical shift range and overlap with the aliphatic peaks, as is typical of aromatic structures.

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Figure 9 The ^{13}C/CP–MAS and ID/CP–MAS NMR spectra of sample P1.