



Article Dechlorination of Polyvinyl Chloride via Solvothermal Treatment with Glycerol

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Abstract: Solvothermal treatment using glycerol effectively removes chlorine from polyvinyl chloride (PVC). Additive-free PVC was dechlorinated by treatment with glycerol in an autoclave at 200–240 °C. Liquid glycerol was coexistent with a red powder after the reaction at 200 °C. At reaction temperatures of 220 and 240 °C, the liquid glycerol disappeared, and carbonization proceeded to form a black powder. In this reaction, the glycerol was directly converted into glycidol. Epichlorohydrin was also produced from the glycerol via 1,3-dichloro-2-propanol as an intermediate. The PVC was converted into the polyethylene oxide structure, following the generation of the polyene structure by zip-elimination. Finally, the converted PVC was resinified by an epoxidation reaction with the glycidol and epichlorohydrin. Thus, glycerol acted as a useful reaction medium for this reaction system. The analysis of the decomposition ratio and dechlorination yield showed that the PVC was solidified by resinification at 240 °C. The effects of the additives on dechlorination were investigated using commercially available PVC sheets. Elemental analysis showed that the calorific value of the solid product dechlorinated at 240 °C was found to be higher than that of standard bituminous coal.

Keywords: waste plastics; dechlorination; solvothermal treatment; glycerol; polyvinyl chloride

1. Introduction

Polyvinyl chloride (PVC) has been used in various fields, such as packaging materials, piping materials, agricultural films, and electric wires, because of its low cost and high performance [1]. Therefore, a large amount of waste, including PVC, is generated every year and requires disposal. Thermal recycling (pyrolysis, gasification, hydrogenation, etc.) and incineration are common waste treatment methods for PVC. Owing to the high chlorine content of PVC (56.8%), the incineration method requires an advanced facility for treating the exhaust gas, which contains large amounts of hydrogen chloride and trace amounts of harmful dioxins. When PVC is disposed of in landfills, phthalates and heavy metals contained in the plasticizers and stabilizers are leached, causing environmental problems. Therefore, a highly efficient method for dechlorinating PVC is required. Yu et al. [2] reviewed the recent advances in PVC pyrolysis. The dechlorination of PVC, which is affected by the characteristics of the PVC and its additives, mainly occurred in the temperature range of 250–320 °C [3]. The results of thermogravimetric analysis–mass spectrometry, the thermal decomposition of the PVC was found to be clearly divided into three stages, and dechlorination occurred mainly in the first and second stages [4,5]. Many methods



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). have been used to improve the efficiency of chlorine removal from PVC. Yuan et al. [6] used a gas–liquid fluidized bed to clarify the dechlorination behavior and reported that the chlorine removal ratio was greatly affected by the temperature; this method was able to remove up to 99.5% of the chlorine in 1 min. at 300 °C. Wu et al. [7] investigated the co-pyrolysis behavior of polyethylene, polyvinyl chloride, and polystyrene and reported that the chlorination of the PVC and the cyclization of the conjugated polyenes occurred simultaneously to produce dioxins. Hydrothermal treatments are widely used to generate energy from waste [8–10], in which supercritical water is employed as a useful reaction medium [11]. Endo and Emori [12] reported that chlorine was completely removed by hydrothermal treatment at 19.3 MPa at 300 °C. NaOH is often used to promote the dechlorination of PVC under mild conditions. Shin et al. [13] reported that the addition of NaOH reduced the hydrothermal treatment temperature from 300 °C to 150–250 °C. Dimethyl sulfoxide [14] and ethylene glycol [15] were added to further promote dechlorination with NaOH. However, in these methods, dechlorination was improved by the addition of an

organic solvent, but solvent recycling to reduce costs becomes an additional problem. Recently, it was reported that PVC was effectively dechlorinated by hydrothermal carbonization (HTC) [1]. Furthermore, the hydrothermal co-carbonization (Co-HTC) of biomass and PVC at temperatures of 200–260 °C has been studied, where the OH groups of the lignocellulosic biomass promoted dechlorination [16–20]. The Co-HTC process can provide dechlorinated char, but the organic matter must be recovered from the wastewater, followed by wastewater treatment.

Crude glycerol is a by-product in the production of biodiesel from waste cooking oil, and its production is equivalent to approximately 10% of all biodiesel production. Purification is required to use crude glycerol as the raw material for chemical products. Glycerol purification using distillation is costly because of the high boiling point of glycerol, and most crude glycerol waste is used as fuel or incinerated. There is a demand for effective methods for utilizing crude glycerol without purification. Kusakabe et al. [21] reported the formation of biochar by the solvothermal co-carbonization of PVC and wood chips in glycerol. In this process, the dechlorination of the PVC was promoted by the reaction with the glycerol or wood chips. At a reaction temperature of 200–220 °C, unreacted liquid glycerol was coexistent with the biochar after the reaction, but when the reaction temperature was raised to 240 °C, the liquid substance disappeared, and a resinized biochar was formed. These results showed that glycerol had a significant influence as a reaction medium on dechlorination and carbonization.

In this study, to understand the details of the dechlorination of PVC by glycerol, the dechlorination of PVC powder in glycerol was conducted at a reaction temperature of 200–240 °C. The effects of additives in PVC on the decomposition ratio and dechlorination yield were investigated by using a PVC reagent and commercially available PVC.

2. Materials and Methods

2.1. Dechlorination of PVC

The powdery, additive-free PVC reagent (hereafter referred to as PVC-P) was purchased from FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan. A commercially available PVC resin sheet with a thickness of 0.1 mm (hereafter referred to as PVC-S) was cut into small pieces of several millimeters in size for use. The additive contained in the PVC-S was partially removed by extraction with tetrahydrofuran (THF), and the resulting sample is hereafter referred to as PVC-ST. The THF and glycerol were purchased from FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan. The PVC and glycerol were loaded into the decomposition container (25 mL) of an autoclave reactor (San-ai Kagaku Co. Ltd., Nagoya, Japan) in an N₂-filled glove box. The dechlorination of the PVC was conducted with the PVC/glycerol mass ratios of 4:3, 2:3, and 1:3 at 200, 220, and 240 °C for 30–120 min. The solid and liquid samples were recovered from the autoclave after dechlorination. The solid product was rinsed with ethanol to remove the glycerol solution and

dried in a vacuum oven at 105 °C for 1 d. The decomposition ratio was calculated via the following equation:

Decomposition ratio = 1 - (Mass of dried solid sample/Mass of feedstock (PVC and glycerol)) (1)

2.2. Characterization

The surface morphologies of the dried solid samples were observed using a scanning electron microscope (SEM, VE-9800, Keyence, Osaka, Japan). The presence of functional groups on the solid products was examined by scanning from 4000 to 650 cm⁻¹ at a resolution of 1 cm^{-1} using a Fourier-transform infrared spectrometer (FTIR, Spectrum 100, PerkinElmer, Waltham, MA, USA). The chlorine content of the solid products was measured using the flask combustion method. The solid products (50 mg) were wrapped with filter paper and tied with a platinum wire. The tip of the filter paper was ignited externally, and combustion in oxygen was carried out in a closed separable flask with a sodium carbonate solution. The chlorine concentration in the sodium carbonate solution was determined using ion chromatography (Dionex Integrion HPIC system, Thermo Fisher Scientific, Waltham, MA, USA). The dechlorination yield of the solid product was calculated using the following equation:

Dechlorination yield = 1 - (Cl content in solid product)/(Cl content in feedstock) (2)

The elemental contents (C, H, and N) of the solid product were analyzed using an elemental analyzer (UNICUBE, Elementar, Langenselbold, Germany). The oxygen content was determined indirectly by the difference, when considering the Cl content. The higher heating value (HHV) is the amount of heat produced from the complete combustion of the sample, including the heat vaporization of the moisture in the sample and the H₂O produced from the reaction. In this study, the calorific value of the solid product was calculated from a developed correlation using the percentages of carbon, hydrogen, and oxygen from ultimate analysis, using the following equation [22]:

HHV
$$(MJ/kg) = 0.3491 \text{ C} + 1.1783 \text{ H} - 0.1034 \text{ O}$$
 (3)

3. Results and Discussion

3.1. Dechlorination of PVC-P

Figure 1 shows the physical appearance of the PVC-P pyrolyzed at 200–240 °C for 120 min. The remaining liquid glycerol from the product pyrolyzed at 200 °C was removed with ethanol, resulting in a red powder. Carbonization proceeded with the disappearance of the glycerol at reaction temperatures of 220 °C and 240 °C, forming a black powder. Figure 2 shows the surface morphologies of the pyrolyzed PVC-P. The unreacted PVC-P powder had a diameter of 100–150 μ m. The PVC-P pyrolyzed at 200 °C expanded slightly, and surface melting was observed. At 220 °C, the dispersed granules remained in the melt. At 240 °C, the entire sample melted, and the granules disappeared.



Figure 1. Physical appearance of pyrolyzed PVC-P; PVC/glycerol mass ratio = 2/3 (PVC = 0.4 g, glycerol = 0.6 g), reaction time = 120 min.



Figure 2. Surface morphology of pyrolyzed PVC-P: (**a**) unreacted PVC-P, (**b**) PVC-P pyrolyzed at 200 °C, (**c**) pyrolyzed at 220 °C, (**d**) pyrolyzed at 240 °C, PVC/glycerol mass ratio = 2/3, reaction time = 120 min.

As indicated in Table 1, the chlorine fraction in the pyrolyzed PVC-P was 47.2, 16.0, and 10.0 wt% for the samples treated at 200, 220, and 240 °C, respectively. Figure 3 shows the mass balance of the pyrolysis products evaluated according to the data in Table 1. During the chemical conversion of PVC, glycerol is thought to be converted into glycidol and epichlorohydrin, according to Equations (4) and (5), respectively, which is in line with reported patents and papers detailing the glycerol chlorination mechanism [23]. These compounds were solidified by an epoxidation reaction with the converted PVC. Therefore, liquid glycerol remained as a reaction product at 200 °C but disappeared at 220 °C. The chlorine content in the solid product decreased sharply from 200 °C to 220 °C, and conversely, the amount of CHO in the solid product increased.

Table 1. Decomposition ratio and dechlorination yield of PVC-P.

Reaction Temperature (°C)	200	220	240
Decomposition ratio (wt%)	61.1	63.3	64.9
Dechlorination yield (wt%)	16.7	71.8	82.4
Chlorine fraction in solid residue (wt%)	47.2	16.0	10.0

PVC/glycerol mass ratio = 2/3; reaction time = 120 min.



Figure 3. Mass ratio of gas, liquid, and solid phases during PVC-P pyrolysis; PVC/glycerol mass ratio = 2/3, reaction time = 120 min.

$$C_3H_8O_3 \rightarrow C_3H_2O_2 + H_2O \tag{4}$$

$$C_{3}H_{8}O_{3} + 2HCl \rightarrow HOCH_{2}CHClCH_{2}Cl \rightarrow C_{3}H_{5}ClO$$
(5)

The FT-IR spectra of the unreacted PVC-P and the pyrolyzed PVC-P in glycerol are presented in Figure 4. In the FT-IR spectrum of the unreacted PVC-P, no OH stretching band was observed in the wavenumber range of $3100-3600 \text{ cm}^{-1}$. At a reaction temperature of 200 °C, the OH stretching absorption was observed, because the PVC was partially converted into a polyene structure by zip-elimination (Equation (6)), and further reacted with water to form a polyethylene oxide structure (Equation (7)). PVC containing a polyethylene oxide structure is thought to be resinified by ring-opening polymerization with glycidol and epichlorohydrin at high temperatures. As a result, the OH stretching absorption decreased at 220 °C and disappeared at 240 °C. The absorption peaks of the C=O stretching vibration at 1710 cm⁻¹ and the CH out-of-plane bending vibration at 740 cm⁻¹ for the sample treated at 220 °C indicated aromatization of the polyene structure.

$$-(CH_2-CHCl)_n - \rightarrow -(CH=CH)_n - + nHCl$$
(6)

$$-(CH_2-CHCl)_n - + [OH] \rightarrow -(CH_2-CHOH)_n - + [Cl]$$
(7)



Figure 4. FT-IR spectrum of PVC–P and that pyrolyzed at 200 °C (PVC–P–200), 220 °C (PVC–P–220), and 240 °C (PVC–P–240); PVC/glycerol mass ratio = 2/3, reaction time = 120 min.

Figure 5 shows the decomposition ratio and dechlorination yield of the PVC-P pyrolyzed at 200–240 °C, respectively. The PVC/glycerol mass ratio was 2:3. According to Equation (1), the initial decomposition ratio was 60% because the feedstock contained 60% liquid glycerol. At a reaction temperature of 200 °C, the decomposition ratio initially decreased and then increased to 61.1% at 120 min, which corresponded to the increase in the dechlorination of the PVC (decomposition) (Figure 5). This indicated that glycerol solidified due to the presence of glycidol at the beginning of the reaction (Equation (4)). However, the dechlorination hardly progressed, as shown in Figure 5b. When the reaction temperature was raised to 220–240 °C, the decomposition ratio increased slightly with time and reached 63–65% at 120 min. The initial processes in the PVC thermal degradation were the zip-elimination of HCl and the simultaneous formation of a conjugated double-bond (Equation (6)), which generated a polyene structure in the polymer backbone [24]. Assuming the complete dechlorination of the PVC, the decomposition ratio was calculated to be 71.3%. The decomposition ratio was almost the same at 120 min. Regardless of the reaction temperature, the large differences in the dechlorination yields cannot be explained by the

direct dechlorination of the PVC (Equation (6)). To explain the unchanged decomposition ratios and the high dechlorination yields at the high temperatures, solidification with dechlorination must be considered. Hydrogen chloride produced by decomposition reacts with glycerol to produce 1,3-dichloro-2-propanol. The dechlorination yields increased with temperature because of the formation of epichlorohydrin by the dechlorination of 1,3-dichloro-2-propanol (Equation (7)). Finally, glycidol and epichlorohydrin were thought to be resinified by an epoxidation reaction with the converted PVC. The reaction scheme, surmised on the basis of these results, is shown in Figure 6.



Figure 5. (a) Decomposition and (b) dechlorination ratios of PVC-P; PVC/glycerol mass ratio = 2/3.



Figure 6. Schematic of dechlorination reaction of PVC in glycerol.

3.2. Effect of PVC/Glycerol Mass Ratio on Dechlorination

The dechlorination of the PVC-P was conducted with PVC/glycerol mass ratios of 1:3, 2:3, and 4:3. To focus on the dechlorination of the PVC, the effect of the PVC/glycerol mass ratio on the reaction characteristics was investigated at the fixed reaction time of 120 min. As shown in Figure 7a, at a PVC/glycerol mass ratio of 1:3, the decomposition ratio of the PVC-P decreased with increasing reaction temperature, despite the progress of the dechlorination. This indicated the progress of the conversion from liquid to solid via resinification with epichlorohydrin. The decomposition ratios of the PVC-P at 240 °C were 67.8, 64.9, and 62.1% for the PVC/glycerol mass ratios of 1:3, 2:3, and 4:3, respectively. The decomposition ratio of the PVC-P at 240 °C was calculated assuming that complete dechlorination proceeded and a portion of the glycerol solidified. As a result, when an amount equivalent to 30% of the

starting glycerol was solidified, the calculated decomposition ratios for the PVC/glycerol mass ratios of 1:3, 2:3, and 4:3 were 66.7, 64.7, and 62.4%, respectively, which were almost the same as the individually measured values. This indicated that the PVC was converted into solid products in high yields via chlorine release, and that 30% of the glycerol was solidified by resinification. As shown in Figure 7b, the dechlorination yield tended to increase with increasing reaction temperature and was not significantly affected by the amount of PVC.



Figure 7. Effect of PVC/glycerol mass ratio on (a) decomposition ratio and (b) dechlorination yield.

3.3. Comparison with Commercially Available PVC-Sheets

The results of the elemental analysis of the unreacted PVC-P, PVC-S, and PVC-TS are listed in Table 2. The amounts of additives in the PVC-S and PVC-TS were calculated by subtracting the amount of intrinsic PVC, which was estimated by considering the Cl fraction from the total amount of PVC. The fraction of additives in the PVC-S and PVC-TS was 37% and 23%, respectively. Table 3 summarizes the decomposition ratios and dechlorination yields for the PVC-P, PVC-S, and PVC-TS at a reaction time of 120 min. The complex behavior of the decomposition ratio was influenced by the shape factor, the relaxation of the polymer network by the THF treatment, the suppression of chlorine elimination by the additives, and the decomposition of the additives. The dechlorination yield increased rapidly from 16.7 to 71.8% in the temperature range of 200–220 °C for the additive-free PVC-P, and a rapid increase in the dechlorination yield was observed in the range of 220–240 °C for the PVC-TS and PVC-S. The shift in the temperature range where dechlorination progressed was due to the suppression of zip-elimination by the additives.

Sample	PVC-P	PVC-S	PVC-TS
C (%)	38.4	48.4	44.6
H (%)	4.8	7.1	6.4
O (%)	0	8.9	5.2
Cl (%)	56.8	35.6	43.8

Table 2. Elementary analysis of various PVC samples.

Table 3. Decomposition ratio and dechlorination y	yield of various PVC samp	les.
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Sample	Fraction of Additive (%)	Deco	mposition Rati	io (%)	Dechlorination Yield (%)		
		200 °C	220 °C	240 °C	200 °C	220 °C	240 °C
PVC-P	0	61.1	63.3	64.9	16.7	71.8	82.4
PVC-TS	22.9	65.2	64.2	66.9	25.0	33.4	82.9
PVC-S	37.3	57.6	61.8	75.0	33.0	38.2	84.6

PVC/glycerol = 2:3; reaction time = 120 min.

3.4. Calorific Value of the Solid Product

Table 4 shows the effects of the PVC/glycerol ratio and the reaction temperature on the elemental composition and calorific value of the PVC-P solid product. Due to the simultaneous occurrence of carbonization and dechlorination, the carbon content increased from 41.2 to 67.1%, and the chlorine content decreased from 47.6 to 15.9% at a PVC/glycerol ratio of 2:3 in the temperature range of 200–220 °C. At the PVC/glycerol mass ratios of 4:3 and 1:3, almost the same trends were observed. In particular, at the ratio of 1:3, the carbon content decreased to 3.60% at 240 °C. The oxygen content decreased with the temperature, owing to the decomposition of the glycerol. As a result, when the carbon content of the solid products exceeded 67%, the calorific values exceeded 33 MJ/kg at 240 °C. The calorific values of the solid products were higher than that of standard bituminous coal (25–32 MJ/kg).

Table 4. Elemental analysis and calorific value for PVC-P solid products.

$C_{1} = 1 \cdot (\mathbf{P} \mathbf{C} \mathbf{a})$	Temp. (%)	Weight Fraction (%)				U/C ($m = 1/m = 1$)	O(C(m + 1/m + 1))	Colorific Volue (MI/kg)
Sample (P/G (**)		С	Н	0	Cl	H/C (mol/mol)	0/C (mol/mol)	Caloffile Value (WJ/Kg)
4:3 ^(b)	-	36.78	6.23	22.39	29.59	2.03	0.46	17.9
4:3	200	41.4	5.48	5.51	47.6	1.59	0.045	20.3
4:3	220	73.0	7.058	4.0	15.9	1.16	0.019	33.4
4:3	240	79.3	7.34	2.66	10.7	1.11	0.011	36.1
2:3 ^(b)	-	38.8	7.14	31.32	22.72	2.2	0.61	18.7
2:3	200	41.2	5.58	7.0	47.2	1.63	0.057	20.2
2:3	220	67.1	7.06	9.9	16.0	1.26	0.05	30.7
2:3	240	73.6	7.63	8.71	10.0	1.24	0.04	33.8
1:3 ^(b)	-	38.93	7.73	39.15	14.2	2.38	0.75	18.7
1:3	200	40.9	5.51	7.72	46.4	1.62	0.064	20.0
1:3	220	54.5	6.45	13.0	26.1	1.42	0.0581	25.3
1:3	240	79.0	7.12	10.3	3.6	1.08	0.044	34.9

^(a) P/G indicates PVC/glycerol mass ratio. ^(b) Calculated value for mixture of PVC and glycerol. Reaction time = 120 min.

Table 5 shows the elemental composition and calorific value of the solid products of the PVC-P, PVC-S, and PVC-TS. The carbon and oxygen contents of the PVC-S and PVC-TS were higher than those of the PVC-P, owing to the presence of additives. The progress of the carbonization and dechlorination reactions of the PVC-S and PVC-TS shifted in the temperature range of 220–240 °C due to the suppression of the reactions by the additives. Compared to the PVC-P, the PVC-S had a carbon content of up to 79.1% and a chlorine content of up to 8.7% at 240 °C.

Table 5. Comparison of elemental analysis and calorific value. ^(a) Calculated value for mixture of PVC and glycerol. PVC/glycerol mass ratio = 2:3; reaction time = 120 min.

	Temp. (%)	Weight Fraction (%)			%)			Colorific Volue (MI/Ico)
Sample		С	Н	0	Cl	H/C (mol/mol)	U/C (mol/mol)	Calofine value (wij/kg)
PVC-P ^(a)	-	38.8	7.14	31.32	22.72	2.2	0.61	18.7
	200	41.2	5.58	7.0	47.2	1.63	0.057	20.2
	220	67.1	7.06	9.9	16.0	1.26	0.05	30.7
	240	73.6	7.63	8.71	10.0	1.24	0.04	33.8
PVC-TS ^(a)	-	41.3	7.76	33.4	17.52	2.26	0.6	20.1
	200	45.4	6.42	6.0	42.6	1.69	0.099	22.8
	220	48.4	6.41	6.39	37.8	1.59	0.099	23.8
	240	78.3	7.49	4.89	9.75	1.15	0.047	35.7
PVC-S ^(a)	-	42.82	8.04	34.88	14.24	2.25	0.61	20.8
	200	44.4	6.35	10.8	38.0	1.72	0.182	21.9
	220	47.6	6.72	10.7	35.1	1.69	0.169	23.4
	240	79.1	7.7	6.52	8.7	1.17	0.062	36.0

4. Conclusions

PVC was dechlorinated by treatment with glycerol in an autoclave at 200–240 °C. For the PVC-P dechlorination, liquid glycerol remained in the product pyrolyzed at 200 °C for 120 min. When the reaction temperature was raised to 220 °C and 240 °C, carbonization proceeded with the disappearance of glycerol, forming a black powder.

Characterization of the solid products showed that the PVC was partially converted into a polyene structure by the zip-elimination of HCl and further reacted with water to form a polyethylene oxide structure. During the chemical conversion of the PVC, glycerol was thought to produce glycidol and epichlorohydrin via the reaction represented by Equations (4) and (5), respectively. These compounds were solidified by an epoxidation reaction with the converted PVC. Thus, the glycerol acted as a useful reaction medium in this reaction system. Analysis of the decomposition ratio and dechlorination yield showed that the PVC was converted into solid products in high yields via chlorine release, and approximately 30% of the glycerol solidified by resinification at 240 °C.

The effects of additives on dechlorination were examined by comparing commercially available PVC sheets (PVC-S and PVC-TS) and PVC-P. Although the decomposition and dechlorination of the PVC-P, PVC-TS, and PVC-S were significantly influenced by the shape factor and the additives at 200–220 °C, the dechlorination yields for all the PVCs converged to 81–85% at 240 °C. The calorific value of the solid product pyrolyzed at 240 °C exceeded 30 MJ/kg, owing to the progress of carbonization and dechlorination.

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