

Feedstock Recycling of PVC and PET by Wet-processes

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PET could be converted into terephthalic acid and ethyleneglycol (EG) by sulfuric acid, nitric acid and NaOH solution quantitatively. On the other hand, resulting EG is oxidized to oxalic acid, which is more expensive than EG, by simultaneous oxidation in nitric acid and oxygen-oxidation in NaOH solution. PVC materials could be converted into carboxylic acids by oxygen-oxidation in alkaline solution without production of organochlorine compounds such as dioxin's. In this case, apparently, the dechlorination proceeded with zero order reaction in water, on the other hand it done with first order reaction in NaOH solution. The apparent activation energies were ca. 46 kcal/mol independent on the NaOH concentration.

Introduction

It is important to choice optimum treatment according to a material, an emission and a treatment technology in the recycling of waste plastics. Some recycling technologies as material-, energy-, and chemical- recycling, have been investigated for that propose.

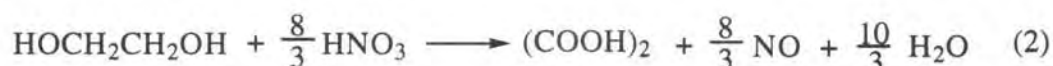
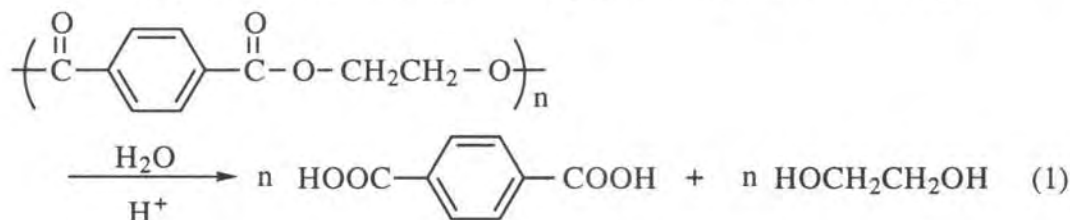
Polyvinylchloride (PVC) materials produce a lot of hydrogen chloride during thermal decomposition, and a trace of harmful organochlorine compounds such as dioxins is formed in its incineration. Additionally, the soil and water pollutions by elusion of phthalic acid esters and heavy metals from some additive in PVC materials have afraid to be impact for the ecological system. On the other hand, Polyethylenterephthalate produced 3.1×10^5 t/y (1998) as bottles in Japan, the separate collection has been promoted by "*The law for promotion of sorted collection and recycling of containers and packaging*", the amount of collected and recycled of PET have increased gradually. But it is difficult to deal with all by material recycling, the development of new chemical recycling technology is necessary.

The purpose of this work is the development of new chemical recycling process for PET and PVC materials, (1) acid and alkali hydrolysis simultaneous oxidation of PET, and (2) oxygen-oxidation and dechlorination of PVC materials in alkaline solution. In this present, the possibility of wet processes is indicated a feedstock recycling of waste plastics.

Chemical Recycling of Polyethylene-terephthalate (PET) using Acids

It is well known that PET is hydrolyzed to terephthalic acid (TPA) and etyleneglycol (EG) easily, and hydolysis is accelerated by acid and base catalysts [1-3]. TPA and EG is produced quantitatively for the degree of hydrolysis, but EG yield decreased with increasing sulfuric acid concentration and temperature owing to carbonization. On the other hand, EG is be able to convert into oxalic acid, which is more expensive than EG, in nitric acid due to the oxidation as shown in Equations (1) - (3). PET is hydrolyzed first under 100 °C at atmospheric pressure as shown in Eq.(1), and resulting EG was oxidized simultaneously to

oxalic acid as shown in Eq.(2). Effect of HNO_3 concentration on the oxalic acid yield at 100°C are shown in Figure 1. The oxalic acid yield was increased with increasing HNO_3 concentration, and reached 23.4 % in 13 M for 4 h, and then was decreased. The reaction time reaching the maximum was decreased with increasing the concentration, and was 16 h in 7 M, 10 h in 10 M and 4 h in 13 M. In this case, nitric acid is reduced to formed NO , which can be recycled as nitric acid by the oxygen-oxidation as shown in Eq.(3).



Chemical Recycling of PET using Alkaline Solution

PET is hydrolyzed quantitatively in alkaline solution. The products are sodium terephthalate (TP-Na) and EG in the case of using NaOH solution. TP-Na and EG yields agreed well with the degree of hydrolysis as shown in Fig.1. TP-Na and EG yields were quantitative in 2 M NaOH at 2 h and 100°C , TPA was recovered quantitatively by acidification. EG is oxidized to oxalic acid as sodium salt by base-catalyzed oxygen oxidation due to the pressurizing of oxygen.

Oxalic acid (Oxa) yield reached 86.3 % in 27.5 mol- $\text{NaOH}/\text{kg-H}_2\text{O}$ at 250°C and P_{O_2} 5 MPa for 3 h [4-5]. This reaction is characterized that TP-Na is stable to oxidation due to participations as sodium salt.

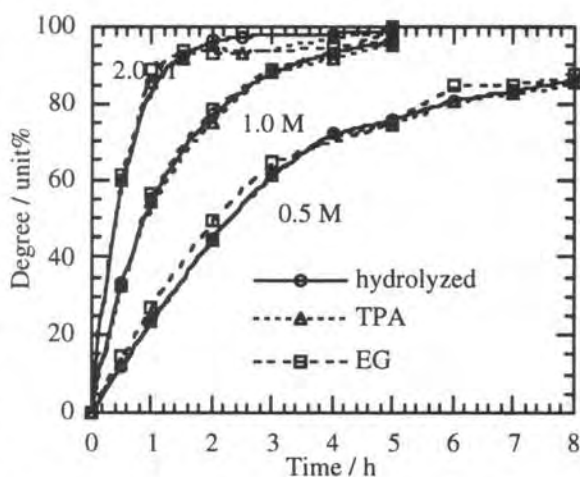


Figure 1 Effect of NaOH concentration on the hydrolysis and the yields of TPA and EG at 100°C

Chemical Recycling of PVC Materials in Alkaline Solution at Elevated Temperatures

PVC materials consist of PVC, plasticizer such as di-octylphthalate (DOP) and many kinds of additives unlike PET. Oxygen-oxidation in alkaline solution can recycle them to carboxylic acids. The major products in the oxidation of carbonaceous materials in flexible PVC were oxalic acid, CO_2 , and water-soluble acids compound of carboxylic acids. The product types are the same as those present in PVC resin [6], VDC-VC copolymer [7], and rigid PVC [8] on oxygen oxidation in alkaline solutions. There are many types of aromatic carboxylic acids present in water-soluble acids. These include phthalic acid, trimellitic acid, pyromellitic acid, and benzenepenta-carboxylic acid, as shown in Table 1. The formation of such aromatic carboxylic acids is caused by the oxidation aromatic rings in dechlorinated PVC as it forms, due to bimolecular addition reaction and/or coiling. However, phthalic acid

was produced mainly by the hydrations of plasticizer.

The effect of reaction time on the products yield is shown in Fig. 2. Water-soluble acid decreased with the simultaneous formation of oxalic acid and CO₂. In contrast, residue is slowly and completely oxidized to finally yield oxalic acid, water-soluble oasis, and CO₂. Consequently, oxalic acid and CO₂ yields continued to increase up to 18 h. However, the yield of water-soluble acids exclusively was decreased in two steps: The first step is the oxidation of phthalic acid from plasticizer, and the second step is the further oxidation of the base-catalyzed mechanism. A large amount of CO₂ is formed from these substances, as in the case of coal tar pitch. The yield of water-soluble acids was constant. It is thought that the rate of oxidation of phthalic acid is almost equal to that of water-soluble acids caused by the oxidation of PVC between the first and the second steps.

In the oxygen-oxidation of PVC in alkaline solutions, the formation of small amount of chlorinated feared including dioxin's, because this system contains chlorine, oxygen and aromatics. According to analytical results of dioxin's GC-MS in reaction solution, the determination of dioxin's concentration was before the limit (0.04 ng/l) and the toxicity equivalent concentration of 2,3,7,8-T₄CDD (TEC) was zero.

Kinetics of Dechlorination of PVC in Alkaline solutions

Dechlorination of PVC powder was studied in water and NaOH solutions (0.01 - 2 M) from 200 °C to 250 °C using an autoclave. PVC powder was introduced in to the autoclave with the same composition reaction solution by pressurized N₂ after the prescribed temperatures reached in order to suppress the effect of dechlorination during heating the autoclave. The degree of dechlorination was increased linearly with time until ca. 80 %, apparently the dechlorination proceeded with zero order reaction. The rates of dechlorination in 0.01 and 0.02 M NaOH almost agreed with that in water, and apparent dechlorination could be regarded as zero order reaction. This probable that NaOH is neutralized with evolved HCl by dechlorination. On the other hand, the dechlorination was first order reaction over 0.1 M until 0.5 M, and the rate was increased with increasing NaOH concentration, it was almost constant over 0.5 M.

Generally, the properties of reactant such as the composition and the structure of do

Table 1 Yield of benzenecarboxylic acids / C%.

mono-benzenecarboxylic acid	1.29
1,2-benzenedicarboxylic acid	8.73
1,3-benzenedicarboxylic acid	0.25
1,4-benzenedicarboxylic acid	0.45
1,2,3-benzenetricarboxylic acid	0.29
1,2,4-benzenetricarboxylic acid	0.99
1,3,5-benzenetricarboxylic acid	0.18
1,2,3,4-benzenetetracarboxylic acid	0.42
1,2,3,4-benzenetetracarboxylic acid	0.35
1,2,3,5-benzenetetracarboxylic acid	0.54
1,2,3,4,5-benzenepentacarboxylic acid	0.35
Total	13.84

(15 m NaOH, 250 °C, 7 h, 5 MPa Po₂)

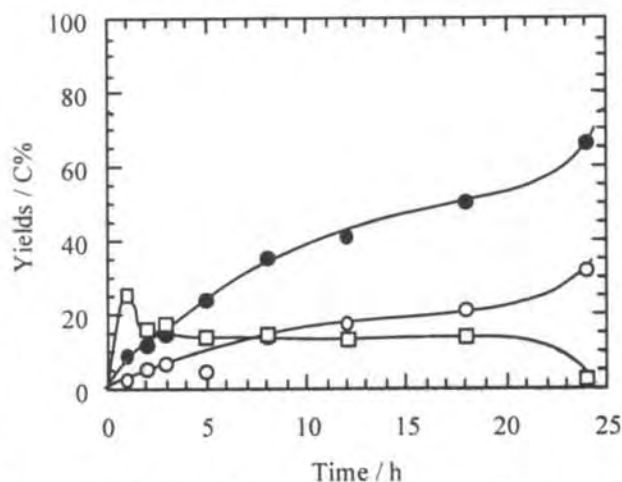


Figure 2 Effect of reaction time on the yields of oxalic acid, CO₂ and water-soluble acids in the oxidation of F-PVC pellet in 15 m NaOH at 250 °C and Po₂ = 5 MPa.
○ oxalic acid, ● CO₂, □ water-soluble acids

not change during the reaction. However, in this case, these are changed with time, because the formation of conjugated double bond, bridge structure and cyclization progress with dechlorination. Considering the dechlorination proceeded with the zipper mechanism and zero order reaction in water, the dechlorination may proceed without the effect of the change of molecular structure. On the other hand, the initial rate of dechlorination, particularly, was increased with NaOH concentration, and then it was clearly that NaOH accelerated the rate of dechlorination.

First order plots in 0.1 M and 0.5 M are shown in Fig. 3. This indicates that the dechlorination proceeds by apparent first order reaction in NaOH solutions. The plots were appreciably linear excluding the dates which the rate was drastically decreased over 2 h at 250 °C. Arrhenius plot of rate constant k including the result in water is shown in Fig. 4. The apparent activation energies were ca. 46 kcal/mol independent on the NaOH concentration. These results approximately agreed with the result (49 kcal/mol) by the result under adding organic solvent [10-11]. The magnitude of activation energy is larger compared to that (ca. 30 kcal/mol) in thermal decomposition in inert gas.

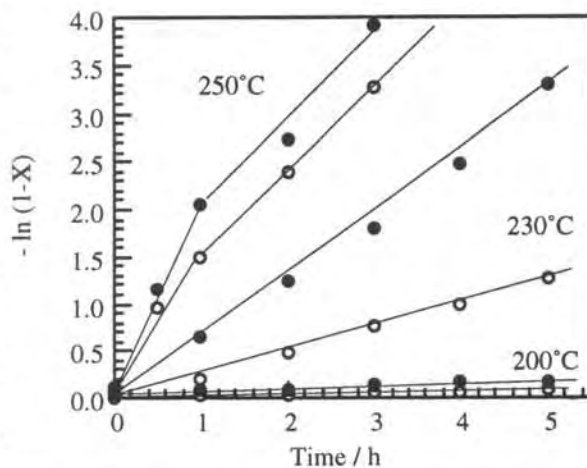


Figure 3 First order plot of the dehydrochlorination of PVC powder in 0.1 M and 0.5 M NaOH solution.

○ 0.1 M ● 0.5 M

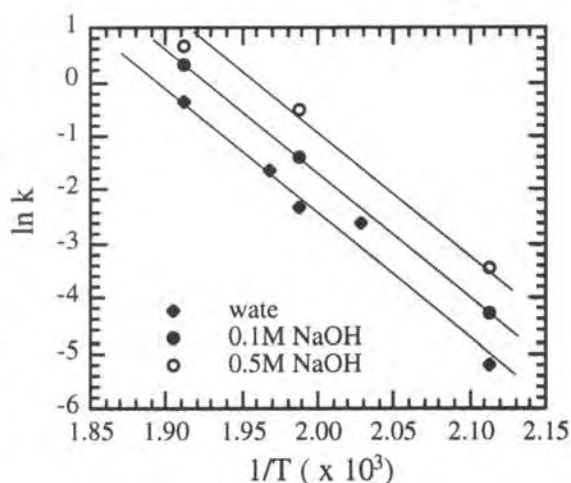


Figure 4 Arrhenius plots of the apparent rate of dehydrochlorination in water, 0.1 M and 0.5 M NaOH solutions.

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