# Leaching of Plasticizer and Chlorine from Mixed Waste Plastics in NaOH Solutions at Elevated Temperatures.

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It is difficult to treat and recycle municipal Mixed Waste Plastics (MWP), since they consist of various plastics. A purpose of this study is dechlorination treatment of MWP and leaching of plasticizers from MWP to produce clean fuel. Dechlorination of MWP proceeded quantitatively at 250°C for 5h, but didn't do at 150°C. On the other hand, the degree of leaching of plasticizers proceeded completely at 150-250°C. Thus new process is proposed, dechlorination and leaching of plasticizers are performed separately.

## Introduction

MWP consists of commodity plastics such as PE, PS, PP, PET, PVC, and metals, etc. Particularly it is difficult to treat and recycle them, since PVC materials are complex materials that contain various additives, such as filler, plasticizer, and stabilizer, etc. (Table 1). On the other hand, it is known that chlorine and plasticizers in PVC materials can be leached by treatment of PVC in NaOH solutions at elevated temperatures [1-3]. Therefore, it is expected to apply this process to treatment of MWP. The present study examines the selective leaching of chlorine and plasticizers treatment of MWP in order to establish the fundamental conditions necessary for a new chemical recycling method for treating waste plastics.

Table 1 Composition of PVC materials ,
a) Rigid PVC : b) Flexible PVC :c) Agricultural PVC

| a) Rigid PVC pellet | (wt%) |
|---|---|
| PVC | 82.7 |
| MBS | 13.2 |
| Sn stabilizer | 2.47 |
| Monoglycelide | 0.99 |
| Processing aid | 0.82 |
| LDPE | 0.082 |
| Pigment | 0.012 |

| b) Flexible PVC pellet | (wt%) |
|---|---|
| PVC | 36.8 |
| $CaCO_3$ | 28.3 |
| DINP | 23.9 |
| Chlorinated paraffin | 6.99 |
| Alkylbenzene | 1.84 |
| Pb stabilizer | 1.10 |
| Calcium stearate | 0.74 |
| Wax | 0.37 |

| c) Agricultural PVC film | (wt%) |
|---|---|
| PVC | 64.5 |
| DOP | 32.2 |
| Epoxy plasticizer | 1.29 |
| Surface active agent | 1.29 |
| Ca-Zn stabilizer | 0.64 |
| UV absorption agent | 0.06 |

## Materials and Methods

MWP samples were collected in Niigata City. These consist of various plastics, so samples for this work needed to be homogeneous. So MWP samples were coarse-ground into about 10mm and these were ground further (fine-ground) by using laboratory grinder.

Determination of chlorine and phthalic acid contents in MWP samples with test tubes.

Fine-ground samples (about 1g) were used in order to determine the composition of MWP samples. These experiments were carried out using 50% NaOH solution (20mg) in SUS 304 tubes lined with a 35mL PTFE flask in an electric oven for 5-48h at 250°C. The product solutions were filtrated and analyzed by IC and by HPLC after cation exchange for determining the degrees of dechlorination and the leaching of plasticizers. Plasticizers consist of phthalic esters (e.g. DOP, DINP), so they were hydrolyzed to phthalic acids in alkali solution (Figure 1). The degrees of leaching plasticizers were converted into phthalic acid yields.

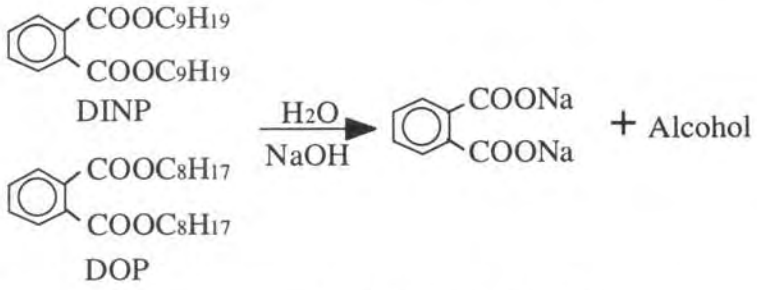


Figure 1 Alkali hydrolysis of phthalic esters.

Leaching of chlorine and phthalic acid from MWP samples with 1L autoclave.

In other experiments, a mixture of 15g of fine-ground MWP and 500g of 50% NaOH solution was placed in a PTFE beaker (1L). The PTFE beaker was placed into a Hastelloy-C lined stainless autoclave fitted with a magnet-driven stirrer under $N_2$ and then heat to 150-250°C. These analysises were carried out above methods.

## Results and Discussions

Determination of chlorine and phthalic acid contents in MWP with test tubes.

The contents of chlorine and phthalic acid were shown in Table 2. Table 2 expressed as weight percents against the feed materials. The degree of dechlorination and leaching of phthalic acid reached 3.94-4.66wt% and 0.67-1.09wt% for 5h respectively. Also, both were

Table 2 The contents of chlorine and phthalic acid in MWP samples

| No. | Amount (g) | Temp. (°C) | Time (h) | chlorine (wt%) | phthalic acid (wt%) |
|---|---|---|---|---|---|
| 1 | 1.012 | 250 | 5 | 4.30 | 0.67 |
| 3 | 1.059 | 250 | 5 | 4.66 | 1.09 |
| 2 | 1.008 | 250 | 5 | 3.94 | 0.87 |
| 4 | 1.036 | 250 | 48 | 4.65 | 0.90 |
| av. | | | | 4.40±0.45 | 0.88±0.21 |

4.65wt% and 0.90wt% for 48h. This shows that chlorine and plasticizers were leached completely from MWP in 50% NaOH solution at 250°C for 5h. Thus, MWP samples contain 4.40±0.45wt% of chlorine and 0.88±0.21wt% of phthalic acid.

Leaching of chlorine and phthalic acid from MWP samples with 1L autoclave.

Figure 2 shows the effect of temperatures and reaction time on the degree of dechlorination. The gray zone means the range of weight percent of chlorine content. Dechlorination only progressed at 150°C but reached gray zone at 250°C at the beginning of reaction. The degree of dechlorination at 150°C was considered as inorganic chlorine compound content in MWP samples originally. And dechlorination at 200°C increased with time gradually, and reached the gray zone over 1h. No chlorine contained in the residues treated at 250°C for 5h.

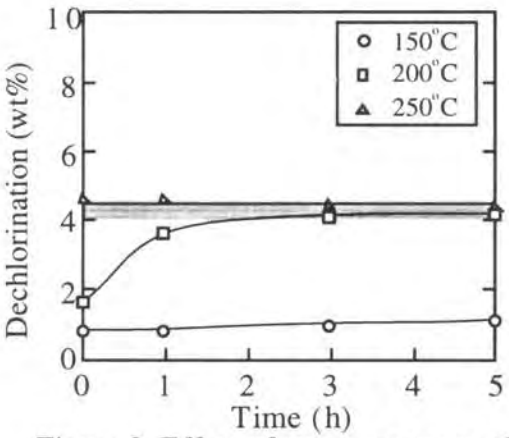

Figure 2 Effect of temperatures on the dechlorination.

Figure 3 shows the effect of temperatures and reaction time on the degree of leaching of phthalic acid being formed from some plasticizers. The gray zone means the range of weight percent of phthalic acid. The degrees of leaching plasticizers as phthalic acid were almost equal at all temperatures independent of time and reached the range of gray zone. This shows that plasticizers were leached completely even at 150°C.

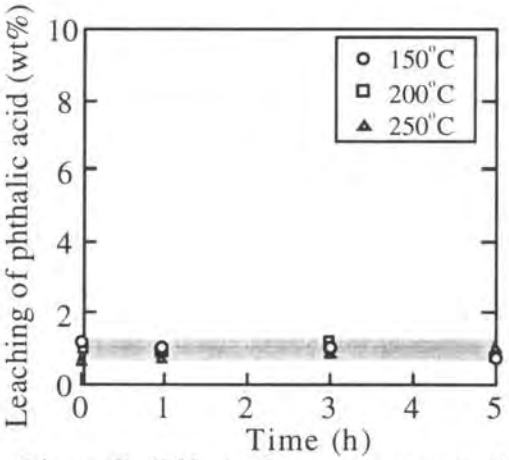

Figure 3 Effect of temperatures on the leaching of phthalic acid.

Consequently it is possible to remove chlorine and plasticizers selectively from MWP by the control of temperature. The first step is leaching the plasticizers under 150°C or so and the second step is dechlorination by heating up to 200-250°C in 50% NaOH solution.

**Conclusions**

In this work, we found a possibility of selective removal of plasticizers and chlorine from MWP in NaOH solution by the control of temperature. So we make proposals of a new process about MWP treatment as shown in Figure 4. Leached plasticizers as phthalic acid at low temperature reaction are used as chemical source and this process can be used as a

pretreatment for such as a hydrocracking process [4-8]. Dechlorinated MWP (residue) by the control of high temperature can be used as a clean resource and fuel due to no chlorine. Organic compounds in the reaction solution are converted to more valuable compounds as oxalic acid or sodium carbonate by base-catalyzed oxidation and they are used as chemical

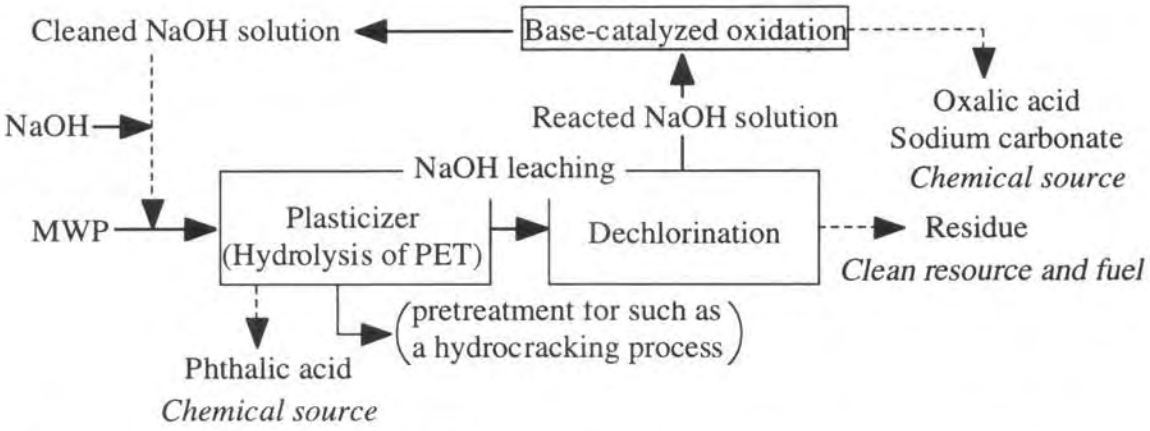


Figure 4 Selective leaching of chlorine and plasticizers process using NaOH solution.

sources.

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