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Dechlorination of Polyvinyl Chloride in NaOH and NaOH/Ethylene Glycol Solution by Microwave Heating

F. Osada and T. Yoshioka

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1. Introduction

The amount of plastic produced in Japan was 14.65 million tons in fiscal year 2007, although this figure has fluctuated, as shown in Figure 1. As a result, the amount of plastic waste has increased to 10.05 million tons/year[1]. Most of that waste is either landfilled or incinerated.

The amount of plastic waste discharged is annually growing. Therefore, it is essential to research and develop technologies to recycle and reuse plastic waste to protect the global environment and effectively to utilize resources. In an effort to promote recycling of plastic waste. The Containers and Packaging Recycling Law was enacted in June 1995 to promote sorted collection of containers and packaging and the recycling of containers and packaging as products. To promote recycling, the scope of this law was expanded to plastic containers and packaging, instead of being limited to polyethylene terephthalate (PET) bottles. When it was amended then reenacted in April 2000, it seemed as if almost 50% of plastic waste was recycled in fiscal year 2000. However, the breakdown of effective utilization in fiscal year 2006 revealed that almost 72% was simply incinerated: [1] 40% was used for power generation, 19% was incineration to release thermal energy, 4% was used as feedstock, 9% was used as solid fuel (Figure 2). Some waste plastic from general household was also incinerated in the metropolitan area. Thus, the current situation is that most waste plastic is still either landfilled or incinerated. There is a limit to how much waste plastic that a landfill can hold, and the option of landfilling waste plastic is becoming more difficult, especially since the amount of landfill space available to bury plastic waste is annually decreasing. In fact, it has been reported that the landfills will be completely full in 14.8 years (as of end of fiscal year 2005) for general waste, and in only 7.7 years (as end of fiscal year 2005) for industrial waste. When plastic waste is landfilled, there is risk of endocrine disruptors and

hazardous substances eluting from the waste. The specific gravity of plastic is low. Therefore, burying it poses risk of loosening the landfill ground. This makes it difficult to reuse the landfill site for other purposes. On the other hand, when waste plastic is incinerated, it tends to corrode the incinerator due to the waste plastic containing halogens such as chlorine. What is more, depending on the incineration condition, it can also generate toxic organic compounds and materials causing acid rain. Burned ash and fly ash that are buried in landfills also contain residual $CaCl_2$ from $Ca(OH)_2$ added to neutralize hydrogen chloride. This also increases the load on the landfill. Among waste plastic, polyvinyl chloride (PVC), whether rigid or flexible, is common because it is used in construction materials and materials for electrical wire sheathing. PVC is used as a durable and enduring product, thus, there is risk of an increase in volume discharged when buildings are renovated or rebuilt in the future.
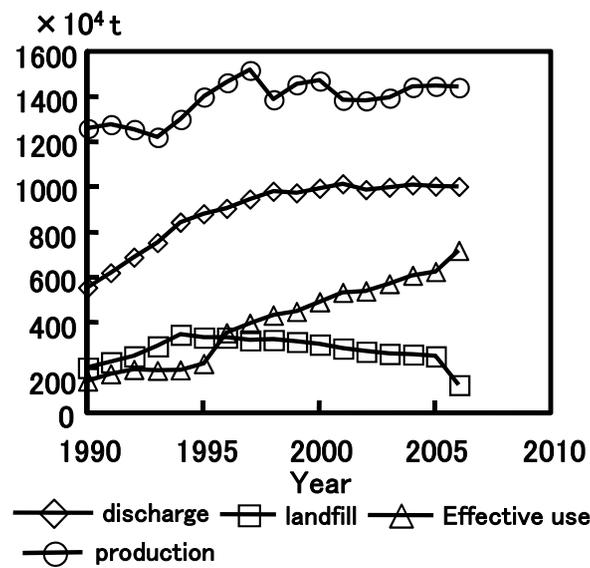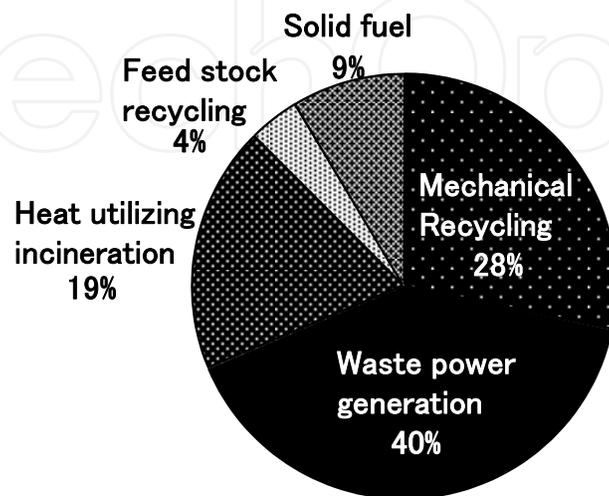

Figure 1. Production and emissions of plastics

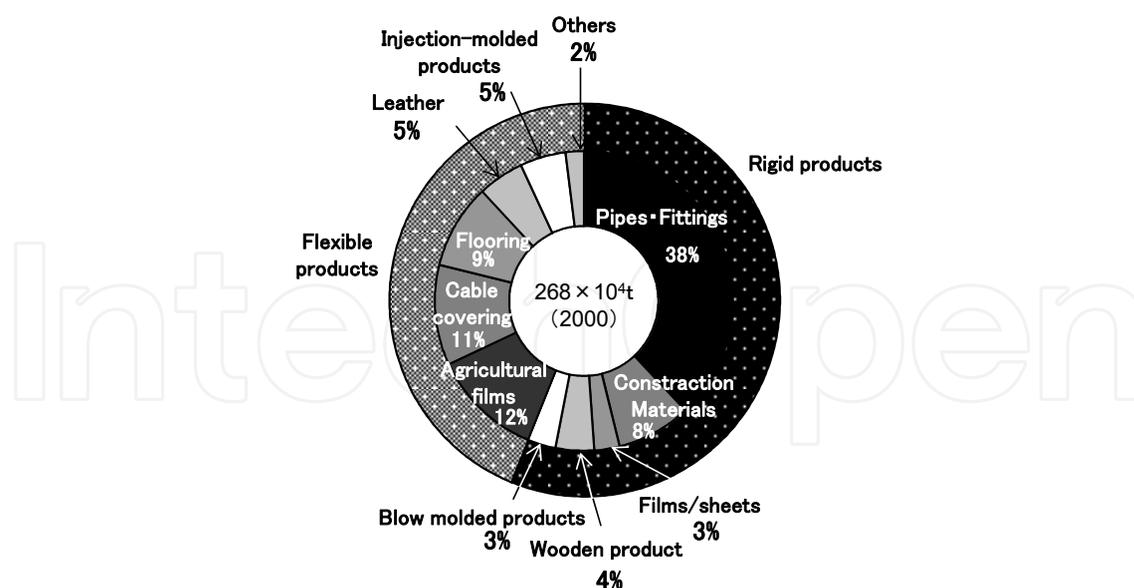**Figure 2.** Breakdown of waste plastics to the effective use (2006)
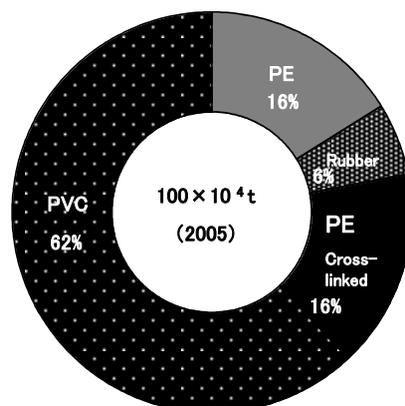
Figure 3. Applications of PVC

Figure 4. Waste material coated cables

There have been many studies on PVC since 1950. However, the objectives of these studies tended to mainly focus on stabilization. Recent reports indicate that more studies have focused on recycling as a study objective. Examples include:

1. Material recycling to make industrial raw materials,
2. Recycling to turn waste vinyl chloride products into new vinyl chloride products,
3. Chemical recycling (feedstock recycling) [2] by fractional precipitation,
4. Recycling PVC waste products into chemicals and raw materials for products through chemical treatment methods [3],
5. Energy recycling by thermal energy recovery from incineration of PVC wastes, dechlorinated via thermal degradation, and by power generation from incineration of PVC waste and gasified or liquefied PVC waste, reusing this energy source to generate power.

PVC studies are largely classified into two types: the dry method by thermal degradation and wet method. When considering the speed of temperature rise during thermal

degradation of pure PVC powder, with the dry method we can get type-A crude oil with an average molecular weight of 280.[4]With the wet method, we can process flexible PVC. The plasticizer additive becomes anhydrous and then NaOH solution is added. PVC undergoes hydrolysis, and the heavy oil contents are pressurized and reheated to make light crude oil, thereby turning PVC into an oil.[5] NaOH solution can be used for dechlorination, then PVC is converted into carboxylic acids.[6] Flexible PVC film can be deplasticized and dechlorinated to synthesize polyene.[7]

We must find new methods to handle PVC waste using approaches that are not dependent on landfills and incineration. To do this, there is a need to create products with a very long usage life, as well as to promote reuse and recycling of products. If it is difficult to reuse or recycle these products, then we must support material recycling by recycling it into something else. Films are the most common form of flexible PVC,[8] as seen in the PVC product breakdown shown in Figure 3. It is most used in agricultural vinyls, as well as in packaging for agricultural fertilizers. Until recently, these items were incinerated. However, we see that tendency has changed, and that they are now often washed of adherents and residue and then reused/recycled or reused/recycled into lower quality PVC products. However, this amounts to only a fraction of the PVC waste discharged. Most of it is either incinerated or exported to Southeast Asia and China to reduce the treatment cost. The second largest waste comes from electrical wire sheathing. Roughly 1 million tons of cable sheathing is discharged as waste every year, of which 62% is PVC [9](Figure 4). About 300,000 tons, or roughly half, of this PVC undergoes material recycling and is made into flooring materials or other lower quality products, and a fraction is recycled into electrical wire sheathing materials. The reality is that the remainder is either landfilled or incinerated. The majority of PVC products discharged from different industrial fields is generally either landfilled or incinerated; however, some may be recycled. In either case, the situation is that the mode of disposal still tends to be mostly dependent on incineration. For waste that can only be incinerated, this study intends to find a way to extract and remove beforehand, thus eliminating the hydrogen chloride that would be generated upon incineration. A flexible PVC tube was used as the source of PVC in the study. We then studied whether use of external heating with a general thermal heater or internal heating with a microwave heater could promote the reaction conditions when used as the heating source for the deplasticization and dechlorination processes. It is generally known that polyvinyl chloride (PVC) is dehydrochlorinated when burnt at temperatures higher than 280°C. However, to effectively accelerate dehydrochlorination process with faster and better heat transport. Substances with low thermal conductivity are generally heated by microwaves because this procedure does not require heat transport. Thus new applications utilizing microwaves are expected to be developed in the near future. In this study, we reviewed the dehydrochlorination of flexible PVC to see if it was possible to use controllable microwave heating as a fast heating mechanism. This assumption was based on conventional wet method studies, [10-16] which indicated that substance containing Cl molecules tended to easily absorb microwaves, and materials made of flexible PVC and ethylene glycol (EG) used as a reacting solution also easily absorbed microwaves. The goal was also to accelerate dehydrochlorination by directly heating PVC molecules for early extraction of plasticizers.

We similarly studied the conditions that best promote dehydrochlorination and improve reaction efficiency through an interactive effect by using substances such as EG that present good intersolubility with flexible PVC.

PVC	59.2
DOP	29.7
Epoxidized soybean oil	3.6
Other substances	7.5
Cl	35.7

Table 1. Composition of flexible polyvinyl chloride (PVC) (wt%)

2. Experimental study

2.1. Sample and reagent

The materials used included flexible PVC with the composition indicated in Table 1. The weight ratio of dioctyl phthalate (DOP) plasticizer was roughly 30%, compared to a weight ratio of roughly 60% for PVC polymer. Other components included the oil added upon molding and UV stabilizers. We confirmed that the PVC polymer contained 35.7% of chlorine according to elementary analysis. We also used NaOH (Merck GR99%) diluted in distilled water as the NaOH solution for extraction and removal treatment in this study. Ethylene glycol was used without adding anything.

2.2. Reactor

A general purpose microwave heater (Milestone General) was used for the reaction experiments.[18] The heater had a fixed microwave frequency of 2.45 GHz, a maximum output of 1kW, a maximum usable temperature of 240°C, a maximum usable pressure of 3.4MPa, with a 100-ml reactor vessel. The reactor vessel was made of tetrafluoroethylene perfluoroalkylvinylether (PFA) copolymer, and the outer tube was made of polyether ether ketone (PEEK). In the container was also a magnetic stirrer so that the contents could be stirred. The mechanism also came with a temperature sensor to measure the temperature of the solution in the container. The temperature sensor measurement was also fed back to control microwave output. The inside of the device, including the reactor vessel, was not easily heated by microwaves, and both the reactor vessel and outer tube protecting the reactor vessel were made of materials that easily transmit microwaves. To ensure even heating distribution, the reactor vessel was also placed on a rotary stand. When heating was completed, the inside of the device and reactor vessels were cooled by a built-in fan. Conditions such as the reaction temperature and heating time were controlled using the exclusive control settings. The temperature elevation time, hold temperature, and temperature hold time can be input into the oven in advance, and the oven operates automatically.

2.3. Experimental method

In this study, we used a reactor vessel with a volume of 100ml and added 0.5g of flexible PVC crushed to a maximum particle size of 1mm and 50ml of NaOH solution. The solution was continuously agitated. The container containing the sample was set on the microwave heater and the sequence program was then started for microwave irradiation according to the preprogrammed target reaction temperature, heating time, temperature hold time, temperature elevation time and other parameters. The reaction start time was defined as the time when the solution in the vessel reached the set temperature. Then the temperature was maintained for the specified time. NaOH was prepared at concentrations of 2, 4, 6, 8 and 16mol/l, and the reaction temperature was set at 100°, 150°, 200°, 225° and 250°C. After the temperatures hold time had elapsed, agitation was stopped and the reaction products were cooled to room temperature. Then the solution was passed through a 0.45-mm polyvinylidene difluoride (PVDF) filter to separate the residue and filtrate, and then distilled water was added to the filtrate to prepare a 50-ml reaction solution. The residue was then washed with distilled water and dried by decompression; it was then weighted and underwent elementally analyzed. In the case of using NaOH/EG solution, the flexible PVC (Table 1.) with a particle size of about 1 mm was charged with 50 ml of EG were placed in the reactor vessel. NaOH was prepared at concentrations of 0.5, 1, 2, and 4 mol/l. The reaction temperature was set at 100, 120, 140, and 160°C.

3. Analysis

3.1. Chlorides and phthalic acid

The anion levels in the filtrate were measured using Ion Chromatograph (Model 7310-20, NIKKISO, Tokyo, Japan) consisting of DIONEX AG15 and AS15 columns. The eluent was mixed with NaOH solution of 35×10^{-3}mol/l, which was continuously added at 0.75ml/min. The ASRS suppressor was operated in recycle mode. The filtrate was then accordingly diluted with distilled water. The phthalic acid ions and chloride ions were quantitatively analyzed by concentrated analysis using concentrated columns.[19]

3.2. Residue

The residue recovered was washed with distilled water and methanol and then dried by decompression. After drying, the residue structure was examined under a scanning electron microscope (Hitachi S-2510). The change in molecular weight was then examined with a gel permeation chromatography (GPC) analyzer (Waters).

3.3. Evaluation method

The dechlorination ratio and deplasticization ratio were defined and evaluated as follows;

$$\text{Dechlorination ratio (\%)} = [Cl_t]/[Cl_0] \times 100 \tag{1}$$

$$\text{Deplasticization ratio (\%)} = [DOP_0]/[DOP_t] \times 100 \qquad (2)$$

Where $[Cl_0]$ is the number of moles of chlorine in the original flexible PVC and

$[Cl_t]$ is the number of moles of chlorine in the in the extracted solution after reaction time t. $[DOP_0]$ is the number of moles of plasticizer in the original flexible PVC and

$[DOP_t]$ is the number of moles of plasticizer in the extracted solution during after reaction time t.

	Thermal process	Frequency
Induction heating (heating of the metal)	Low frequency heating	50/60Hz
	High frequency heating	Several hundred KHz
Dielectric heating (heating of the insulator)	Dielectric heating	1～400KHz
	Microwave heating	0.3～300GHz

Table 2. Thermal processes and frequency

4. Results and discussion

An electric heater is generally used as the heat source of an autoclave. The external heating method heats the surface of an object with a heat source. With this method, the object is gradually heated from the outside to the inside according to the thermal conductivity of that object. In other words, heat is transferred from the surface in which the treatment vessel and electric heater come in contact. The heat is then sequentially propagated from the liquid to the object being heated. In contrast, internal heating by high-frequency dielectric heating by electromagnetic waves or microwave heating are intense heating methods where objects are heated from the inside then outward. This tends to be a highly efficient heating method since there is practically no heat escaping outside; the system delivers swift item heating, as we know from what a domestic microwave oven can do. Polarization takes place when a dielectric is exposed to an electric field, since charged carriers (electrons and ions) in a dielectric move around, while the dipoles try to face the direction of the electric field. Heating method and their associated frequency ranges are illustrated in Table 2.[20] In microwave electric fields, the polarity reverses 2.45 billion times per second. Heat is generated through intense rotation, collision, vibration and friction of the dipoles influenced by the oscillating electric field.[21] This exothermic reaction is expressed in Eq.3, showing the amount of electric power (P) consumed per unit area in the dielectric;

$$P = (E/d)^2 \times 5.56 \times 10^{-11} \times f \times \varepsilon r \times \tan\delta \, (W/m^3) \qquad (3)$$

Where E is the intensity of the electric field (V), d is the distance between electrodes (m), f is the frequency (Hz), εr is the relative permittivity, $\tan\delta$ is the dielectric tangent, and P is the electric power consumption per cubic meter (W/m^3).

Material	Tangent*δ (× 10)
Water	1570.0
Sodium Chloride	2400.0
Ethylene glycol	10000.0
Fused Quartz	0.6
Ceramic	5.5
Nylon66	128.0
Polyvinyl Chloride	55.0
Polyethlene	3.1
TeflonPFA	1.5

Table 3. Material loss factor (at 3GHz)

The product of εr and tanδ is called as loss coefficient, which is specific to each material.[20] and also changes with the temperature and frequency. According to Eq.3, we see that the level of heating energy increases when the intensity of the electric field, the frequency, and the loss coefficient increase.
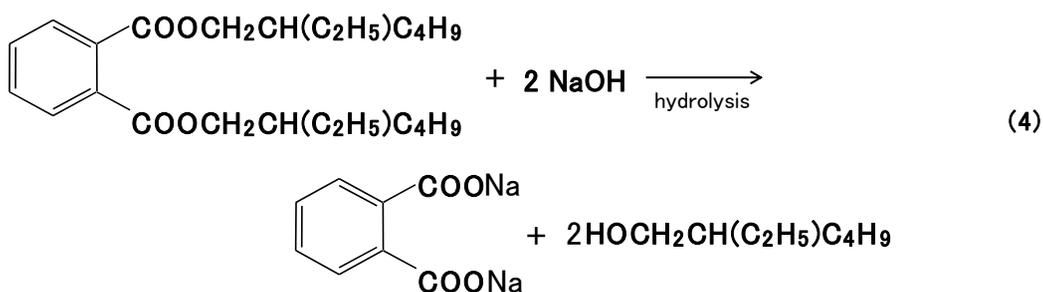
PVC shows asymmetries in polarization due to its molecular structure. Therefore, it is classified as a plastic with a polarity. Other examples include acrylonitrile butadiene styrene (ABS) resin, nylon, and polyvinyl acetate. As indicated in Table 3, plastic with a polarity have a larger loss coefficient; therefore, they easily absorb microwaves.[22] On the other hand, plastic without polarity, such as Teflon, polyethylene, and polypropylene, have a smaller loss coefficient; therefore, microwaves easily pass through them. For this reason, Teflon is used as a structural material when using microwaves, or as a heat- and chemical-resistant container for chemical experiments using microwaves. Polyethylene and polypropylene are used as containers for preserved food and meals that are to be heated, with regard to their heat- resistant properties. On the other hand, plasticizer is mixed with and coexists with flexible PVC. It does not form a chemical bond with PVC. Significant vibration and heat is generated between the molecules since plasticizer is mixed/coexists with PVC and because plasticizer itself absorbs microwaves.

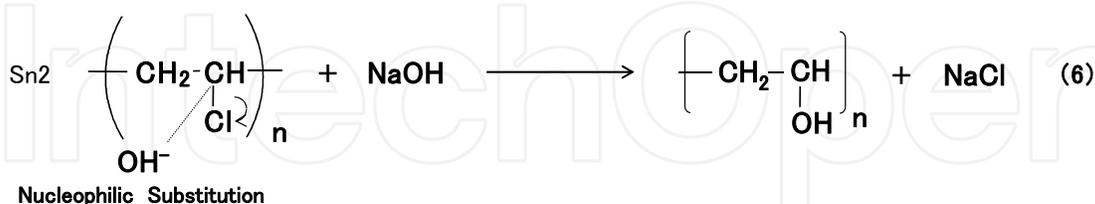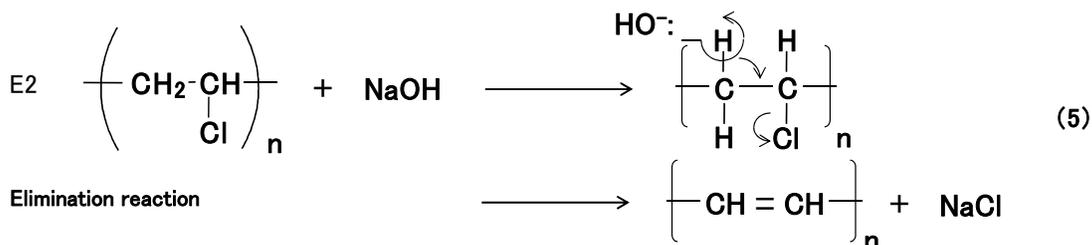As a result, the plasticizer and PVC are easier to separate.

It was discovered that deplasticization and dechlorination could take place separately by changing the reaction temperature. The purpose of this study was to separately isolate and recover extracted and chlorides in the same reaction solution in a way that the plasticizer and chlorides do not coexist, and to do this to the greatest extent possible by setting the reaction temperature at two different levels. We detected chloride ions, phthalate ions, isooctanol and hexanol in the solution extracted after the reaction.[7] The residue was yellow, brown, or black and was smaller in volume than the initial flexible PVC sample. It has been reported that when there are more than seven conjugated double bonds created by

PVC dechlorination, they absorb visible light, which makes dechlorinated PVC appear yellow, brown or black.[21] Under the initial temperature conditions to solely extract plasticizers, the plasticizer was hydrolyzed and extracted into phthalic acid and isooctanol, then extracted as sodium phthalate in the solution (Eq.4). At this point, no chloride ions were detected. Thus, it is conjectured that dechlorination has not yet taken place. Next, we detected chloride ions by raising the reaction temperature to the temperature condition to only perform the second level of dechlorination. Based on the detection of chloride ions, it was conjectured that PVC dechlorination selectively occurred according to the reaction temperature (Eps.5, 6). From the above findings, we found that it was possible to both extract plasticizer and dechlorinate PVC in high-temperature alkaline solution using microwave heating (internal heating) by simply changing the reaction temperature, as illustrated in the reaction process of Scheme 1.[7]

First reaction

$$\text{COOCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9$$

$$\text{COOCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9 \quad + \; 2\,\text{NaOH} \xrightarrow{\text{hydrolysis}} \tag{4}$$

$$\text{COONa}$$
$$\text{COONa} \quad + \; 2\,\text{HOCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9$$

Second reaction

$$\text{E2} \quad \left(\!\!\begin{array}{c}\text{CH}_2\text{-CH}\\ |\\ \text{Cl}\end{array}\!\!\right)_n + \text{NaOH} \longrightarrow \quad \text{HO}^-: \quad \left(\!\!\begin{array}{cc}\text{H} & \text{H}\\ \text{C} & \text{C}\\ \text{H} & \text{Cl}\end{array}\!\!\right)_n \tag{5}$$

Elimination reaction $\longrightarrow \left(\text{CH}=\text{CH}\right)_n + \text{NaCl}$

$$\text{Sn2} \quad \left(\!\!\begin{array}{c}\text{CH}_2\text{-CH}\\ |\\ \text{Cl}\end{array}\!\!\right)_n + \text{NaOH} \longrightarrow \left(\!\!\begin{array}{c}\text{CH}_2\text{-CH}\\ |\\ \text{OH}\end{array}\!\!\right)_n + \text{NaCl} \tag{6}$$

$$\text{OH}^-$$

Nucleophilic Substitution

When using conventional external heating sources, we found that both the extracted and removed chlorides coexisted in the reaction solution after deplasticizing and dechlorinating flexible PVC.[7,24] With our microwave-heating method, we found that it was possible to extract plasticizer and remove chlorides at different temperatures. First the plasticizer is extracted from NaOH solution. Then the same NaOH solution is heated at a higher reaction temperature to remove the chlorides. By using this method, we successfully removed the chlorides from PVC without mixing them with any plasticizer. We speculate that the reactions are dependent on reaction temperature. As a result, we can say that internal

heating using microwaves allows us to selectively and individually extract plasticizer and remove chlorides one after the other by simply changing the reaction temperature, which is not possible when using external heating sources such as conventional electric heaters. In the case of using the NaOH/EG solution, plasticizer that is mixed with flexible PVC will be easy to heat since EG (with high loss coefficient) can easily permeate it. Since the plasticizer is not chemically bonded with PVC, exposure to microwave radiation generates, powerful motion between molecules and generates heat. By separately heating the plasticizer and PVC, and by setting the reaction temperature at two different levels, we assume that it becomes easier to separate and extract the plasticizer.
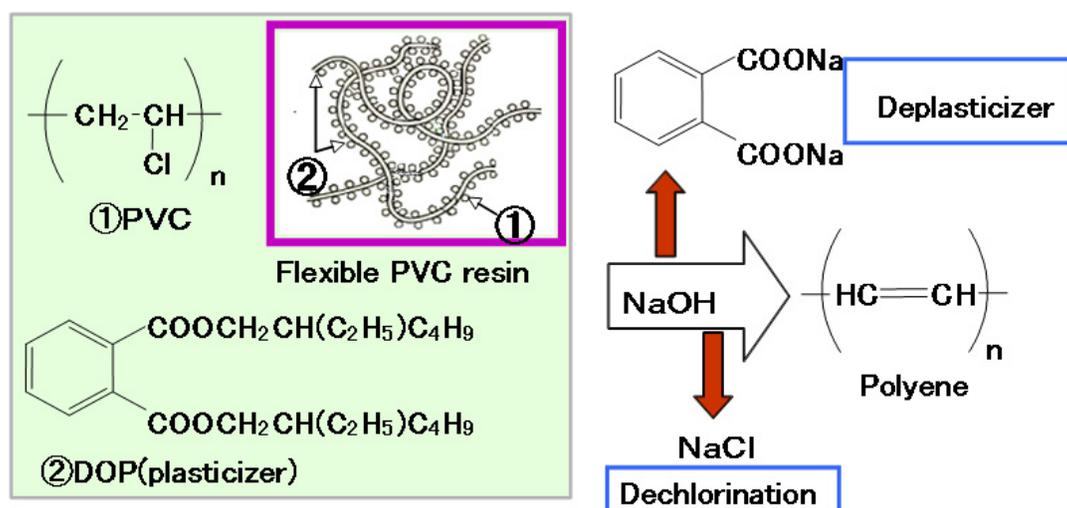
Scheme 1. Processing method of flexible PVC, DOP, dioctyl phthalate

4.1. Dehydrochlorination

Weight loss was measured when using 8mol/l NaOH solution at a reaction temperature between 150° and 250°C for a reaction time of 30min. The measured values are shown in Figure 5. The weight loss ratio was 24.4% at 150°C, 34.8% at 200°C, 62.5% at 225°C, and 71% at 250°C. Since the DOP plasticizer content was 29.7% of the total compound weight, 82% of DOP was hydrolyzed at 150°C and almost all was hydrolyzed and extracted at 200°C. What is more, since weight loss reached 71% at 250°C, this further change in weight indicates the removal of additives other than DOP and, mainly, the dechlorination of PVC. These results indicate that it is possible to selectively extract plasticizer and remove chlorides in a NaOH solution by changing the reaction temperature to achieve deplasticization and dechlorination. This suggests the possibility of inhibiting the generation of organic chloride compounds by extracting the plasticizer beforehand from the flexible PVC. The results of the dechlorination of flexible PVC tube using 2-16mol/l NaOH solution at a reaction temperature of 150°-250°C are shown in Figure 6. Our results indicate that the concentration of NaOH solution did not affect dechlorination, but the reaction temperature did greatly affect dechlorination. Flexible PVC has two levels of degradation that are dependent on

reaction temperature. Below 200°C, hydrolysis and extraction of DOP mainly took place, but dechlorination did not.
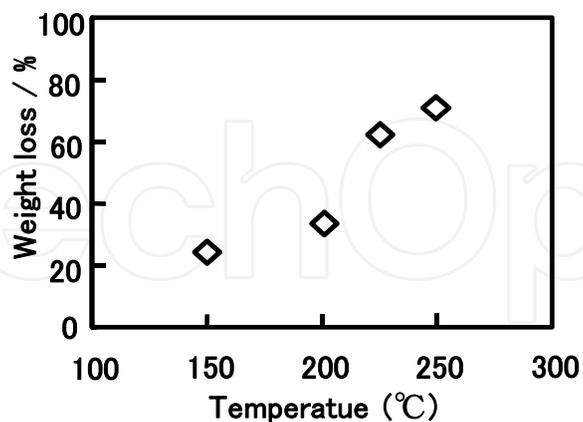

Figure 5. Effect of temperature on the weight loss in 8mol/L NaOH for 30 min by microwave heating
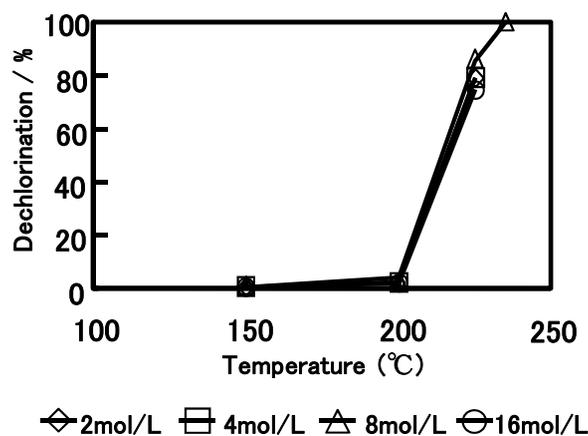

Figure 6. Dechlorination as a function of temperature and NaOH concentration for 30 min by microwave heating
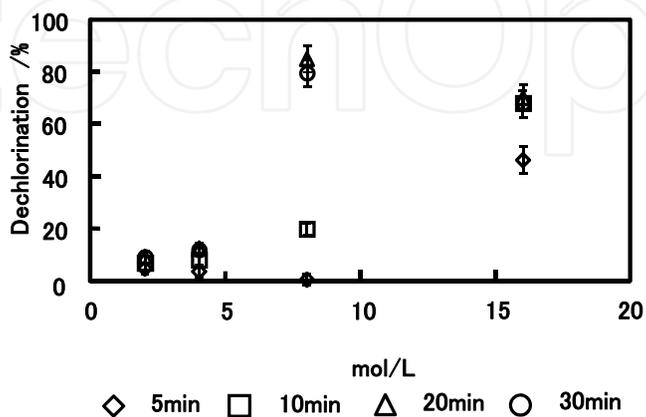

Figure 7. Dechlorination of flexible PVC as a function of NaOH concentration and reaction time at 225°C with microwave heating

It was assumed that once the DOP plasticizer was completely hydrolyzed and extracted, the microwaves rapidly promoted dechlorination, since the hydrolyzed DOP was in a state in which it could be absorbed by PVC chlorides. The results of dechlorination using 2-16mol/l NaOH solution at reaction temperature of 225°C for various reaction time are shown on Figure 7. In 2 and 4mol/l NaOH solution, there was no significant increase in dechlorination ratio, even when the reaction time was increased. In 8mol/l NaOH solution, the dechlorination ratio was 0% at 5min, 20% at 10min, 85% at 20min, and 80% at 30min, showing almost constant progress. In 16mol/l NaOH solution, the dechlorination ration reached 45% at 5min., however, the ration remained constant at 70% although the reaction time was extended. After DOP plasticizer was hydrolyzed and extracted, the tendency was for the flexible PVC sample to became smaller and decrease in surface area, as shown in the surfaces presented in Figure 8a-e. At 150°C, when DOP plasticizer was hydrolyzed and phthalic acid was extracted, it created micro-pores measuring roughly 3µm in diameter size (Figure 8b). The micro-pores grew in size as the reaction temperature was elevated. According to Figure 8d, micro-pores were formed of about 1-2µm in size overall as a result of rapid progress of dechlorination. It was also found that the sample reduced in size compared to the pre-reaction state of Figure 8a. Based on these states, the contact area with the NaOH solution was no longer sufficient. As a result, although the reaction time was extended, it resulted in delayed progress of dechlorination. Further, it may be considered that the dechlorination ratio did not improve or was not complete because the microwave output for internal heating was automatically controlled according to the liquid temperature of the NaOH solution.
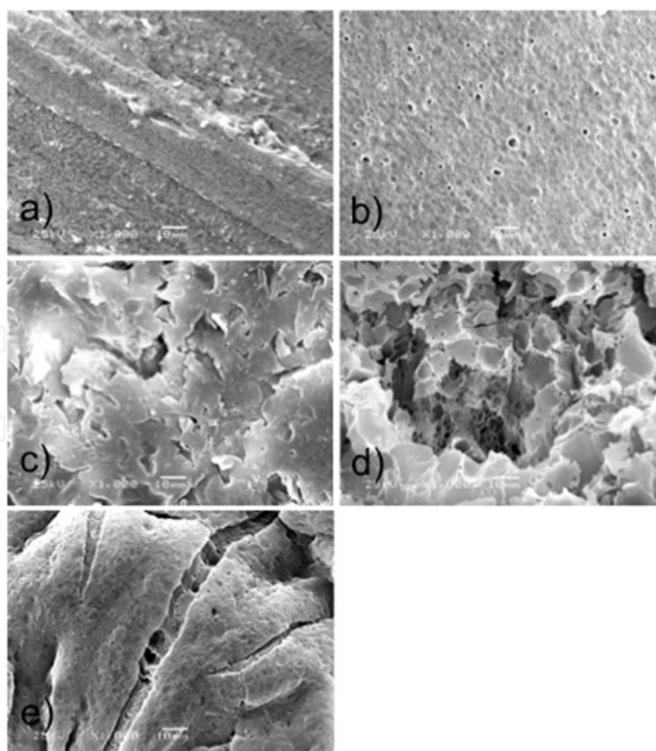
Figure 8. Scanning electron microscope images of residues from treatment of PVC with 8mol/l NaOH: a before reaction, b at 150°C, c at 200°C, d at 225°C, and e at 235°C

Table 4 illustrates the elemental analysis of the solid residue obtained after reactions in 8mol/l NaOH solution. As can be seen, the chlorine ratio was higher in the residue at 150°C than the sample that was used in our experiment. Based on the results described earlier, we know that the deplasticization ratio is 100% at this temperature. It is speculated that this is mainly due to hydrolysis of DOP plasticizer and extraction of phthalic acid. It is also obvious that the amount of chlorine in the residue decreased as the reaction temperature was elevated above 150°C. Although H/C is 1.62 in the residue formed at a reaction temperature of 150°C, this ratio tended to decrease as the reaction temperature was elevated, and H/C was 1.05 at 235°C a temperature at which 100% DOP plasticizer extraction and dechlorination is achieved. After dechlorination, H/C was close to 1.0, the level at polyene is generated. Therefore, this is indicative of the solid residue containing 96% polyene. It is conjectured that the remaining 4% was a result of the reaction substituting the OH group. When carrying out the reaction for the same time with external heating instead of microwave heating, we obtained the results shown in Figure 9. At a reaction temperature of 250°C when the plasticizer was 100% removed, 20% dechlorination had already occurred. This means that the reaction solution contained coexistence phthalic acid extracted from the plasticizer and chloride ions at the same time. This makes it difficult to separate them later. However, with microwave heating, there is only the need to change the reaction temperature to allow the plasticizer and chlorides to be recovered separately. On the other hand, in the case of NaOH/EG solution, we studied the weight loss of flexible PVC for NaOH concentrations in NaOH/EG solution of 0.5,1, and 2mol/l at reaction temperature between 100 and 160°C and a reaction time of 10 min. A maximum weight loss of 74.7 % was identified at 160°C. There was no difference in dehydrochlorination results up to 120°C, although the NaOH concentration was modified, and dehydrochlorination was about 8% in a 1mol/l NaOH/EG solution. The dehydrochlorination rate increased in the 1mol/l NaOH/EG solution when the reaction temperature rose above 130°C and reached a maximum rate99.7% at160°C (Figure 10). We presume that the DOP hydrolysis reaction mainly occurred up to 130°C, and suggest that the PVC dehydrochlorination reaction mainly occurred at temperature above 130°C. Based on these results, we found that dehydrochlorination was possible at temperature that were 50°C lower than conventional external heating systems. This indicates that EG permeates the PVC particle, and when directly heated, the EG loss coefficient is large, thereby making it easy to absorb microwaves. The NaCl created around the PVC particles further improved microwave absorption (Table 3), showing reaction-promoting effects. This potentiation supported a rapid start to dehydrochlorination and efficient progress of the procedure (Table 3).[11]

|	Content (wt%)			Atomic ratio	
	C	H	Cl	H／C	Cl／C
PVC*	51.6	6.8	35.7	1.56	0.23
150℃	42.3	5.8	48.8	1.62	0.4
225℃	84.4	7.8	6.2	1.1	0.03
235℃	88.1	7.8	N.D.**	1.05	–

*PVC : raw material, **N.D. : not detected

Table 4. Elemental analysis of residue formed at different temperatures

4.2. Removal of the plasticizer

The DOP plasticizer that present in flexible PVC is hydrolyzed in high-temperature alkaline solutions yielding phthalic acid and isooctanol that can be extracted from the solution. We studied the optimal reaction conditions to extract phthalic acid from DOP plasticizer.
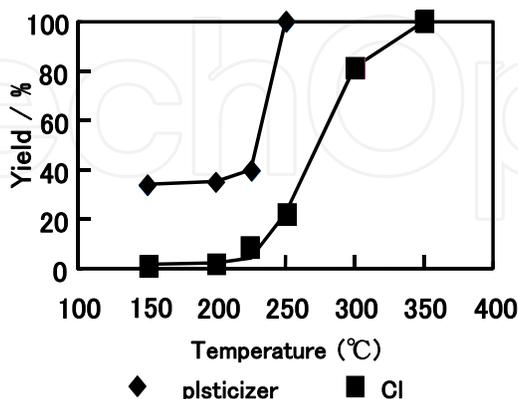

Figure 9. Effect of temperature on the yield of phthalic acid and Cl in 16mol/L NaOH solution using conventional heating
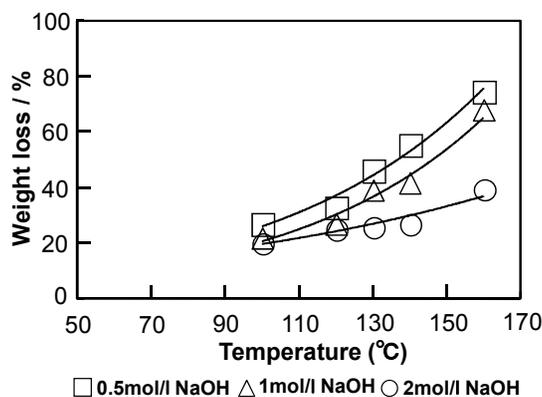
Figure 10. Effect of NaOH concentration on the weight loss from flexible PVC due to dechlorination and deplasticization on microwave heating for 10 min. Concentration of NaOH: squares, 0.5 mol/l; triangles, 1mol/l; circles, 2mol/l
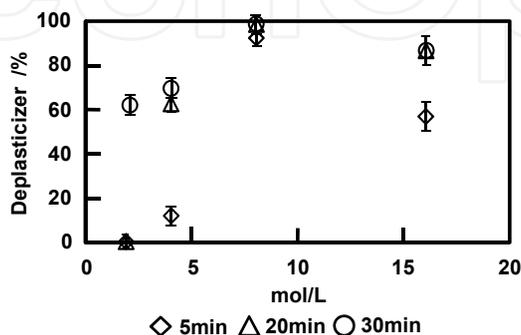
Figure 11. Deplasticization of flexible PVC as a function of NaOH concentration and reaction time at 150°C with microwave heating
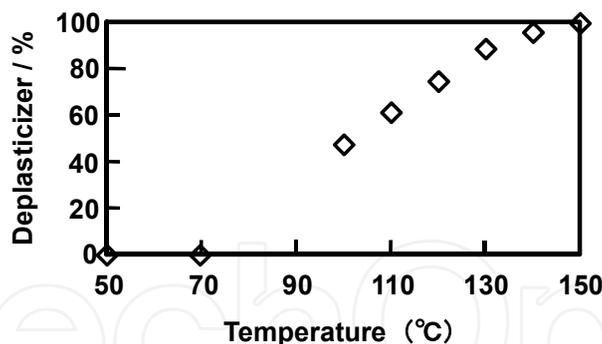
Figure 12. Deplasticization of flexible PVC as a function of temperature in 8mol/L NaOH for 30 min

We investigated the effects of NaOH solution concentration on the deplasticization ratio by microwave heating at a reaction temperature of 150°C for 30min (Figure 11). As can be seen, the recovery of phthalic acid from DOP plasticizer tended to be elevated at higher NaOH concentrations. The maximum recovery ratio was 63% in 2mol/l NaOH solution, 70 % in 4mol/l NaOH solution, 99% in 8mol/l NaOH solution, and 87% in 16mol/l NaOH solution. In 8mol/l NaOH, the recovery ratio was optimum. There was a tendency for the deplasticization ratio to drop when the concentration of NaOH solution increased further. As indicated in Figure 8b-e, when the plasticizer was eluted, the PVC sample became smaller. As a result, it was presumed that there was not enough contact with the NaOH solution at a high concentration. For this reason, there was not sufficient hydrolysis and the deplasticization ratio dropped as a result.

We studied the effects of reaction temperature on recovery ratio of phthalic acid in 8mol/l NaOH solution (Figure 12). The recovery ratio of phthalic acid was 0% at 50- 70°C. However, the recovery ratio of phthalic acid drastically increased when the reaction temperature exceeded 100°C, and reached 50% at 100°C and 100% at 150°C. This indicates that DOP plasticizer was hydrolyzed and extracted as sodium phthalate by microwave heating, since DOP plasticizer absorbed microwaves and effectively reacted with the NaOH solution.

Before the chemical reaction, the flexible PVC tube was translucent. At 70°C or lower, the color was the same as the raw material. However, at 100°C it turned light cream in color, and darkened as the temperature was elevated, finally turning orange at 150°C. This color change is speculated to be the result of an increase in double bonds due to some chlorides slightly escaping from the side chain of the PVC polymer.

The GPC results for molecular weight analysis of flexible PVC after treatment are shown in Table 5. Mn is the number-average molecular weight and Mw the weight-average molecular weight, expressed as shown inEq.7, when the number of molecules of component *i* with molecular weight *Mi* of a sample is *N* (i=1, 2, … q):

$$M_n = \sum_{i=1}^{q} M_i N_i \Big/ \sum_{i=1}^{q} N_i \quad M_w = \sum M_i^2 N_i \Big/ \sum_{i=1} M_i N_i \tag{7}$$

Mn and Mw showed a declining tendency with increasing temperature. This seems to indicate that the molecular weight decreased when the principal PVC chain broke. However, we believe there is a possibility that the residues after deplasticization can be recycled by mixing it with virgin PVC materials. In either case, there is a need for more detailed evaluation because this process results in product with a darker pigmentation. In the case of NaOH/EG solution, the effect was studied of NaOH concentration and reaction temperature on the extraction of plasticizer in NaOH/EG solution in the range 1-4mol/l at reaction temperatures between 100° and 160°C and a reaction time of 10 min. As a result, we found that the maximum plasticizer extraction effect was attained in 1mol/l NaOH/EG solution at a reaction temperature of 140°C and with a reaction time of 10 min. However, plasticizer extraction tended to drop as the NaOH concentration increased (Figure 13). This is presumed to be caused by the high NaOH surface tension making it difficult for the plasticizer and NaOH to sufficiently come into contact and thereby making it difficult to extract, or because DOP was assessed in terms of phthalate ions (and with the promotion of hydrolysis it might become impossible to detect phthalate ions). Figure 14 indicates the rate of extraction of plasticizer in 1mol/l NaOH/EG solution for a reaction time of 10 min and different reaction temperature. The highest extraction rate was 98 % in 1mol/l NaOH/EG solution at a reaction temperature of 160°C and a reaction time of 10 min (Figure 14). It is also indicated that the 1mol/l NaOH/EG for a reaction time of 10 minutes (Figure 14). It is indicated that the plasticizer hydrolyzed to form phthalic acid on microwave heating.
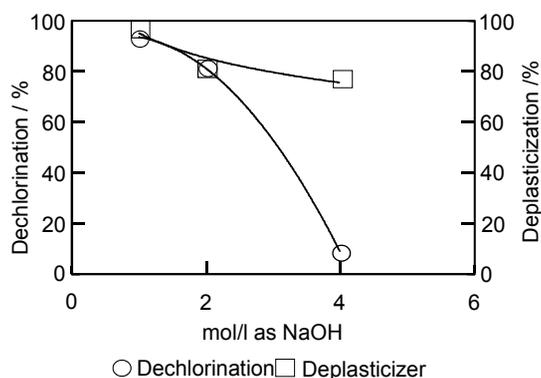
Figure 13. Extraction of plasticizer (*squares*) and dechlorination (*circles*) as a function of NaOH concentration using microwave heating at 190°C for 10min
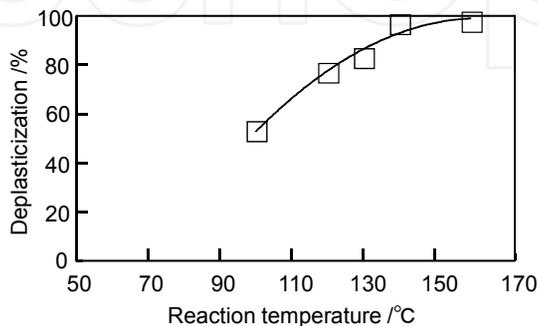
Figure 14. Extraction of plasticizer as a function of the reaction temperature in 1mol/l NaOH/EG using microwave heating for 10 min

	Mn	Mw
Before the reaction	114K	210K
100° C	111K	205K
110° C	108K	205K
120° C	109K	204K
130° C	108K	202K
140° C	104K	202K
150° C	96K	190K

Mn, number average molecular weight; Mw, weight average molecular weight K=10^3

Table 5. Molecular weight determination results from gel permeation chromatography (GPC)

4.3. Effect of NaCl in promoting heating

Let us consider water to illustrate the dynamics of the loss coefficient. When water gets hotter, the loss coefficient gets smaller (Table 6), which indicates lower microwave absorption. When looking at the NaOH or NaOH/EG solution and flexible PVC composition in the reactor vessel, we find that the constituents, NaOH, EG, PVC, and plasticizer, have different abilities to absorb microwaves. When the reaction solution and reagent temperature rises, making it more difficult to absorb microwaves their respective potentiating effects will promote extraction of the plasticizer. What is more, the HCl released by PVC dehydrochlorination reacts with NaOH to become NaCl, As a result, the loss coefficient increases; the NaCl created around the PVC absorbs microwaves and promotes the rise in inside temperature. This makes it possible to effectively dehydrochlorination PVC.

Temperature (°C)	Tangent*δ (× 10)
15.0	2050
25.0	1570
35.0	1270
45.0	1060
55.0	890
65.0	765
75.0	660
85.0	547
95.0	470

Table 6. Effect of temperature on the dissipation factor of water at 3GHz

5. Conclusion

In this study, we investigated how flexible PVC decomposed in a high-temperature alkaline solution heated by microwave to learn about the hydrolysis and extraction of DOP plasticizer and dechlorination process. We came to the following conclusion as a result of the study.

1. We found a way to selectively hydrolyze/extract DOP plasticizer and remove chlorides using high-temperature alkaline solutions by internally heating flexible PVC (made of defined sample components) using microwave heating.

2. The suitability of microwave heating was acknowledged. It was also possible to separately deplasticize and dechlorinate the sample by changing the reaction temperature or the reaction control temperature. When external heating was applied using a general electric heater (Figure 9), plasticizer and chlorides were found to coexist in solution since chloride removal takes place at 250°C, the reaction temperature required to extract 100% of the plasticizer. This requires an additional step to individually separate the plasticizer and chlorides. However, using microwave heating, it is possible to separately extract plasticizer and remove chlorides by simply controlling or changing the reaction temperature without the plasticizer and chlorides coexisting in the reaction solution.

3. We believe that it is possible to use microwave heating to extract 100% of the plasticizer with no dechlorination occurring by changing/controlling the reaction temperature. The residues in this case can be reused as materials recycled into PVC.

4. According to studies using external heating, the reaction temperature for deplasticization was 250°C and for dechlorination it was 350°C, using the same flexible PVC samples in a 16mol/l NaOH solution and using external heating with an autoclave with an electric heater. However, by using microwave heating as presented in this study, 100% deplasticization is possible at 150°C and 100% dechlorination is possible at 235°C in a 8mol/l NaOH solution, which was only half the concentration required when using an external heating sources.

5. It was found that microwave heating with NaOH/EG was suitable for flexible PVC dehydrochlorination and extraction of plasticizer.

6. Using an NaOH/EG solution, it was found that microwave heating possibly allowed the reaction temperature to be lowered from 190°C to 160°C, and shortened the reaction time from 60 to 10 min.

7. When microwave heating was used as a heating source and NaOH/EG solution was used, it was possible to lower the concentration of NaOH to 1 mol/l instead of the conventional 8 mol/l solution used to remove the chlorides from PVC. Further, the reaction time was also shortened from the conventional 30 min to 10 min, and thus, this procedure is considered as energy saving method.

Author details

F. Osada
Analysis Solution Engineering Section,
2nd Engineering Department Higashimurayama Plant Industrial Division, NIKKISO, LTD., Japan

T. Yoshioka
Graduate School of Environmental Studies, Tohoku University

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