Synthesis of hydroxyapatite with the mechanochemical treatment products of PVC and CaO

J. Kano, Q. Zhang, F. Saito, Michel Baron, Ange Nzihou

SYNTHESIS OF HYDROXYAPATITE WITH THE MECHANOCHEMICAL TREATMENT PRODUCTS OF PVC AND CaO

J. KANO[1]*, Q. ZHANG[1], F. SAITO[1], M. BARON[2] and A. NZIHOU[2]

[1]*IMRAM, Tohoku University, Sendai, Japan*
[2]*Ecole des Mines d'Albi Carmaux, Albi, France*

Polyvinyl chloride (PVC) is one of the most excellent plastic materials because of its chemical stability. It is widely used in many fields. Burning PVC generates HCl gas which must be treated properly. We have developed a non-thermal process for dechlorinating of PVC, and this process is composed of two steps: The first step is to grind the PVC waste with an active grinding additive such as CaO, leading to transformation of organic chlorine into water soluble chloride mechanochemically. The second step is to remove the formed chloride from the milled product by washing with water. The solid residue after filtration has been already dechlorinated, so that it can be recycled safely as fuel. When the filtrate is mixed with solution which contains phosphate ion PO_4^{2-}, hydroxyapatite (HAp) fine particles formed. It is known that the precipitate (HAp) formed has a sorption ability for heavy metals such as Pb^{2+}.

Keywords: PVC; dechlorination; hydroxyapatite; heavy metals; mechanochemical reaction.

INTRODUCTION

Polyvinyl chloride (PVC) is well known and widely used not only in commodities but also industrial in materials in construction, agriculture, medical fields and so on, since it has excellent properties such as good chemical stability and cost performance. Used PVC products, when not recycled become wastes that must be disposed of adequately. Four disposal methods for PVC wastes have been mainly proposed so far: (1) The first method is to use PVC waste as a raw material for blast furnace (Nemoto, 1999); (2) the second is thermal decomposition (Tsuruga, 1999); (3) the third is to use it as a fuel (Ueno, 1999); (4) the fourth is to use it as a source for liquefying technology (Ogata, 1999). These are all possible, however, operational cost and maintenance of the equipments represent drawbacks in implementation.

The authors have proposed an alternative and novel process for dechlorinating a PVC waste by its grinding with a reagent such as CaO, followed by water rinsing (Zhang *et al.*, 1999; Saeki *et al.*, 2001; Mio *et al.*, 2002; Inoue *et al.*, 2004). The grinding causes mechanochemical reaction between PVC and CaO, which forms water soluble CaOHCl. The CaOHCl can be separated from the product by washing with water, so that this process results in the emission of a amount of CaOHCl solutions. This has a possibility to react with phosphate to form hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$), which is one of the most attractive materials for sorption of heavy metals such as Zn, Cd and Pb (Chen *et al.*, 1997; Ma *et al.*, 1994; Takeuchi and Arai, 1990; Takeuchi *et al.*, 1988; Bailliez *et al.*, 2004). As for the solid residue, it could be used safely as a fuel because most of chlorine has been removed.

The main purpose of this paper is to propose pre-treatment of PVC wastes by a mechanochemical method and their recycling of decomposition products.

EXPERIMENTAL

Mechanochemical Reaction Between PVC and CaO

A PVC powder sample used in this experimental was a chemical reagent (Wako Chemical Co., Ltd, Japan), and its mean particle diameter is about 133 μm. The molecular weight is about 55 000. CaO was prepared by heating calcium hydroxide [$Ca(OH)_2$ (Wako Chemical Co., Ltd, Japan)] powder at 800°C, and its mean particle diameter is about 1.8 μm. The PVC sample was mixed with the CaO one so that the molar ratio of CaO to Cl in the PVC sample is unity, and 3.0 g of the mixture was ground in air by using a planetary ball mill (P-7, Fritsch, Germany). The mill is composed of a pair of pots having 50 ml in volume. The speed was set at 700 rpm. The grinding time was varied up to 12 h, and the ground product was removed

Correspondence to: Dr J. Kano, IMRAM, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan.
E-mail: kano@tagen.tohoku.ac.jp

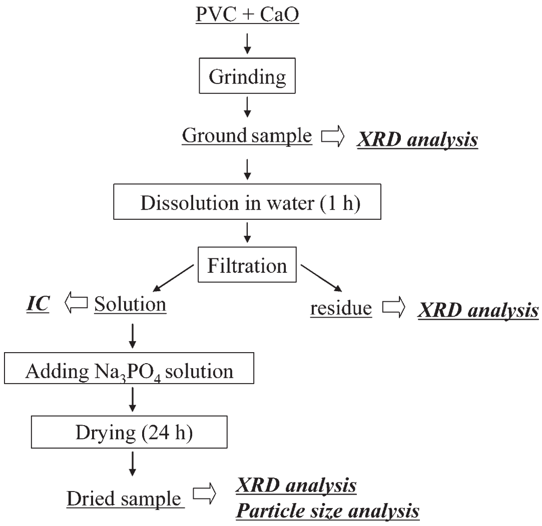

Figure 1. Flow chart of the sample preparation of and the characterization.

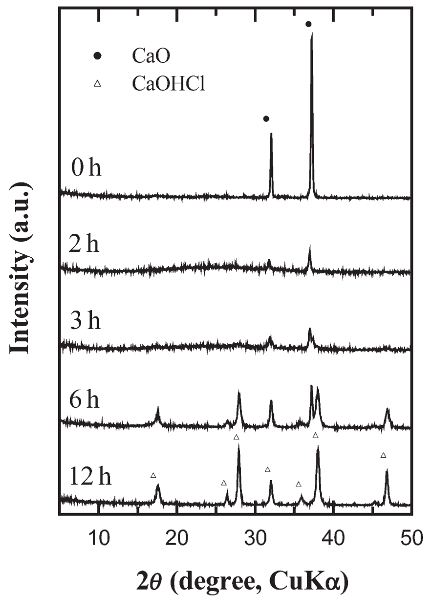

Figure 2. XRD patterns of samples ground for various periods of time.

completely from each pot after grinding. Of the ground product, 1.0 g was dispersed in 100 ml-distilled water by stirring for 1 h to dissolve soluble compounds formed mechanochemically in the ground sample, subsequently, it was filtered to separate filtrate from the solid. Total volume of the filtrate was set to 250 ml.

Synthesis of Hydroxyapatite (HAp)

A method for formation of HAp fine particles in suspension is as follows: first of all, 0.02 mol l^{-1} Na_3PO_4 (Aldrich, Japan) solution was prepared. Then 250 ml of Na_3PO_4 solution was mixed with the filtrate (12-h-ground sample) in the same volume in an ambient air. pH value of the Na_3PO_4 solution was measured as 11.8 and that of the solution after mixing with the filtrate was 11.7. The filtration was done with a vacuum pump and the powder sample was dried at an oven for 24 h at 100°C.

The samples were characterized by X-ray diffraction (XRD) analysis (RAD-B system, Cu–Kα, Rigaku, Japan), and the concentration of chlorine ion in the solution was determined by an ion chromatograph (IC) (LC10 series, Shimadzu Co., Ltd, Japan). The experimental procedure is shown in Figure 1. The particle size was measured with a laser diffraction particle analyzer (Microtrac MT33000EX, Nikkiso, Japan). The morphology of the sample was observed with SEM (S-4100L, Hitachi Co., Ltd, Japan).

RESULTS AND DISCUSSION

Figure 2 shows XRD patterns of the PVC–CaO mixtures ground for various periods of grinding time. The intensity of peaks corresponding to CaO is decreasing with an increase in the grinding time. New peaks, which correspond to CaOHCl, appear after 6-h grinding, and their intensities go up. This indicates that mechanochemical reaction between PVC and CaO took place, and that CaOHCl formed as monomer expression given by equation (1):

$$[CH_2CHCl]_n + CaO \rightarrow CaOHCl + [CH=CH]_m \quad \text{(n,m: polymerization degree, n > m)} \tag{1}$$

The peaks corresponding to CaO disappear after 12-h-grinding. This reason why could be that most of CaO convert to CaOHCl or that CaO loses crystallinity. According to the previous work (Zhang *et al.*, 1999; Inoue *et al.*, 2004), the double bonds in the ground mixture have been confirmed by FT-IR analysis. It is clearly observed from the pattern of the solid residue after filtration that CaOHCl has been removed from the ground mixture by washing with water, being concentrated in the filtrate (Figure 3). The peaks of $CaCO_3$ are observed in Figure 3, due to the carbonation of unreacted CaO during the operation.

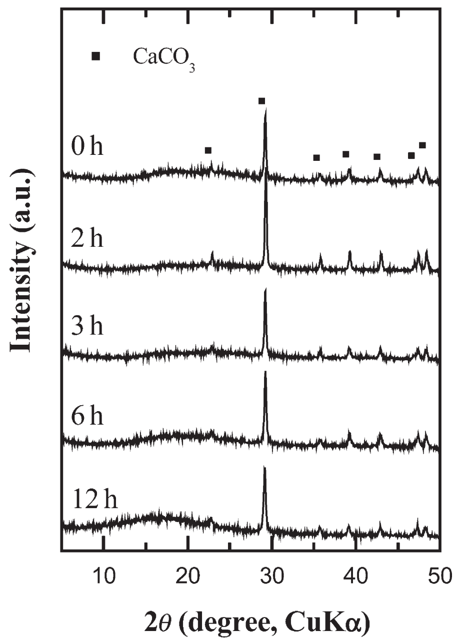

Figure 3. XRD patterns of ground samples after washing with water (solid residue).

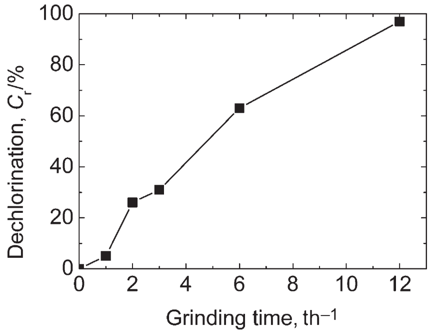

Figure 4. Change in the dechlorination with grinding time.

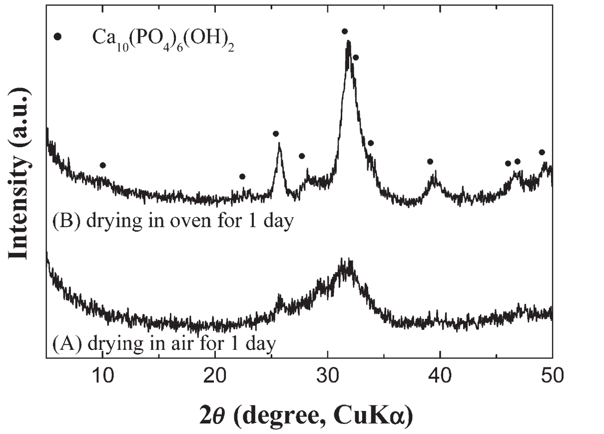

Figure 5. XRD patterns of the sediments dried (A) in air and (B) in oven at 100°C.

Figure 4 shows change in the dechlorination of PVC with grinding time. The dechlorination increases with an increase in grinding time, and almost reaches 100% after 12-h-grinding.

XRD patterns of precipitate formed in the solution after mixing the two CaOHCl (12-h-gound sample) and Na_3PO_4 solutions is shown in Figure 5. One is the powder dried in air (A) and the other the dried one at 100°C in an oven (B). It is difficult to identify the powder (A) dried in air to be HAp, while the particles (B) dried in the oven is identified as HAp. It is therefore conformed that the composition of the powder formed from the solutions is HAp, and the total reaction between the two components in the solution is given as follows:

$$10CaOHCl\ (l) + 6Na_3PO_4\ (l) = Ca_{10}(PO_4)_6(OH)_2\ (s) + 10NaCl\ (l) + 8NaOH\ (l) \quad (2)$$

Figure 6 shows a cumulative size distribution curve of HAp particles dried in air. A SEM photograph of the HAp particles dried at 100°C in an oven was also shown in this figure. The curve clearly shows that the size of particles ranges from about 1 to 100 μm and the mean particle size is about 15 μm. Thus, CaOHCl in the wastewater emitted from the mechanochemical dechlorination process of PVC using CaO as a reactant can react with PO_4^{3-}, forming HAp fine particles in the solution.

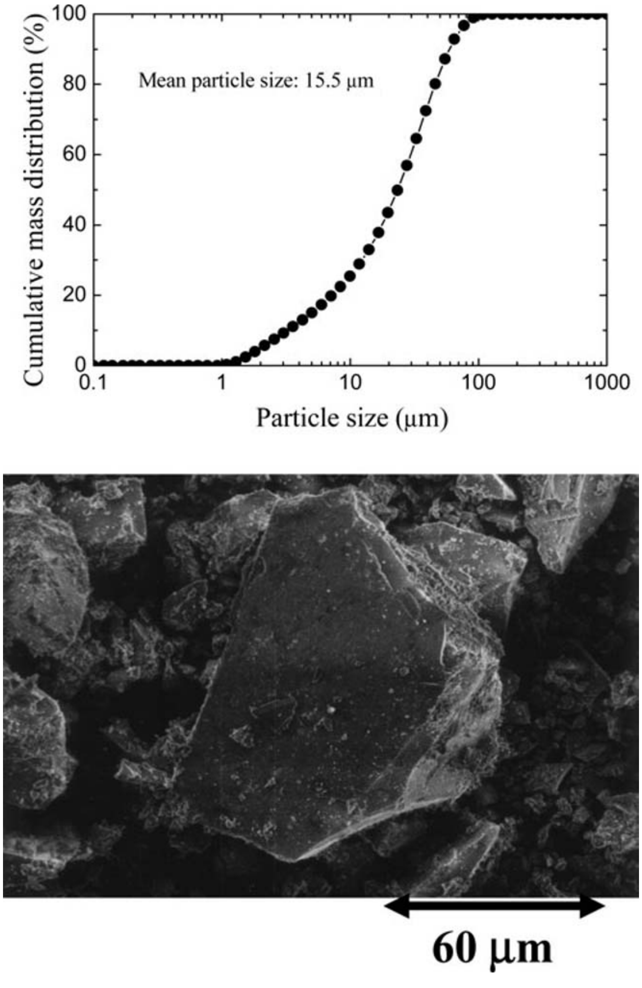

Figure 6. Size distribution curve and SEM photograph of HAp.

CONCLUSION

A non-thermal process for dechlorinating polyvinyl chloride (PVC) has been presented in this paper, and this process is composed of two steps: one is to grind the PVC waste with CaO, and the second one is to remove the formed chloride from the ground mixture by washing with water. The residue after filtration has been already dechlorinated, so that it can be recycled safely as fuel. The formed chloride reacted with PO_4^{3-} and hydroxyapatite (HAp) was formed.

REFERENCES

Bailliez, S., Nzihou, A., Bèche, E. and Flamant, G., 2004, Removal of lead (Pb) by hydroxyapatite sorbents, *Trans IChemE, Part B, Process Safe Env Prot*, 82(B2): 175–180.

Chen, X., Wright, J.V., Conca, J.L. and Peurrung, L.M., 1997, Effect of pH on heavy metal soption on mineral apatite, *Environ Sci Technol*, 31: 624–631.

Inoue, T., Miyazaki, M., Kamitani, M., Kano, J. and Saito, F., 2004, Mechanochemical dechlorination of PVC by co-grinding with various metal oxides, *Advanced Powder Technology*, 15: 215–225.

Ma, Q.Y., Logan, T.J. and Traina, S.J., 1994, Effect of NO^{3-}, Cl^-, F^-, and CO^{3-} on Pb^{2+} immobilization by hydroxyapatite, *Environ Sci Technol*, 28: 408–418.

Mio, H., Saeki, S., Kano, J. and Saito, F., 2002, Estimation of mechanochemical dechlorination rate of poly(vinyl chloride), *Environ Sci & Technol*, 36: 1344–1348.

Nemoto, K., 1999, Enkabiniru no Koro Genryoka risaikuru Gijutsu, in *Haienkabiniru no Datsuensoka Risaikuru Gijutsu*, 79–93 (NTS, Tokyo, Japan).

Ogata, H., 1999, Enkabiniru wo Fukumu Haipurasuchikku no Yukagijutu, in *Haienkabiniru no Datsuensoka Risaikuru Gijutsu*, 95–114 (NTS, Tokyo, Japan).

Saeki, S., Kano, J., Saito, F., Shimme, K., Masuda, S. and Inoue, T., 2001, Effect of additives on dechlorination of PVC by mechanochemical treatment, *J of Mater Cycles Waste Manag*, 3: 20–23.

Takeuchi, Y. and Arai, H., 1990, Removal of coexisting Pb^{2+}, Cu^{2+} and Cd^{2+} ions from water by addition of hydroxyapatite powder, *J Chem Eng, Japan*, 23: 75–80.

Takeuchi, Y., Suzuki, T. and Arai, H., 1988, A study of equilibrium and mass transfer in processes for removal of heavy-metal ions by hydroxyapatite, *J Chem Eng, Japan*, 21: 98–100.

Tsuruga, S., 1999, Enkabiniru no Netsubunkai Gijutu, in *Haienkabiniru no Datsuensoka Risaikuru Gijutsu*, 61–77 (NTS, Tokyo, Japan).

Ueno, A., 1999, HaikiPVC no Kanshikishori to Ensogasu no Kaishuu Gijutsu, in *Haienkabiniru no Datsuensoka Risaikuru Gijutsu*, 23–43 (NTS, Tokyo, Japan).

Zhang, Q., Saito, F., Shimme, K. and Masuda, S., 1999, Dechlorination of PVC by a mechanochemical treatment under atmospheric condition, *J Soc Powder Technol Japan*, 36: 468–473.