

# Mechanochemical decomposition of PVC by using $\text{La}_2\text{O}_3$ as additive

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Received 6 March 2006; received in revised form 4 April 2006; accepted 6 April 2006

Available online 22 April 2006

## Abstract

A polyvinyl chloride (PVC,  $[-\text{CH}_2-\text{CHCl}-]_n$ ) sample was ground with one of the following oxide samples, lanthanum oxide ( $\text{La}_2\text{O}_3$ ) and calcium oxide (CaO), as a reference, to investigate its mechanochemical (MC) decomposition. According to the XRD patterns for the ground products, peaks of lanthanum oxy-chloride,  $\text{LaOCl}$  which is water insoluble, were observed to appear in the patterns of the mixture samples at a molar ratio of (PVC:  $\text{La}_2\text{O}_3 = 1:2$ ) and (1:4), after 20 min grinding, while the patterns of the ground PVC–CaO mixtures show the formation of  $\text{CaOHCl}$ , which is water soluble, in the products after 2 h grinding. TG patterns taken for the PVC– $\text{La}_2\text{O}_3$  mixtures ground for different periods of time do not indicate significant weight loss in the range from 200 to 300 °C, and this suggests that  $\text{La}_2\text{O}_3$  is more effective additive than CaO in the MC decomposition for PVC. FT-IR patterns for organic phases in the ground mixture show the reduction of C–Cl bindings in the PVC structure. The MC reaction between PVC and  $\text{La}_2\text{O}_3$  is accompanied by the formation of C–O single bonds, to form  $\text{LaOCl}$ , which is insoluble in water at ambient condition. This is the reason why the yield of Cl extracted by the water leaching reaches only less than 50%, while it reaches almost 100% in the yield of Cl from the PVC–CaO mixture ground for 2 h or more.

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**Keywords:** Mechanochemistry; Grinding; Polyvinyl chloride; Lanthanum oxide; Lanthanum oxy-chloride

## 1. Introduction

Polyvinyl chloride plastics (PVC) are well known and most widely used as vinyl plastic and is easily recognized that an enormous amount of PVC has ended up as waste material after the usage. Since more than half of weight in PVC contains chlorine (56.7 wt.%), it causes a serious environmental problem when it is burned out, even if as fuel. Combustion results in emission of harmful gases such as hydrochloride and harmful substances such as dioxins. It is therefore required that safe and novel methods for disposing the waste PVC to prevent air and soil pollution would be developed.

Recently, mechanochemical (MC) decomposition of these substances has attracted much attention because of the easy operation and evident merit for the disposal of vast amount of samples contaminated by chlorinated polymers in quite a low concentration. Inorganic compounds such as CaO,  $\text{CaCO}_3$ , MgO, ZnO,  $\text{Ca}(\text{OH})_2$ , KOH, NaOH,  $\text{LiCoO}_2$  and others have been investigated and these additives have shown to decompose target

samples effectively. From the additives investigated [1–8], complete decomposition of PVC was achieved with CaO within 2 h of grinding. Under similar experimental conditions, more than 95% of Cl in PVC was removed by  $\text{CaCO}_3$  and  $\text{Ca}(\text{OH})_2$  in 4 and 12 h, respectively. Other additives also gave lower results when compared to CaO. According to these literatures, when CaO is ground with the chlorinated substance, mechanically induced solid-state reactions takes place to transform chlorine in the organic chemicals and polymers into the inorganic chloride, achieving MC decomposition. However, the time needed is quite long in order to complete the reaction of MC decomposition of organic polymers.

There exists the need to improve the reaction efficiency. The analysis of functions for grinding and designing an ideal mill to exhibit a high grinding efficiency are worth consideration, but not easy to realize soon. Selecting new additives for the decomposition of chlorinated compounds is another route and has been discussed by various researchers [4–6,8]. Lee and co-workers [9,10] report their findings on the mechanochemical synthesis of  $\text{LaOF}$  from poly(vinylidene fluoride) and  $\text{LaOX}$  ( $\text{X}=\text{Cl}, \text{Br}$ ) from  $\text{LaCl}_3$  and  $\text{LaBr}_3$  using  $\text{La}_2\text{O}_3$  as a rare earth oxide additive. Use of  $\text{La}_2\text{O}_3$  to capture Cl from PVC during decomposition by heating is reported by Matsusaka and co-workers [11].

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This paper demonstrates the effect of lanthanum oxide ( $\text{La}_2\text{O}_3$ ) as an additive to decompose PVC and discusses the reaction mechanisms during the MC reaction.

## 2. Experimental

### 2.1. Samples

PVC  $[-\text{CH}_2-\text{CHCl}-]_n$  sample used in this experiment was a chemical reagent with original particle sizes from about 40 to 300  $\mu\text{m}$ , and its mean particle size is about 130  $\mu\text{m}$ . Chemical reagents of  $\text{La}_2\text{O}_3$  (purity = 99.5%) was selected as an additive for the decomposition of PVC sample. The original particle sizes of the  $\text{La}_2\text{O}_3$  was ranged from 5 to 176  $\mu\text{m}$ , and its mean particle size is about 44  $\mu\text{m}$ . Chemical reagents of CaO (purity = 98%) was also used as an additive for the decomposition of PVC sample. The average particle size of the CaO powder was ranged from 1 to 300  $\mu\text{m}$  and the mean particle size was about 84  $\mu\text{m}$ . All chemical reagents were supplied from Wako Chemicals Co., Ltd., Japan and their sizes were measured by a particle size analyzer (PSA-Microtrac MT300).

### 2.2. Mechanochemical reaction and water leaching

The PVC sample was mixed with  $\text{La}_2\text{O}_3$  at 1:0.5, 1:1, 1:2 and 1:4 in molar ratio and the mixture of 3.0 g was subjected to grinding in ambient condition by a planetary ball mill (Pulverisette—7, Fritsch, Germany) for different periods of time and at a mill rotational speed of 780 rpm. Mill pots (45  $\text{cm}^3$  inner volume) made of steel with seven steel balls of 15 mm diameter were used for the grinding. From the ground mixtures of PVC- $\text{La}_2\text{O}_3$ , 0.5 g samples were dispersed in 100 ml distilled water for 1 h to extract chlorine from the formed compounds, mainly  $\text{LaOCl}$  and  $\text{La}(\text{OH})_3\text{Cl}$  from low molar ratios. The suspensions were filtered and the solid residues were washed with 50 ml distilled water followed by drying in oven at 353 K for 24 h. The filtrates as well as the solid residues were characterized by several analytical methods, described in the following section.

## 3. Characterization

X-ray diffraction (XRD) analysis (Rigaku, RINT-2200/PC system, Cu  $\text{K}\alpha$ ) was conducted for the ground and washed samples as well as the starting mixture to determine their phases and observe changes in phase formations. Thermo-gravimetric analysis was conducted by a TG/DTA analyzer (Rigaku—Thermo plus TG-8120) at a heating rate of 10 K/min in one of air or argon gas at a flowrate of 150  $\text{ml min}^{-1}$  to monitor decomposition profile of PVC in the ground mixture. Weight of sample for TG analysis was fixed at 10.0 mg. A Fourier transform infrared spectrometer (FT-IR) (DIGILAB EXCALIBUR SERIES, FTS-3000) was used to analyze the chemical species near the surface of ground powder particles using KBr as a diluent. A liquid ion chromatograph instrument (Shimadzu L10 Series) was used to determine the concentration of chlorine in the filtrate.

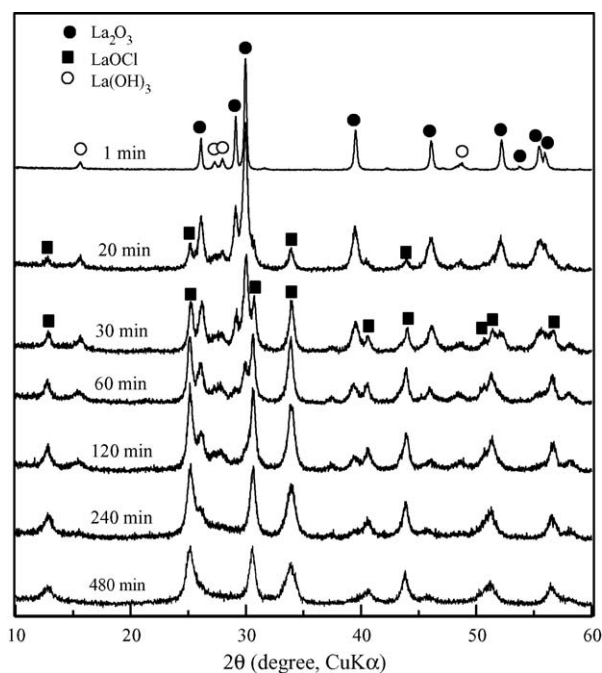


Fig. 1. XRD patterns of PVC  $\text{La}_2\text{O}_3$  [1:2] milled for different times at a mill rotational speed of 780 rpm.

## 4. Results and discussion

### 4.1. MC reaction between PVC and $\text{La}_2\text{O}_3/\text{CaO}$

Fig. 1 shows XRD patterns of the mixture of PVC: $\text{La}_2\text{O}_3$  [1:2] ground at 780 rpm for different periods of time. The intensity of the peaks of  $\text{La}_2\text{O}_3$  in the patterns of the mixtures is observed to decrease as the grinding progresses. On the other hand very weak new peaks of  $\text{LaOCl}$  (Tetragonal, JCPDS No. 34-1494) appear in the patterns ground for 20 min due to dechlorination reaction and their intensity becomes clear in the range from 30 min to 8 h. Fig. 2 shows XRD patterns of the mixture of PVC: $\text{La}_2\text{O}_3$  at 1:4 in molar ratio ground at 780 rpm for different periods of time. The intensity of the peaks of  $\text{La}_2\text{O}_3$  is observed to decrease rapidly and reduced to amorphous phase as grinding progresses from 2 to 8 h. Weak new peaks of  $\text{LaOCl}$  appear in the patterns ground for 20 min and remain consistent up to 1 h of grind and then reduced to amorphous phase as grinding progresses from 2 to 8 h. This may be attributed to further reaction among un-reacted  $\text{La}_2\text{O}_3$ , oxidized carbon during the grinding and formed  $\text{LaOCl}$ . At a molar ratio of [1:1],  $\text{LaOCl}$  peaks were observed after 1 h grinding and  $\text{La}(\text{OH})_2\text{Cl}$  (Monoclinic, JCPDS No. 85-0839) peaks were observed after 3 h grinding for the PVC- $\text{La}_2\text{O}_3$  mixture at 1:0.5 in molar ratio. Detection of  $\text{LaOCl}$  is delayed further when the mill rotational speed is reduced.

Fig. 3 shows XRD patterns of the mixture of PVC:CaO at 1:2 in molar ratio ground at 780 rpm for different periods of time. The intensity of the peaks of CaO in the patterns of the mixtures is observed to decrease as the grinding progresses. On the other hand, very weak new peaks of  $\text{CaOHCl}$  (Hexagonal, JCPDS No. 36-0983) appear in the patterns ground for 2 h due to

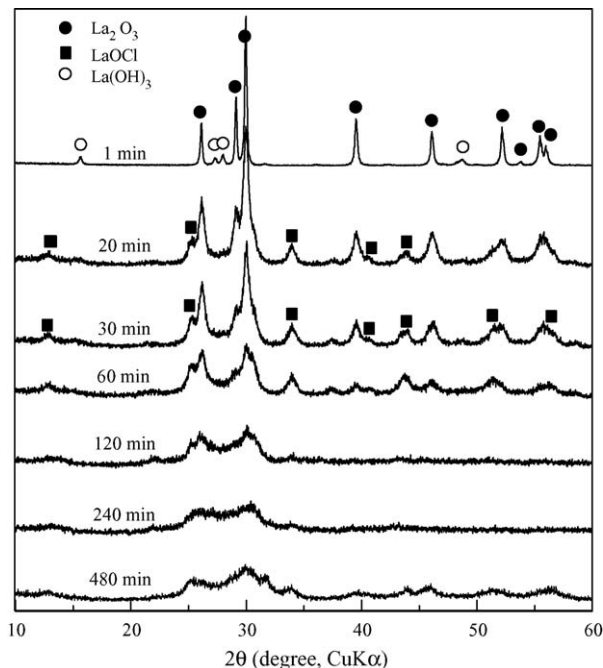


Fig. 2. XRD patterns of PVC and  $\text{La}_2\text{O}_3$  [1:4] milled for different times at a mill rotational speed of 780 rpm.

dehydrochlorinating reaction and their intensity becomes clear in the range from 3 to 8 h. When the (PVC:CaO) molar ratio is decreased to [1:4] and ground for different times at 780 rpm, no new peaks of CaOHCl is observed but only a decrease of intensity of CaO patterns. Amount CaOHCl may be below detection limit.

From the XRD patterns, it is found that the MC reaction takes place to form LaOCl for PVC– $\text{La}_2\text{O}_3$  mixture and CaOHCl for

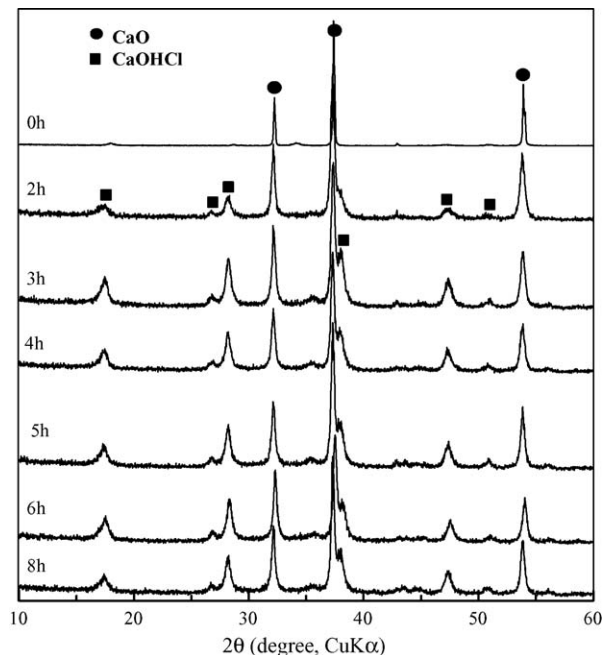


Fig. 3. XRD patterns of PVC and CaO [1:2] milled for different times at a mill rotational speed of 780 rpm.

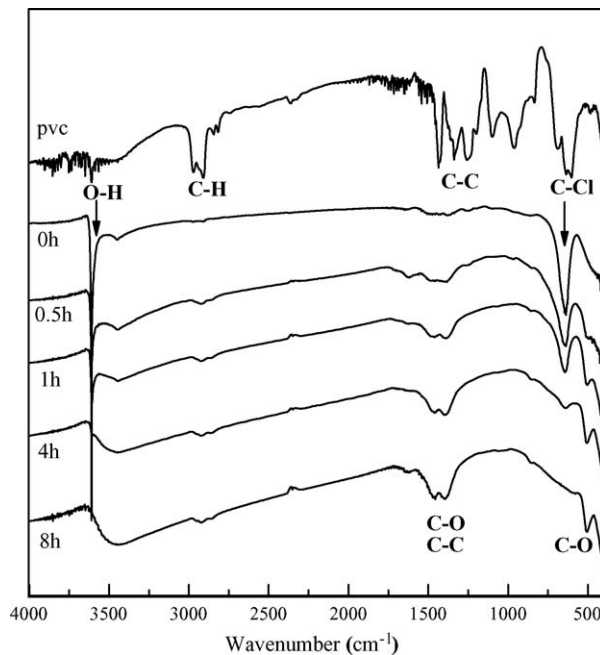
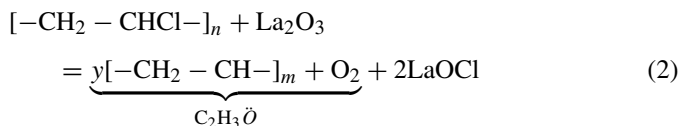
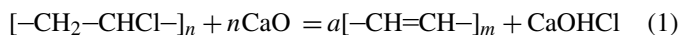


Fig. 4. FT-IR patterns of PVC: $\text{La}_2\text{O}_3$  [1:2] mixture ground for different times at 780 rpm.

PVC–CaO system. The major reactions as anticipated can be expressed by the following equations, respectively.



The above reactions were verified by FT-IR analysis. Zhang and co-workers [1] have observed that the dehydrochlorinating reaction (Eq. (1)) was accompanied by the formation of C=C double bond for the PVC–CaO mixture, while the dechlorination (Eq. (2)) was accompanied by the formation of C–O single bond for the mixture of PVC and  $\text{La}_2\text{O}_3$ . FT-IR patterns for the mixture of PVC– $\text{La}_2\text{O}_3$  at 1:2 in molar ratio are shown in Fig. 4. The C–Cl binding between the wavenumber 800–600  $\text{cm}^{-1}$  was observed to decrease rapidly as grinding progressed and no peaks of C=C bindings appeared around 1700  $\text{cm}^{-1}$ . The C–O inplane bend clearly observed at  $\sim 740 \text{ cm}^{-1}$  may indicate formation of inorganic carbonate ( $\text{La}_2\text{O}_2\text{CO}_3$ ) during MC reaction [12]. Prolonged grinding and increase in molar ratio of PVC and  $\text{La}_2\text{O}_3$  mixtures results in further reaction with excess  $\text{La}_2\text{O}_3$  as given by Eq. (3), which further reacts with LaOCl as given by Eq. (4). It is suggested that during decomposition of PVC, carbon from PVC structure and oxygen released by  $\text{La}_2\text{O}_3$  react first to form  $\text{CO}_2$ , which then reacts with excess  $\text{La}_2\text{O}_3$  to form  $\text{La}_2\text{O}_2\text{CO}_3$ .

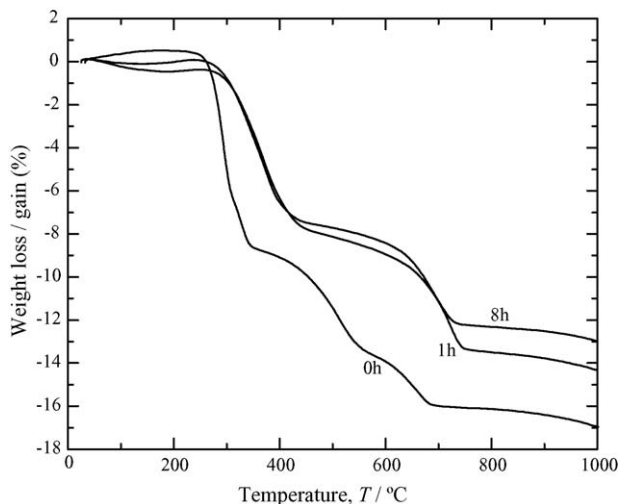


Fig. 5. TG patterns taken under air of PVC:La<sub>2</sub>O<sub>3</sub> [1:2] mixture ground for different times at a mill speed of 780 rpm.

The product La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> is believed to react with LaOCl formed during dechlorination to give LaCO<sub>3</sub>Cl and remains in amorphous phase as grinding progresses.

Figs. 5 and 6 show TG curves of the PVC:La<sub>2</sub>O<sub>3</sub> [1:2] and [1:4] mixtures respectively, ground for different periods of time taken under air environment. For the mixture of PVC–La<sub>2</sub>O<sub>3</sub> at 1:2 in molar ratio, as shown in Fig. 5, the mixture before ground is seen to decompose at around 250 °C and records 16% in weight loss. The mixtures ground for more than 1 h begin to decompose at 300 °C and total weight loss decreases as grinding progresses. The mixtures ground for more than 1 h all show a weight loss of around 13%. Overall significant weight loss of the mixtures can be seen in the temperature range from 250 to 700 °C which is attributed to the thermal decomposition of PVC into HCl, CO<sub>2</sub>, H<sub>2</sub>O, and a like. The shift in decomposition temperature from 250 °C for the mixture before ground to 300 °C for

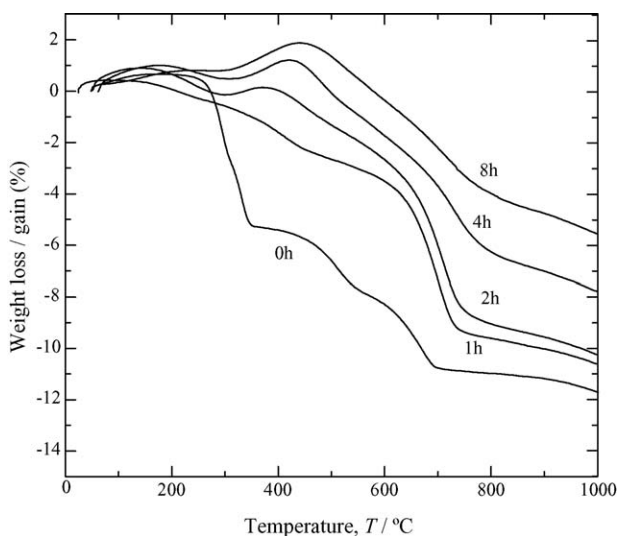


Fig. 6. TG patterns taken under air of PVC:La<sub>2</sub>O<sub>3</sub> [1:4] mixture ground for different times at a mill speed of 780 rpm.

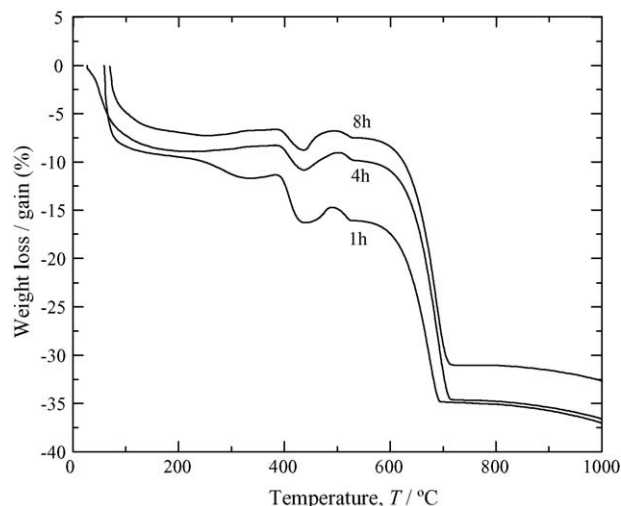


Fig. 7. TG patterns taken under air of PVC:CaO [1:4] mixture ground for different times at a mill speed of 780 rpm.

the samples ground for more than 1 h and significant decrease in total weight loss as the grinding time for the PVC–La<sub>2</sub>O<sub>3</sub> mixture indicates that the MC reaction proceeds quickly in this range. As the Cl in the mixture is transferred into the inorganic phase, the weight change becomes small correspondingly. Regarding to the TG curves taken for the PVC–La<sub>2</sub>O<sub>3</sub> mixture at 1:4 in molar ratio, the un-ground (0 h) mixture is seen to decompose at around 250 °C and records 11% in weight loss, as shown in Fig. 6. The mixtures ground for more than 1 h decompose gradually and the total weight decreases as grinding progresses. That is, the mixtures ground for 1, 4 and 8 h show weight loss of 9%, 7% and 5%, respectively. The shift in decomposition temperature and decrease in weight loss as a function of grinding time is clearly seen in the TG patterns. The weight increase is observed in the range from 400 to 500 °C, and this is attributed to the reaction between carbon formed during the MC reaction and La<sub>2</sub>O<sub>3</sub>, to form La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> (Monoclinic, JCPDS No. 23-0435). The formation of this compound was confirmed by the XRD patterns taken after heating the ground mixture at 450 °C.

Fig. 7 shows TG curves of the PVC:CaO mixture at 1:4 in molar ratio ground for different periods of time taken under air. The weight loss of the mixture was observed in the range from 100 to 500 °C, however, the weight increase is seen at about 450 °C. The weight decrease may be due to the release of H<sub>2</sub>, H<sub>2</sub>O, HCl, and a like and the weight increase is due to the formation of CaCO<sub>3</sub>. Significant weight loss in the range from 600 to 700 °C is due to the decomposition of CaCO<sub>3</sub>, releasing CO<sub>2</sub>. At around 420 °C, a weight loss of about 16% for the mixture ground for 1 h is seen, but it is decreased to around 10 wt.% as grinding progresses in the mixture ground for 4 h. The change in the weight loss during the grinding from 1 to 4 h suggests that the MC reaction proceeds quickly. The TG curves taken under argon gas show no significant increase, but gradual decrease in weight from decomposition of PVC, due to the absence of O<sub>2</sub>.

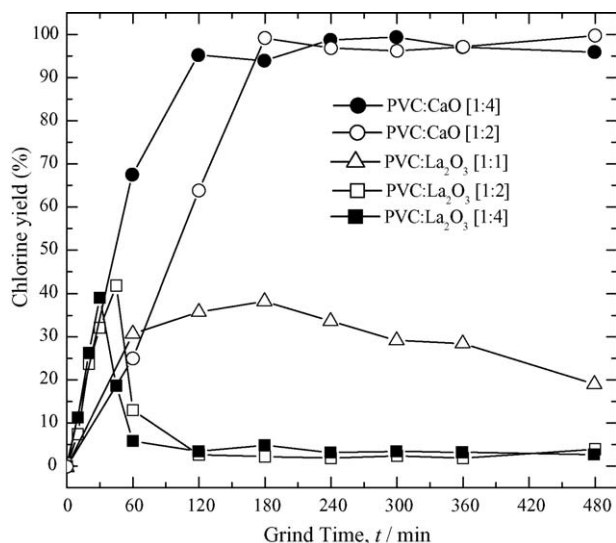


Fig. 8. Chlorine yield as a function of grinding time for PVC mixed with  $\text{La}_2\text{O}_3$  and  $\text{CaO}$  at different molar ratios (mill speed = 780 rpm). Ground mixture washed in water at room temperature.

#### 4.2. Water leaching the ground products

Fig. 8 shows yield of chlorine (Cl) extracted by water from the ground mixtures of PVC– $\text{La}_2\text{O}_3$ , at different molar ratios. For the mixture of PVC: $\text{La}_2\text{O}_3$  at 1:1 in molar ratio, the Cl yield increases gradually as the grinding progresses, and reaches the maximum value of 30% for the mixture ground for 3 h. Further increase in grind time up to 8 h has not been expected, and slight decrease is seen. When the molar ratio of PVC: $\text{La}_2\text{O}_3$  was decreased at 1:2 and 1:4, the yields of Cl increase sharply to 40% in the first 45 min of grinding, however, with an increase in grinding time within 1 h, the Cl yield decreases sharply down to 13%, and reaches to less than 3% in the further grinding time range over 2 h. Profile for Cl yield for the mixture at (1:2) is observed to be very similar to (1:4) when molar ratio is increased to (1:4).  $\text{LaOCl}$  formed in the ground product is insoluble in water, but the result shows the initial increase in Cl yield. It is suggested that water soluble compounds such as  $\text{La}(\text{OH})_2\text{Cl}$ ,  $\text{LaCl}_3$ ,  $\text{LaCl}_2(\text{OH})$  may be formed by disruption of PVC bonds during grinding with an aid of  $\text{La}_2\text{O}_3$ . As grinding progresses, the reaction proceeds fast with an aid of excess  $\text{La}_2\text{O}_3$  to form crystalline form of  $\text{LaOCl}$ , which is stable and does not easily dissolve in water at room temperature. Comparing the fact that the Cl yield has reached about 90% for the mixture ground for 2 h or more [1], the Cl yield for the PVC– $\text{La}_2\text{O}_3$  mixture is low. However, it is concluded that  $\text{La}_2\text{O}_3$  is more effective additive than  $\text{CaO}$  in terms of the decomposition of PVC.

#### 5. Conclusions

This paper reports the effect of  $\text{La}_2\text{O}_3$  as an additive for the decomposition of PVC, conducted at room temperature using

a planetary mill. And the result obtained is compared to PVC decomposition behavior with  $\text{CaO}$ .

The experimental results are summarized as follows:

- (1) Grinding of PVC with  $\text{La}_2\text{O}_3$  enables to accelerate the dechlorination reaction. The  $\text{La}_2\text{O}_3$  plays a significant role to decompose PVC, and is superior to that of  $\text{CaO}$ .
- (2) The dechlorination of PVC with  $\text{La}_2\text{O}_3$  is improved with an increase in molar ratio of PVC: $\text{La}_2\text{O}_3$ , grinding periods of time and rotational speed of the mill.
- (3) The dechlorination of PVC with  $\text{La}_2\text{O}_3$  is accompanied by the formation C–O single bond, while dehydrochlorination of PVC with  $\text{CaO}$  is accompanied by the formation of C=C bond.
- (4)  $\text{LaOCl}$  formed through the MC reaction between PVC and  $\text{La}_2\text{O}_3$  is quite insoluble in water at room temperature, and this is the reason why the Cl yield reaches less than 50%, in spite of the promotion of effective dechlorination of PVC.

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