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# Mechanochemical Dechlorination of PVC by Utilizing Eggshell Waste

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Within this work, the dechlorination of polyvinylchloride (PVC) chemical as a model by co-milling with eggshell was performed in a planetary ball mill in order to show that mechanochemistry can be utilized for the simultaneous treatment of two wastes, while the products of the treatment can be used in further applications. The products of the reaction are water-soluble calcium chloride ($CaCl_2$), which can be used e.g. for de-icing of roads in winter and organic residue on the basis of ethylene, which can be recovered as energy source. The highest dechlorination yield (almost 97%) was achieved under following milling conditions: molar ratio between Ca and Cl: 2.34, ball-to-powder ratio: 65, rotation speed of the planet carrier: 550 rpm, milling time: 4 h and material of milling media: tungsten carbide. The optimum conditions were then applied for the removal of chlorine from industrial waste — the abandoned PVC window parapet. In this case, 95% dechlorination was evidenced.

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## 1. Introduction

Polyvinylchloride (PVC) waste represents an actual environmental issue, because of the problems occurring during its combustion [1]. Therefore seeking alternative solutions of its decomposition is of big interest. The most beneficial way could be the utilization of another abundant waste material for this purpose.

The eggshell (ES) is one of the most common natural wastes. The main component of the ES is $CaCO_3$ [2], which predetermines it to very wide spectrum of applications [3, 4]. The industrial ES waste contains also fibrous eggshell membrane (ESM), which is also suitable for plenty of applications [5]. The treatment of ES by various techniques can broaden its application spectrum even more. One of such approaches is the mechanochemical one.

Mechanochemistry is an interesting branch of chemistry, which has multidisciplinary applications in both inorganic and organic chemistry [6, 7]. Also waste treatment is one of such areas [8].

The positive effect of milling on the dechlorination of PVC was demonstrated in the past [9–11]. In paper [11] by Tongamp et al., the similarity with ES can be found, because another calcium carbonate-containing natural biomaterial (oyster-shell) was used for the same purpose. According to the authors, one of the possible ways of dechlorination is via the following equation:

$$\mathrm{PVC} + \mathrm{CaCO_3} \rightarrow$$

$$[-\mathrm{CH}=\mathrm{CH}-] + \mathrm{CO_2} + \mathrm{H_2O} + \mathrm{CaCl_2}. \quad (1)$$

The products of reaction (1) can be utilized in further applications. Calcium chloride is applicable as road de-icing agent and the organic residue, probably on the basis of ethylene, can be used as energy source. The possibility of PVC dechlorination was confirmed also for ES in the preliminary experiments performed by our group, however not complete dechlorination was evidenced [12].

Within this work, both PVC chemical and an example of industrial waste (window parapet) were co-milled with ES in order to achieve complete dechlorination.

## 2. Experimental

### 2.1. Materials

Eggshell was provided by local canteen in Košice and after the separation of the ESM and pre-milling was used in further experiments. Low-molecular weight PVC chemical (Alfa Produkte, Germany) $Na_2CO_3$ (LACHEMA, Czech Republic) and ZnO (MikroCHEM, Slovakia) were used without further purification. The abandoned window parapet was kindly provided from the company Tieniace systémy s.r.o., Slovakia.

### 2.2. Separation of the eggshell membrane and pre-milling of the ES

The separation of the ESM was achieved by the same procedure as described by Baláž et al. in [13]. After subsequent drying and crushing in mixer, the purified ES was subjected to pre-milling, in order to obtain powder with particles smaller than 160 $\mu$m.

### 2.3. Crushing of PVC window parapet

The as-received window parapet was firstly crushed into coarse particles on the cutting mill Ø200×100 with a vertical shaft (Apritógépgyár Jászberény, Hungary) at 1400 rpm. Subsequently, it was ground into fine particles on the cutting mill SM 2000 with a horizontal shaft (Retsch, Germany) at 1500 rpm. After crushing, it was sieved under 160 $\mu$m.

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### *2.4. Co-milling of PVC and ES*

The co-milling was conducted in a planetary ball mill Pulverisette 6 (Fritsch, Germany) on air. Other milling parameters were optimized throughout the work (see Table). The optimum conditions were then used for the co-milling of the window parapet and ES. The reaction mixture after milling was subjected to the measurement of amount of chlorides.

### *2.5. Calcination of the milling mixture in order to determine total chlorine content*

After the milling process, 0.5 g of the reaction mixture was put into a nickel crucible together with 5 g of $Na_2CO_3$ and 0.5 g of ZnO. The mixture was then heated up to 950 °C for 20 min. After this it was gradually cooled down to laboratory temperature and afterwards dissolved in hot distilled water and finally filtered. The content of chloride ions was measured in the filtrate.

### *2.6. Dissolution in distilled water in order to determine soluble chlorine content*

After the milling experiment, 1 g of the milled mixture was put into 200 mL distilled water and stirred at laboratory temperature for 1 h, in order to achieve complete dissolution of produced calcium chloride. Then, the suspension was filtered and the amount of chloride ions in the filtrate was determined.

### *2.7. Measurement of chloride ions content*

The amount of chlorine was measured by ion chromatograph Dionex ICS 5000 (Sunnyvale, CA, USA), using an IonPac AS11-HC 2×250 mm anion column, 30 mM KOH eluent (isocratic mode) and suppressed conductivity detection.

### *2.8. Determination of dechlorination activity*

The dechlorination yield $D$ was determined by the following equation:

$$D = \frac{c_s}{c_t} \times 100[\%], \tag{2}$$

where $c_s$ is the concentration of chlorides obtained after the dissolution in distilled water and $c_t$ is the total concentration of chlorides measured in the mixture after milling.

### *2.9. Specific surface area measurements, $S_A$*

The specific surface area was determined by the low-temperature nitrogen adsorption method using NOVA 1200e Surface Area & Pore Size Analyzer (Quantachrome Instruments, UK). The values were calculated using the Brunauer–Emmett–Teller (BET) theory.

### *2.10. Powder X-ray diffraction*

Powder XRD patterns were recorded using the D8 Advance diffractometer (Bruker, Germany) equipped with Cu $K_\alpha$ radiation (40 kV/40 mA), secondary graphite monochromator and scintillation detector. The peaks of the corresponding phases were assigned to both phases according to JCPDS-PDF2 database.

## 3. Results and discussion

### *3.1. Optimization of milling parameters*

Altogether 18 experiments were performed until five milling parameters were optimized. The results are summarized in Table.

TABLE

Optimization of milling parameters. For each set of experiments, different milling parameter was optimized, which is marked by bold face in frames. #1 — Exp. No., #2 — Ca:Cl molar ratio, #3 — Ball-to-powder ratio, #4 — Milling speed [rpm], #5 — Milling time [h], #6 — Milling media, #7 — Dechlorination [%]

| #1 | #2 | #3 | #4 | #5 | #6 | #7 |
|---|---|---|---|---|---|---|
| 1 | 2.35 | 33 | 550 | 4 | WC | 88.4 |
| 2 | **1.00** | 33 | 550 | 4 | WC | 39.8 |
| 3 | **1.50** | 33 | 550 | 4 | WC | 27.1 |
| 4 | **2.00** | 33 | 550 | 4 | WC | 66.3 |
| 5 | **3.84** | 130 | 550 | 4 | WC | 90.5 |
| 6 | **6.00** | 130 | 550 | 4 | WC | 79.5 |
| 7 | **8.00** | 130 | 550 | 4 | WC | 85.1 |
| 8 | 2.35 | **65** | 550 | 4 | WC | 96.8 |
| 9 | 2.35 | **130** | 550 | 4 | WC | 92.0 |
| 10 | 2.35 | 65 | **350** | 4 | WC | 17.2 |
| 11 | 2.35 | 65 | **450** | 4 | WC | 52.3 |
| 12 | 2.35 | 65 | 550 | **0.5** | WC | 8.3 |
| 13 | 2.35 | 65 | 550 | **1** | WC | 14.7 |
| 14 | 2.35 | 65 | 550 | **2** | WC | 27.8 |
| 15 | 2.35 | 65 | 550 | **3** | WC | 58.6 |
| 16 | 2.35 | 65 | 550 | **5** | WC | 85.4 |
| 17 | 2.35 | 65 | 550 | 4 | **$ZrO_2$** | 76.5 |
| 18 | 2.35 | 65 | 550 | 4 | **achate** | 74.1 |
| WP | 5.06 | 65 | 550 | 4 | WC | 95.7 |

In the first set of experiments, Ca:Cl molar ratio was optimized. For the first experiment, the one from work [11] was taken. In case of lower molar ratios, i.e. the stoichiometric ratio 1:1 (exp. 2) and also 1.5 and 2 (exp. 3 and 4, respectively), a considerable decrease in dechlorination yield was evidenced. Higher molar ratios (exp. 5–7) also did not increase the yield, however it has to be noted that higher ball-to-powder ratio (BPR) was used in these experiments. It was necessary, because very small amount of PVC would be used otherwise. It was concluded that Ca:Cl molar ratio 2.35 is the optimum value.

For the optimization of ball-to-powder ratio (BPR), which is the weight ratio between the mass of the milling media and the milled powder, the experiments 1, 8 and 9 were realized. BPR 33 was also taken from paper [11] (exp. 1). The yield in this case was under 90%, which could be possibly explained by the fact that the energy input provided by the milling media is not high enough for the dechlorination reaction to proceed to such extent as in the case of BPR 65 (exp. 8). In the case of BPR 130 (exp. 9), there is lower mass of both reactants, due

to which they are less prone to react among each other, because they are more often subjected to the impact of the milling media instead. The best result was obtained for BPR 65, so this value was taken as the optimum one.

Another optimized parameter was milling speed (experiments 8, 10 and 11). The expected results were confirmed, being the higher the milling speed, the better the result. The optimum milling speed was 550 rpm.

As another parameter, milling time was pursued (experiments 8 and 12–16). As can be seen, 4 h of milling were sufficient, because both shorter and longer time provided worse dechlorination yield. After 5 h of milling, the yield decreases, which could be attributed to possible aggregation process, a known phenomenon in mechanochemistry [14].

Finally, different milling media were used (tungsten carbide, zircon oxide and agate — experiments 8, 17 and 18, respectively). As expected, the best results were obtained for the material with the highest density (WC), due to which the highest grinding stress intensity is observed. In both other cases, the yield under 80% was observed.

From all the experiments, the experiment 8 was selected as optimum and therefore for the dechlorination of window parapet (exp. WP), the conditions used in this experiment were applied, with the exception of Ca:Cl molar ratio was increased to 5.06. This is because the mass of powdered parapet containing much less chlorine was the same as the mass of pure PVC in experiment 8.

Figure 1 illustrates the effects of various milling parameters on the dechlorination.

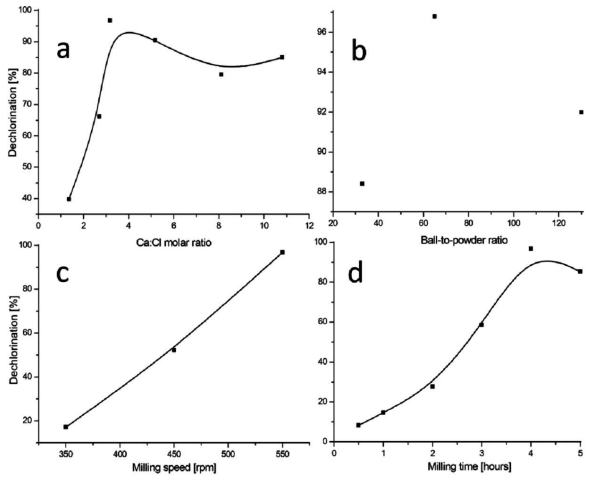


Fig. 1. Dechlorination as a function of various milling parameters: (a) Ca:Cl molar ratio, (b) ball-to-powder ratio, (c) milling speed, (d) milling time.

### 3.3. Specific surface area

In order to pursue the changes taking place during the milling process, specific surface area of the milled mixture was measured. The results are provided in Fig. 2a. For better understanding of the dechlorination process, also the dependence of dechlorination on the specific surface area is provided (Fig. 2b).

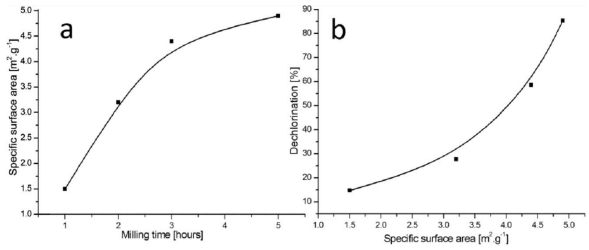


Fig. 2. (a) The dependence of specific surface area on the milling time, (b) the dependence of dechlorination on the specific surface area.

The increase of the specific surface area with the milling time can be clearly seen from Fig. 2a. However, after 3 h, the rate of the increase starts to slow down. This could be attributed to possible aggregation process mentioned earlier. However, another phenomenon can be observed when dechlorination is plotted against $S_A$ (Fig. 2b). The dechlorination yield increases more rapidly when the specific surface area is higher. This could be explained by the fact that when $S_A$ is higher, more reactive sites are available for the interaction between calcium from the ES and chlorine from PVC.

### 3.4. Powder X-ray diffraction analysis

The dechlorination process was pursued also by means of X-ray diffractometry. The XRD patterns of pre-milled ES and of the products after the milling process in the experiments 2 and 8 are shown in Fig. 3.

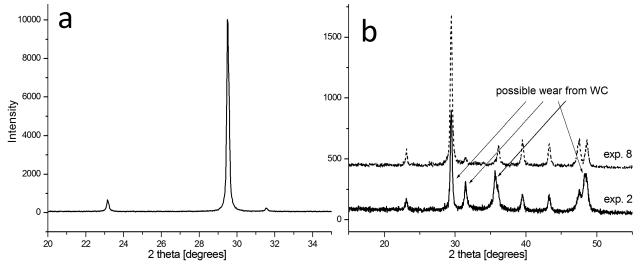


Fig. 3. XRD patterns of: (a) pre-milled ES, (b) product obtained after milling in the experiments 2 and 8. The non-assigned peaks belong to calcite phase.

In Fig. 3a, only the peaks corresponding to calcite as the main component of the ES can be seen in the pre-milled ES. In Fig. 3b, the XRD patterns of the products after milling in case of experiments 8 and 2 are compared. In the first case (optimum experiment no. 8), only the peaks of calcite are present, because it has been used in excess and its amount is too large for any other products to be visible. Therefore the XRD pattern of the sample from experiment no. 2 (larger Ca:Cl molar ratio 1:1) was taken with the aim to observe any signs

of the product $CaCl_2$. Although the XRD pattern has changed considerably, $CaCl_2$ can be hardly identified because of the large peak overlap, and it was found that all visible changes are associated with the presence of tungsten carbide, as a result of wear from the milling media. It is therefore clear that the more the PVC chemical is present, the more wear from milling media occurs. This is a result of the fact that tungsten carbide is too hard for milling the organic material, for milling of which also milder conditions would be sufficient.

### *3.5. Dechlorination of window parapet*

The optimum milling conditions were applied for the co-milling of crushed and sieved window parapet (see exp. WP in Table). As a result, 95.7% dechlorination was evidenced. It means that eggshell waste biomaterial is able to extract chlorine also from the industrially prepared PVC, thus significantly broadening its application.

## 4. Conclusions

Within this work, waste eggshell was successfully applied for the dechlorination of PVC. In the set of experiments, optimum milling conditions were determined, which were then applied for the dechlorination of PVC window parapet, as an example of industrial waste. The rate of the specific area increase is reduced in the later stages of milling. The dechlorination process takes place more rapidly when the value of specific surface area is higher. This contribution represents a unique example of using mechanochemistry for simultaneous treatment of two wastes, yielding usable products. It was also shown that an industrial waste can be treated in this way.

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