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# Enhanced Dry Separation of Aluminium from Composites by Ozone

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The paper presents preliminary results of experimental use of ozone in degradation of polymers in the field of recycling of metal-polyurethane (PUR) composites. By treating of aluminium-PUR segments waste by use of ozone at low flow rates ( $\sim 300 \text{ mg}\cdot\text{h}^{-1} \text{ O}_3$ ) followed by dry techniques (hammer mill crushing followed by air separation) it is possible to enhance (almost double) the efficiency of polymer removal from the composite. The amount of removed polymer increased with increasing concentration (flow rate) of

ozone in reactor atmosphere. This process enables recovery of more pure aluminium product from such construction waste streams which is suitable for direct industrial applications in accordance with EU Council regulation No. 333/2011.

Keywords:

Separation – Metal – Composite – Polyurethane – Ozone

## Verbesserte trockene Abtrennung von Aluminium aus Composites durch Ozon

Dieser Artikel präsentiert die Ergebnisse der experimentellen Anwendung von Ozon im Bereich des Recyclings von Metall-Polyurethan(PUR)-Composites. Durch die Behandlung von Aluminium-PUR-Schrott mit Ozon bei niedrigen Durchflussraten ( $\sim 300 \text{ mg}\cdot\text{h}^{-1} \text{ O}_3$ ) und anschließender Aufbereitung im trockenen Zustand (Zerkleinerung mit Hammermühle und Trennung durch Druckluft) ist es möglich, die Effizienz der Abtrennung der Polymere zu verbessern (nahezu zu verdoppeln). Der Anteil des ab-

getrennten Polymers nimmt mit steigender Konzentration (Durchflussrate) von Ozon in der Reaktoratmosphäre zu. Dieses Verfahren ermöglicht die Wiedergewinnung eines reineren Aluminiumprodukts aus Bauschuttströmen, das für direkte industrielle Anwendungen geeignet ist, gemäß Verordnung (EU) Nr. 333/2011 des EU-Rates.

Schlüsselwörter:

Abtrennung – Metall – Composite – Polyurethan – Ozon

## Meilleure séparation à sec d'aluminium des composites à l'aide d'ozone

## Mejorada separación seca de aluminio desde compuestos a través de ozono

## 1 Introduction

One of the problems with recycling of some composite materials from construction/demolition or packing industry is the lack of effective methods of separating the polymer fraction from the metallic one. In order to gain the End of Waste criteria for metals (Council Regulation (EU) No. 333/2011) the composite waste requires thoughtful pre-treatment and separation of the components [1]. Thanks to the excellent oxidation effect, ozone could find application in treatment of metal-polymer and composite scrap via polymer ageing.

Studies that take interest in impact of ozone on materials can be divided principally into two groups in dependence on what material is used. One group is oriented on primary raw materials processing containing copper, antimony or precious metals. Ozone helps to oxidize the ore components and finally gain better extraction efficiencies [2,3]. The second group is dealing with using of ozone in degradation of some polymers, rubber or organic pollutants. From most often used polymers today the most degradable by ozone are considered polypropylene, polymethyl methacrylate

and polyethylene [4-6]. On the other hand, most of metals is oxidized by ozone but some of them cause ozone cleavage or acts as its decomposition catalysts [7]. The utilization of ozone in recycling and waste metal-polymer composite treatment is relatively new. Nevertheless studies exist in this field, but they do not provide sufficient information [8,9].

The paper presents preliminary results of experimental use of ozone in degradation of polymers in the field of recycling of composite materials on metal-polymer base. The aim of study was to achieve more efficient separation of polymer (polyurethane) from composites and ultimately obtaining metal of higher purity.

## 2 Experimental

### 2.1 Materials and methods

Samples of aluminum segments coated with paint and filled with polyurethane (PUR) were exposed to ozone ageing (Figure 1a). The segments were cut before the experiment into smaller pieces, approximately 15 mm wide and 40 mm long. Thickness of segments was 2.5 mm. Figure 1b shows the FTIR spectrum (spectrometer Perkin-Elmer Spec-

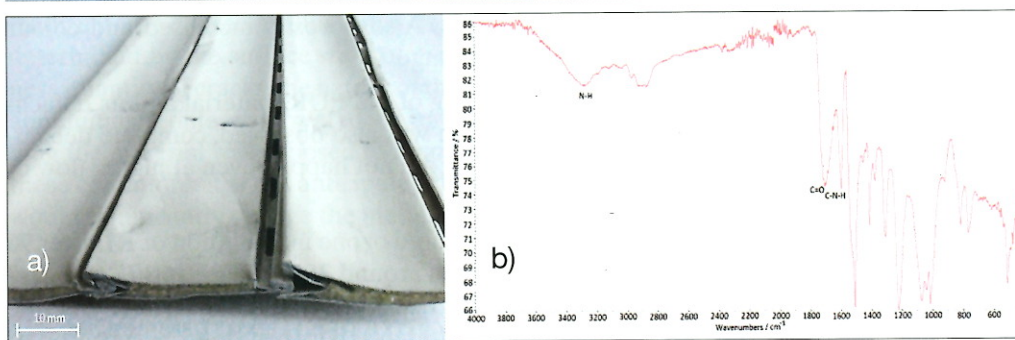


Fig. 1: a) Original input sample; b) FTIR spectrum of filler of aluminum segment (PUR foam)

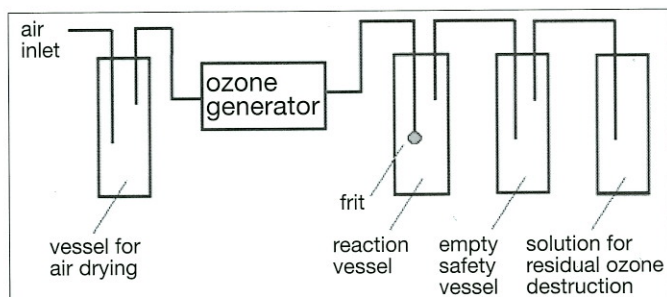


Fig. 2: The apparatus for waste metal-polymer composite treatment by ozone

trum-100) of polymer filler, which confirmed that it is made of polyurethane.

The apparatus (Figure 2) for experiments consists of a small commercial ozone generator, with production of 700 mg O<sub>3</sub> per hour, compressor, flow rate-meter, washing vessel (air dryer), glass reactor (600 ml) and a vessel for residual ozone destruction (150 ml). Air was dried before blowing to the ozonizer by bubbling it through the washing vessel loaded with 100 ml of concentrated H<sub>2</sub>SO<sub>4</sub>. Generated ozone was blown continuously with defined flow rate through the reaction vessel where it reacted with samples for defined time. Excess of ozone was caught in the wash-out vessel filled with potassium iodide solution.

The flow rate of produced ozone as well as the concentration (amount) of produced and consumed ozone in the process was determined by iodometric titration (titrated with sodium thiosulfate). The flow rate of ozone in the first and second experiment was 288 mg·h<sup>-1</sup> and 488 mg·h<sup>-1</sup>, respectively. With the air flow around 180 l·h<sup>-1</sup> the concentration of ozone in reactor represented 747 ppm and 1265 ppm. Samples of trimmed aluminum segments were exposed to ozone atmosphere (at defined ozone flow rate)

for 96 hours. After the experiment, the amount of ozone captured by potassium iodide, after reaction with studied material was determined. The amount of ozone in solution was calculated as follows: the volume of 1 cm<sup>3</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (c = 0.1 mol·dm<sup>-3</sup>) is equal to 2.4 mg of O<sub>3</sub>.

After established time of reaction of ozone with samples, change of appearance and morphology of samples was observed by using magnifier DinoCapture 2.0. Then the samples after ozone ageing were mechanically treated by crushing in hammer mill ŠK-600 followed by air separation. The efficiency of separation of non-metallic parts in composite from metal (in mass-%) was then calculated. Difference between samples exposed to ozone and samples that were not exposed to ozone was compared. The weights of treated and untreated samples were comparable (~25 g).

## 2.2 Results and discussion

Figure 3b shows the sample after ozone treatment (288 mg·h<sup>-1</sup>) and after crushing and air separation. Table 1 and Figure 3a shows the effect of ozone flow rate on efficiency of PUR foam separation from aluminum pieces. The separation of polymer from composite without using ozone was accomplished, too, but evidently with lower efficiency.

Table 1: The results of PUR foam separation efficiency after crushing

O <sub>3</sub> flow rate [mg·h <sup>-1</sup> ]	Weight of sample [g]		Amount of separated polymer	
	Before separation	After separation	[g]	[mass-%]
0	24.45	22.87	1.58	6.46
288	24.23	21.48	2.75	11.35
488	25.52	21.30	4.22	16.54

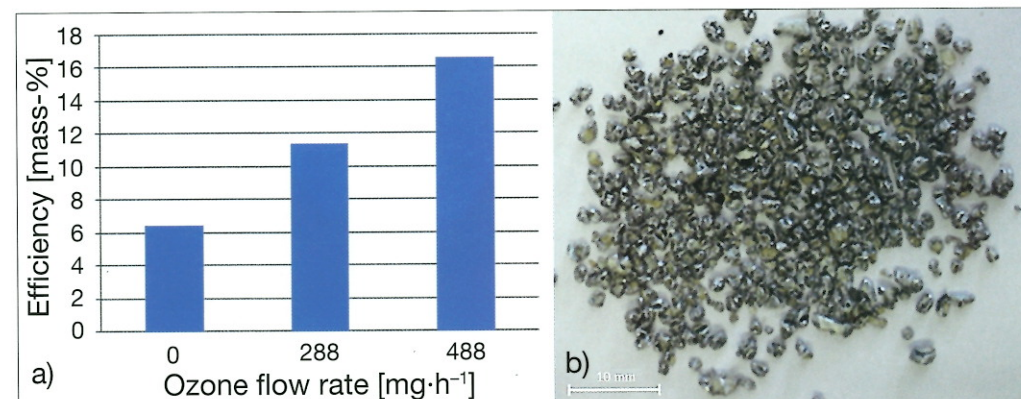


Fig. 3: a) Efficiency of PUR separation as a function of ozone flow rate; b) crushed sample after ozone exposure (96 hours; 288 mg·h<sup>-1</sup> O<sub>3</sub>) and after air separation

From Table 1 it is obvious that with help of ozone, even at low concentrations (747 ppm), almost twice as much material was separated, compared to samples that were not exposed to ozone. By increasing concentration of ozone in reactor (up to 1265 ppm) the amount of separated polymer fraction increased by 250 % compared to untreated sample.

On the samples of aluminum segments, especially of PUR foam exposed to ozone ageing, visible change in morphology and color occurred (Figures 5 and 6) compared to samples that were not exposed (Figure 4).

The morphology and appearance of PUR foam at lower ozone flow rate was not changed as much as on those exposed to higher ozone flow rate. In the case of ozone flow rate 288 mg of ozone per hour the colour changed from light yellow to light orange. PUR foam of samples subjected to ozone ageing at flow rate 488 mg of ozone per hour was evidently more degraded and these samples

considerably shrink. Also porosity increased and colour changed to dark orange.

Nevertheless, flaking of the PUR material and its detaching from aluminium was also observed, complete decomposition of polymer did not happen even at higher flow of ozone ( $\text{mg}\cdot\text{h}^{-1}\text{O}_3$ ).

The amount of captured ozone in a solution of KI, after 96 hour of reaction with around 25 g of segments ( $288\text{ mg}\cdot\text{h}^{-1}\text{O}_3$ ) was  $4471.20\text{ mg O}_3$ . It represents the amount of  $46.58\text{ mg O}_3$  per hour. The difference between the concentration of ozone in the atmosphere of the reaction chamber before adding the material and after executing the experiment shows the amount of ozone that reacted with material, or was decayed on oxygen (or other products) throughout polymer degradation. This amount was equal to  $241.42\text{ mg O}_3$  per hour. These results suggest that most of the ozone was consumed by reaction with given polymer. On the other hand, ozone can react also with aluminium and

Fig. 4: Details of: a) input composite sample (magn. 60×); b) PUR filler (190×)

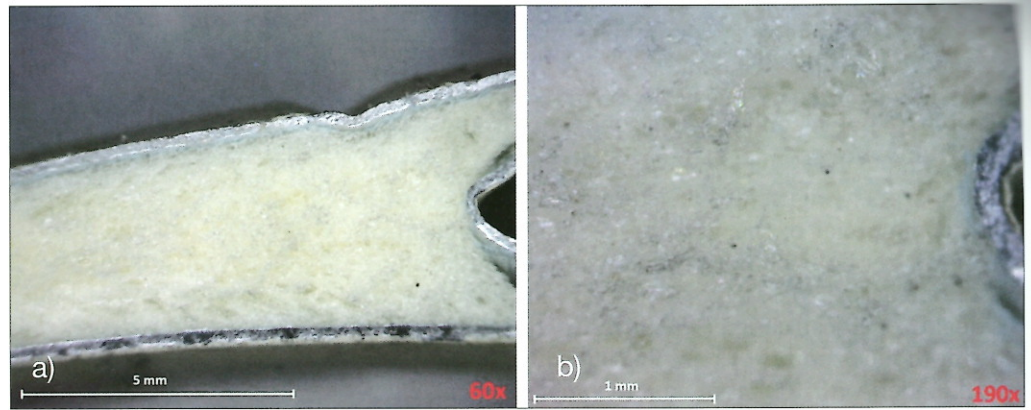


Fig. 5: Sample after ozone exposure: a) 96 h at  $288\text{ mg}\cdot\text{h}^{-1}\text{O}_3$ ; b) 96 h at  $488\text{ mg}\cdot\text{h}^{-1}\text{O}_3$

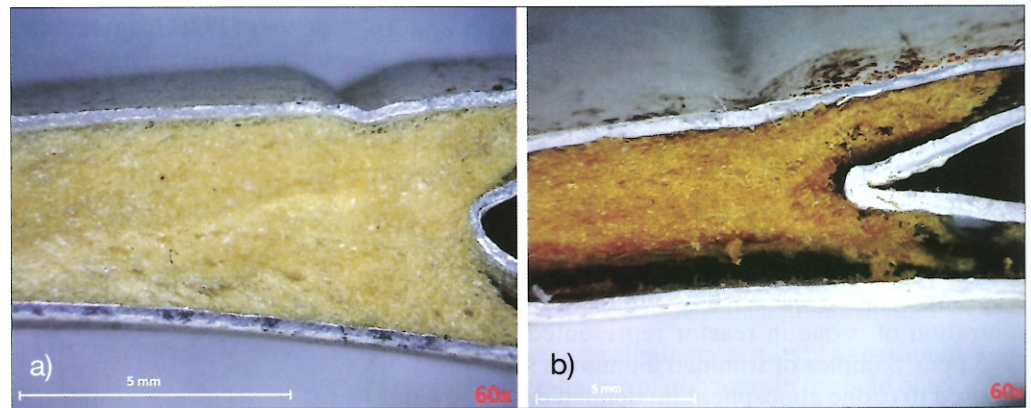
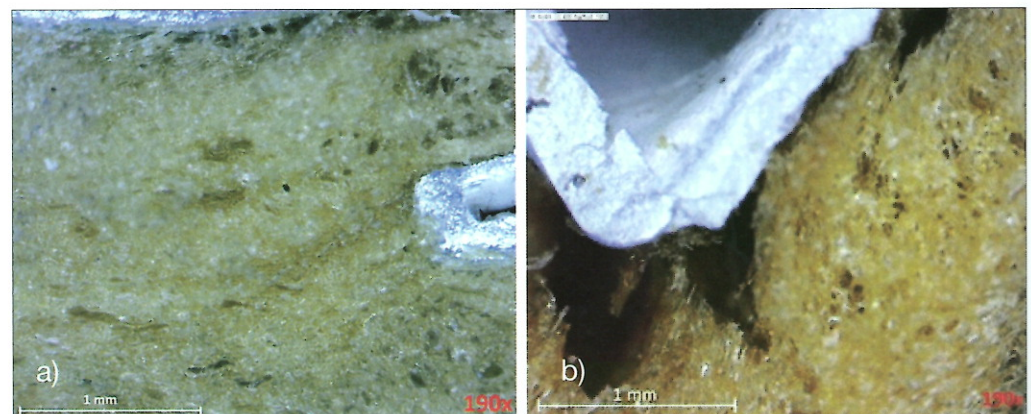


Fig. 6: Sample after ozone exposure: a) 96 h at  $288\text{ mg}\cdot\text{h}^{-1}\text{O}_3$ ; b) 96 h at  $488\text{ mg}\cdot\text{h}^{-1}\text{O}_3$



oxidize it. The degree of aluminium oxidation could be also determined by the surface state of metal – surface roughness, quantity of cracks, the nature of the material and if the aluminium profile was treated by anodic oxidation, how long the material was exposed to air oxidation, etc. Under these conditions, it is not anticipated that the use of ozone would significantly oxidize the metal.

### 3 Conclusions

The preliminary results confirmed that relatively low concentration of ozone (750 ppm) can significantly increase degradation of PUR foam from metal composite waste. By treating this type of waste by use of ozone at low flow rates ( $\sim 300$  to  $500 \text{ mg}\cdot\text{h}^{-1}$ ) and dry techniques (crushing followed by air separation) it is possible to double the efficiency of polymer removal from the composite. The amount of removed polymer increased with increasing concentration (flow rate) of ozone in atmosphere. This process is able to enhance the PUR separation from construction aluminium-polyurethane composite waste and recover more pure metal from those waste streams. Moreover, it seems that also coating paint exposed to ozone was more attacked compared to untreated sample. The process could be even more improved by use of another type of mill or crusher. The aluminium plates tend to bundle in the hammer mill, thus the polymer and coating is hidden inside granules and then it is more difficult to separate them. It can be assumed that increasing the concentration of ozone or using a different type of crusher (for example friction mill), even higher efficiency of process and higher purity of secondary aluminium could be achieved. Ozone can make treatment of these composites easier and more effective. By the proposed process the product for further direct application (steel industry) can be achieved in accordance with EU Council regulation No. 333/2011. In the future, it is also necessary to study in detail the composition of the coating, the impact of higher concentration/flow rate of ozone as well as mill type on efficiency of the separation process. Also gaseous products of the reactions with ozone in this process are necessary to monitor due to environmental issues.

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