Influence of the Zinc Oxide Level in Rubber Compounds on the Amount of Zinc Leaching

Recently the reduction of the zinc oxide level in rubber compounds has become an important issue because of the harmful effect of zinc ions to aquatic organisms. In the present study the effect of reducing the zinc oxide level in rubber compounds on the amount of zinc leached from rubber granulate and powder was investigated. Leaching tests were performed according to DIN 18035-7 on rubber compounds used for truck tyre re-treading containing standard zinc oxide and active one, as well as on commercially grinned rubber made from truck and car tyres by ambient and cryogenic grinding.

It was found that the surface specific area of the zinc oxide has no significant influence on the amount of zinc leached. The amount of zinc leached increases with increase of zinc oxide level up to around 3 phr and then levels off. The most influencing factor is the particle size distribution of the rubber granulate. Smaller amounts of zinc are leached from cryogenic rubber granulate and powder than from ambient rubber granulate and powder having the same particle size.

Der Einfluss des Zinkoxidgehalts in Kautschukmischungen auf die Menge an ausgelaugtem Zink

Zinkoxid Gummimehl Auslaugen


Experimental

A commercial SBR/NR/BR compound used for retreading truck tyres was chosen to evaluate the influence of the zinc oxide level on the amount of zinc leaching. Two grades of zinc oxide were applied. The first one was obtained by the so called French process and was produce at Huta Olawa, Poland. The product consists of large parti-
ber content was determined by TG analysis and the zinc oxide content was obtained from chemical analysis of every commercial rubber granulate.

Results and discussion
As it can be shown from Table 2, the reduction of zinc oxide amount from 4 phr to 1 phr in the commercial truck tyre retreading compound has only minor influence on the curing characteristics. In the case of the standard zinc oxide the scorch time \( t_1 \), the optimum vulcanization time \( t_{90} \) and the increase in torque (\( \Delta M = M_{\text{max}} - M_{\text{min}} \)) which is a simplified measure of crosslink density, demonstrate stable values. Somewhat larger changes are observed in the case of the active zinc oxide where the reduction of the zinc oxide level results in a tendency toward a decrease of \( t_{90} \) and \( \Delta M \). These dependencies can be a result of the poorer dispersion of the active zinc oxide. The SEM pictures shown in Figure 2 demonstrates a different dispersion of the active zinc oxide (Fig. 2b) than the standard one in rubber matrix (Fig. 2a).

However, the reduction of the zinc oxide level has no significant influence on the tensile strength, the elongation at break and the hardness of the vulcanizates (Table 3).

### Particle size distribution and leaching tests
To evaluate influence of zinc oxide level on the amount of zinc leaching rubber powders of particle size below 0.7 mm were used. As it can be shown from the sieve analysis about 80% of particles were smaller than 0.5 mm (Fig. 3). For comparison granulates prepared on the rubber mill having about 50% of particles larger than 1 mm were also used.

From the extraction experiments it was found that the specific surface area of the zinc oxide incorporated into the rubber matrix has no significant effect on the amount of zinc leached. As expected very high amounts of zinc were leached from rubber powders with water saturated with CO2. The concentration of zinc in acidic eluates increased proportionally with increase of zinc oxide level to 3 phr and then leveled off (Fig. 4).
SEM pictures of zinc oxide agglomerates in rubber compounds: standard zinc oxide (a), active zinc oxide (b)

Sieve analysis of rubber granulate and powder prepared from the retreading compound

Vulcanisate properties of the commercial retreading compound containing various amounts of zinc oxide

<table>
<thead>
<tr>
<th>ZnO content [phr]</th>
<th>Active 44 m²/g</th>
<th>Standard 5 m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Tensile strength [MPa]</td>
<td>21.0</td>
<td>21.1</td>
</tr>
<tr>
<td>Elongation at break [%]</td>
<td>336</td>
<td>346</td>
</tr>
<tr>
<td>Hardness [Sh]</td>
<td>70</td>
<td>68</td>
</tr>
</tbody>
</table>

Influence of particle size of rubber granulates on amount of zinc leached

<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>Nominal particle size range, [mm]</th>
<th>Grinding method</th>
<th>Zinc oxide content, [phr]</th>
<th>Total rubber content [%]</th>
<th>Amount of zinc leached [mg/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Truck tyre buffings</td>
<td>0.5 – 1</td>
<td>Buffing and additional ambient grinding</td>
<td>5.6</td>
<td>56</td>
<td>1.69</td>
</tr>
<tr>
<td>2</td>
<td>Car tyre buffings</td>
<td>0.5 – 1.5</td>
<td>Buffing and additional ambient grinding</td>
<td>4.2</td>
<td>58</td>
<td>0.44</td>
</tr>
<tr>
<td>3</td>
<td>Truck tyre buffings</td>
<td>0.5 – 1.5</td>
<td>Buffing and additional ambient grinding</td>
<td>5.3</td>
<td>59</td>
<td>1.44</td>
</tr>
<tr>
<td>4</td>
<td>Truck tyre 1–3</td>
<td>1 – 3</td>
<td>Ambient grinding</td>
<td>4.8</td>
<td>56</td>
<td>1.39</td>
</tr>
<tr>
<td>5</td>
<td>Car tyre 1–4</td>
<td>1 – 4</td>
<td>Ambient grinding</td>
<td>3.3</td>
<td>54</td>
<td>0.69</td>
</tr>
<tr>
<td>6</td>
<td>Mixed car and truck</td>
<td>2 – 5</td>
<td>Ambient grinding</td>
<td>3.8</td>
<td>55</td>
<td>0.04</td>
</tr>
</tbody>
</table>

By extracting granulates with 50% of particles larger than 1 mm a significant reduction of the zinc leached (ca. 20%) was observed. This result can be easily attributed to the reduced rubber surface available in the extraction experiment. The zinc concentration in neutral water leachates of rubber powders was also much higher than acceptable but half of that in acidic ones. Additional leaching tests with water were performed on buffings from truck and car tyres and commercial rubber granulates produced from end-of-life car and truck tyres. The truck and car tyre buffings contained 5.3 and 4.2 phr zinc oxide respectively.
The amount of zinc leached from buffings by water was two orders lower than for the powders made of vulcanisates shortly after vulcanisation. The zinc content in leachates of the truck tyre buffings was three times higher than acceptable. The effect of particle size distribution was also visible. Only car tyre buffings met the requirement of DIN 18035-7: 0.5 mg Zn/l (Table 5).

The commercial granulates produced from truck tyres, car tyres and mixed ones contained 4.8, 3.3 and 3.8 phr of zinc oxide respectively. The car and truck tyre granulates had similar particle size distribution. The particle sizes were in the 1.4 – 3.2 mm range. The mixed granulate comprised particles in the 2 – 4.3 mm range (Fig. 5).

The mixed granulate characterized very low zinc leaching so it indicates clearly that possibility of zinc leaching by water from large rubber particles of small specific surface area is low. Larger amounts of zinc were leached from the truck tyre granulate than car tyre one. It is connected with higher level of zinc oxide in truck tyres and probably different composition of byproducts of crosslinking reactions and products created during use of tyres on roads and production of granulate.

It is worth to remember that not only the particle size distribution but also the shape and the surface area of rubber particles are important. There is a significant difference between the shape and surface area of granulates produced by the ambient and cryogenic grinding and also tyre buffings.

The results of the leaching test are shown in Table 5. The smaller amounts of zinc are leached from cryogenic rubber granulate and powder than ambient granulate and powder. The amount of zinc leached decreases with increase of particle size. It was also found that even very fine cryogenic powder fulfils the DIN-Standard requirements.

**Conclusions**

1. The amount of zinc leaching from rubber granulates produced from end-of-life tyres depends mainly on zinc oxide level in virgin tyre rubber compounds, particle size distribution and surface area of rubber granulates. The specific surface area of zinc oxide has no special effect on amount of zinc leached.

2. The amount of zinc leaching increases proportionally to zinc oxide concentration in tyre compounds up to certain level and then levels off. This level of zinc oxide concentration is probably different for truck and car tyres.

3. The particle size distribution and specific surface area of rubber granulate have very significant influence on amount of zinc leaching. Fine powder should be accurately removed from rubber granulate to decrease amount of zinc leaching.

4. Larger amounts of zinc are leached from truck tyre granulate than from car tyre one with the same particle size distribution. In our tests the amount of zinc leached from truck tyre ambient granulate with water exceeded significantly the acceptable limit 0.5 mg/l.

5. Smaller amounts of zinc are leached from cryogenic rubber granulate and powder than from ambient rubber granulate and powder having the same particle size.

6. In the case of granulate and powder produced from mixed car and truck tyres more samples should be tested to evaluate their susceptibility to zinc leaching.

**References**


