NANOSCALE ZINC OXIDE – HIGH PERSPECTIVE NANOMATERIAL

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Abstract

Zinc oxide (ZnO) is a white solid inorganic powder (a diameter of common type 0.2-3 μm) that is widely used in a lot of industrial segments. The main applications include rubber and ceramics, but also include paints, animal food, pharmaceuticals and numerous other products and processes of our daily life. In fact the global usage of ZnO is over 1 billion tons per year. Nanoscale ZnO (nano = a diameter less than 100 nm) is a much younger type of this material, nevertheless it currently ranks among commonly, plentifully used and fast-growing nanomaterials. Nano ZnO has attracted great interest due to its better (in some cases unique) properties (e.g. anti-microbial, anti-corrosion, photo-catalytic, UV filtering), compared to the common type, which is awarded to its nanoscale. From literature but most importantly from our experiments in selected applications, we can say that nano ZnO shows comparable or better properties than common type ZnO even at a lower dosage. The usage of nano ZnO is thus advantageous from an economic as well as an environmental view. Nowadays prognoses say that nano could completely replace common type ZnO in near future. BOCHEMIE has dealt with zinc chemistry over a long period of time and plans to be a leader producer of nano ZnO in middle Europe. We have done vast research in the area of nano ZnO preparation and have studied its anti-microbial, photo-catalytic and vulcanizing activity. In this contribution we would like to present some of these results.

Key words: Nanomaterial, Zinc Oxide, Rubber, Paints

1. INTRODUCTION

In the last three years BOCHEMIE has done vast research in the area of nano ZnO preparation and has studied its application properties. The main goal of this contribution is to present some of our results from these areas, for example parametric comparison of our nanomaterials with competitive products that are presently available on the market and application possibilities of nano ZnO in different industry segments, especially in rubber and paint. From our experiments in these segments, nano ZnO seems to be a very interesting substitute of ordinary zinc oxide (o-ZnO), especially because of its better functional properties (e.g. anti-microbial and vulcanizing activity), which are reached, compared to o-ZnO, even at lower dosage. The usage of nano ZnO is thus interesting from economic but also from the environmental issues in relation to the amount of zinc in final products. ZnO itself is non-toxic, but classified as very toxic for aquatic environment [1].

2. EXPERIMENTAL

For the preparation of nano ZnO it is possible to use processes in liquid, gas (more precisely vapour) or solid phase. We focused strictly on wet (i.e. liquid) processes, due to easily available zinc raw material in BOCHEMIE. A demonstration of various morphology of our nano ZnO samples that is depended on used preparation process, shows **Fig. 1**. In **Table 1** the comparison of parameters of our nano ZnO samples with competitive nanomaterials and also o-ZnO is mentioned. You can see, that the quality of our materials is comparable or even better than quality of competitive products. Actually we are able to produce nano ZnO with a size of primary particles approximately 7 nm (XRD) or 10-20 nm (HRTEM) and specific surface area higher than 50 $m^2 \cdot g^{-1}$ (BET). Material has a good purity (XRF). The nanoscale of our materials absolutely confirms images from HRTEM.

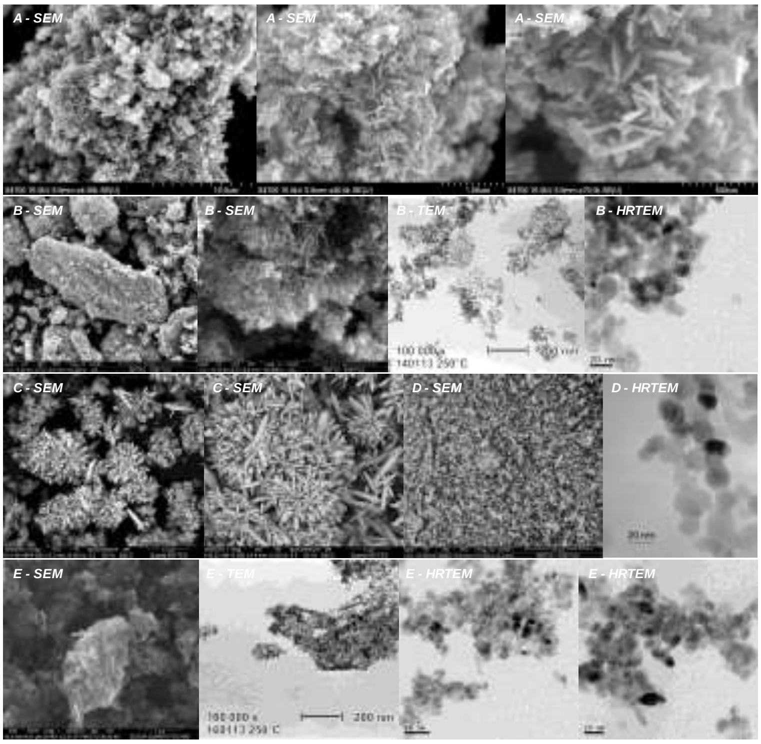

Fig. 1 Images of five nano ZnO samples (A-E) with various morphology

Table 1 Comparison of parameters of our nano ZnO samples with competitive nanomaterials and o-ZnO

Vzorky	XRD			BET	XRF		DLS
	ZnO (%)	**Particle size (nm)**	**Amorphous phase (%)**	**Specific surface area ($m^2 \cdot g^{-1}$)**	**ZnO (wt. %)**	**Cl^- (wt. %)**	**Mean (nm)**
Nano ZnO samples of BOCHEMIE	100	7 ± 2	18	105	99.91	0	103
	100	7 ± 1	17	106	99.93	0	558/92
	100	7 ± 1	13	94	99.93	0	134
	100	7 ± 1	15	86	99.90	0.051	671
	100	6 ± 1	19	72	99.84	0.040	102
	100	7 ± 2	17	54	99.94	0	-
Competitive nano ZnO products	100	9 ± 1	10	70	99.47	0.041	577
	100	12 ± 1	20	64	99.10	0.107	-
	100	12 ± 4	1	58	99.98	-	79
	100	7 ± 1	30	44	98.91	0.832	209
	100	15 ± 3	11	44	98.91	-	579
	100	13 ± 2	2	40	99.91	-	218
	100	22 ± 5	2	35	99.96	-	97
	100	18 ± 6	0	30	99.96	-	100
	100	12 ± 2	7	24	99.97	-	123
	100	29 ± 8	0	17	99.98	-	138
o-ZnO	100	66 ± 9	20	6	99.84	-	434
	100	69 ± 8	0	3-5	99.50	-	333

Relevant application tests were done with nano ZnO samples with varying parameters. The main goal of these tests was to obtain a better idea about crucial parameters of this nanomaterial in a given application and find sufficient dosage of nano ZnO which is necessary for a required functional activity. In **Tabel 2** are the summarized characteristics of samples used in vulcanizing tests in which were nano ZnO tested as a potential new activator.

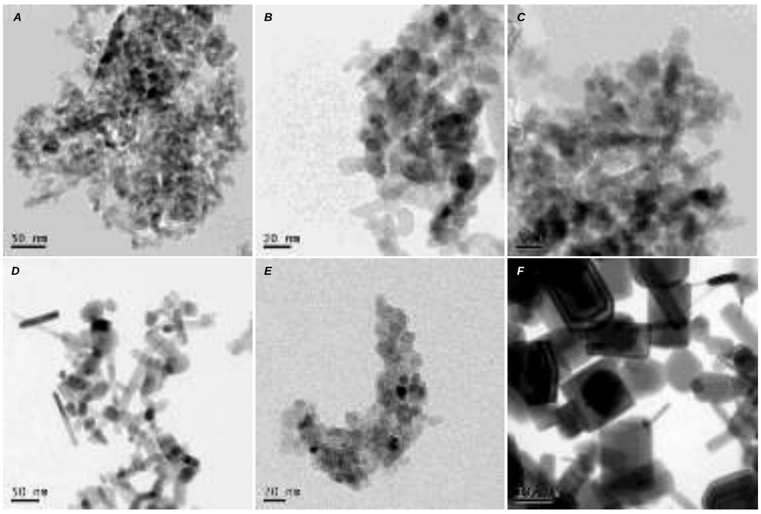

Fig. 2 HRTEM images of nano ZnO BOCHEMIE (A-C), competitive nanomaterials (D and E) and o-ZnO (F)

Table 2 Characteristics of the nano ZnO samples tested as a new vulcanizing activator

Series I	Specific surface area ($m^2 \cdot g^{-1}$)	Particle size (nm)	ZnO content (wt.%)	Series II	Specific surface area ($m^2 \cdot g^{-1}$)	Particle size (nm)	ZnO content (wt. %)
1	27	17 ± 2	99.73	7	114	6 ± 1	99.75
2	102	7 ± 1	99.45	8	84	7 ± 1	99.95
3	73	8 ± 1	99.36	9	105	7 ± 2	99.91
4	37	8 ± 2	-	10	85	7 ± 2	99.75
5	72	8 ± 1	99.58	**Standard (o-ZnO):** Golden Seal R Q3 (Olawka Huta, Poland), specific surface area: 5-6 $m^2 \cdot g^{-1}$			
6	52	10 ± 1	98.96				

Firstly, we tested vulcanization properties (vulcanizing activity and influence on the strength properties of the cross-link density) of nano ZnO samples in a basic model rubber mixture (recipe: 100 phr natural rubber, 5 phr ZnO, 2 phr stearic acid, 2 phr sulphur and 1 phr MBTS [2]). Quantities of nano ZnO in model mixtures were 100, 50, 25 and 12.5 % in comparison with the standard. The samples, which were evaluated from the aspect of the best properties in the model mixtures, were subjected to the more complex evaluation (determination of vulcanizing characteristic and mechanical properties of vulcanizates) in relation to the rubber mixture used for tire manufacturing (a real mixture). A standard amount of ZnO in this mixture was 3 phr and tested quantities of nano ZnO were 3, 1.5, 0.75 and 0.375 phr (100, 50, 25 and 12.5 % in comparison to the standard ZnO).

Samples of similar characteristics as were showed in **Table 1** were also tested for a preparation of hygienic coatings. Antibacterial activity of prepared coatings was measured in accordance with ISO 27447:2009(E) and an internal accredited method of Health Institute in Ostrava.

We also have studied photocatalytic properties of our nanomaterials and compared them with commercial nano ZnO products and TiO_2 P25 (Evonik Degusa). Photocatalytic activity was determined in suspension of model dye Acid Orange 7 (AO7). Intensity of UV radiation was 2 $mW \cdot cm^{-2}$.

3. RESULTS AND DISCUSSION

3.1 Nano ZnO as the vulcanizing activator

From vulcanizing properties of nano ZnO series I (**Table 2**) in model mixture, samples 2, 3 and 5 achieved good properties even at 50 and 25 % dosage. When the dosage was 12.5 %, it was not sufficient. These samples had the largest surface from this series. Cure rate coefficient was increased with decreasing amounts of nano-ZnO - it may mean that higher doses (100 %) were beyond the limit. This paradox is described in literature and it is connected with the fact that too large amount of ZnO in the composition can have the opposite effect on activation [3].

These three samples were afterwards subjected to the more complex evaluation in the real mixture. The measured values are shown in **Table 3**. From these results is clear that samples 3 and 5 showed good properties (comparable to the 100 % of o-ZnO) at amount between 50 to 25 % (1.5 to 0.75 phr) and sample 2 even at 25 % (0.75 phr).

Table 3 Vulcanizing properties and mechanical properties of vulcanizates with nano ZnO series I

Sample series I	ZnO (phr)	Vulcanizing characteristics			Cross-link density $\cdot 10^{-4}$ ($mol \cdot cm^{-3}$)	Mechanical properties of vulcanizates		
		t_s (min)	$t_{c(90)}$ (min)	R_V (min^{-1})		Strenght (MPa)	Tensibility (%)	Modulus 300 (MPa)
o-ZnO	3.00	4.43	9.84	18.48	1.9534	29.66	469	18.30
2	3.00	5.23	11.60	15.70	2.1202	29.94	422	18.70
2	1.50	5.01	10.86	17.09	2.1811	30.04	426	20.58
2	0.75	4.51	10.23	17.48	2.1945	29.56	432	20.06
3	3.00	3.20	6.52	30.12	1.8724	25.24	401	18.62
3	1.50	4.50	10.20	17.54	2.1801	26.04	437	17.26
3	0.75	3.98	7.49	28.49	1.5900	28.90	473	16.96
5	3.00	5.01	11.29	16.13	2.1517	29.20	435	19.40
5	1.50	4.76	10.44	17.06	2.2022	28.68	433	19.12
5	0.75	3.58	7.33	26.67	1.6019	26.52	446	16.78

To confirm this discovery verifying tests we performed on subsequently produced samples with higher specific surface area - nano ZnO series II (**Table 2**). These samples were subjected to the same tests under the same conditions as series I. The compared results (**Table 4**) show that the dosage of 0.375 phr (12.5%) of nano ZnO was already insufficient in real mixtures. The samples of series II exhibited better curing and mechanical properties of vulcanizates at lower dosage (0.75 phr respectively 25%) compared to Series I. It was caused by the higher specific surface area and smaller particle size of ZnO.

Table 4 Vulcanizing properties and mechanical properties of vulcanizates with nano ZnO series II

Sample series II	ZnO (phr)	Vulcanizing characteristics			Cross-link density $\cdot 10^{-4}$ ($mol \cdot cm^{-3}$)	Mechanical properties of vulcanizates		
		t_s (min)	$t_{c(90)}$ (min)	R_V (min^{-1})		Strenght (MPa)	Tensibility (%)	Modulus 300 (MPa)
7	3.00	6.11	13.12	14.27	1.4042	29.39	438	19.69
7	1.50	5.93	11.39	18.32	2.1614	29.12	426	20.02
7	0.75	5.38	9.89	22.17	1.4883	28.47	504	15.31
7	0.375	3.40	5.32	52.08	2.0821	24.23	502	13.34
8	3.00	5.89	12.68	14.73	2.1427	28.57	415	19.79
8	1.50	5.35	11.26	16.92	1.9469	26.91	404	19.35
8	0.75	5.19	9.38	23.87	2.0509	25.70	503	14.18
8	0.375	3.11	5.09	50.51	1.8588	23.29	494	12.45
9	3.00	6.10	12.80	14.93	1.8202	28.98	432	19.36
9	1.50	5.75	11.72	16.75	2.0144	28.66	443	18.53
9	0.75	5.30	9.48	23.92	1.6567	26.66	508	13.97
9	0.375	3.49	5.59	47.62	1.4005	22.03	482	11.94

3.2 Nano ZnO as the additive in a paint or lacquer

A very interesting functional property of ZnO is its antimicrobial activity, which was first mentioned in 1995 [4,5]. We have done comparative antimicrobial tests (6 microorganisms) of our samples with competitive nano ZnO materials and o-ZnO. ZnO samples were tested in powder state and also in tailor-made lacquers.

In powder form our samples show a lower activity, in comparison with competitive materials, which is possible to award to high agglomeration of primary particles. Absolutely opposite results were obtained when we have tested an activity of nano ZnO in lacquers, where well dispergated nanoparticles are presented and our samples showed the best activity. Examples of selected results are mentioned in **Table 5** and **6**.

Table 5 Antimicrobial activity (*Escherichia Coli*) of lacquers (on water-based) with nano ZnO and o-ZnO

Lacquer with	Concentration of ZnO (wt. %)	0 h CFU/50 µl	Exposition 4 h, CFU/50 µl	
			Darkness	UV radiation
pure glass (blank)	0	7 300	4 300	3 000
nano ZnO BOCHEMIE	0.3		17	5
nano ZnO BOCHEMIE	1.0		0	0
o-ZnO	0.3		1 400	668
o-ZnO	1.0		976	364

Table 6 Antimicrobial activity (*Staphylococcus Aureus*, density 10^8, day-light) of lacquers (on solvent-based) with nano ZnO BOCHEMIE and competitive nanomaterials (C1 - nano ZnO and C2 - nano ZnO)

Exposition in minutes	180			240			300		
Lacquer with — Test	1	2	3	1	2	3	1	2	3
without ZnO	uncountable amount			uncountable amount			uncountable amount		
nano ZnO BOCHEMIE - 1 wt. %	uncountable amount			uncountable amount			43	13	5
nano ZnO BOCHEMIE - 3 wt. %	uncountable amount			78	38	28	23	12	11
C1 - nano ZnO - 3 wt. %	uncountable amount			uncountable amount			uncountable amount		
C2 - nano ZnO - 3 wt. %	uncountable amount			uncountable amount			185	75	31
pure glass (blank)	uncountable amount			uncountable amount			uncountable amount		

A next significant advantage is, compared to o-ZnO and also some competitive nanoproducts, that our nano ZnO samples are highly transparent in an appropriate matrix, which is a very interesting property for preparation of functional transparent lacquers. A demonstration of these lacquers shows **Fig. 3**. The antibacterial activities of these lacquers were mentioned in **Table 6**.

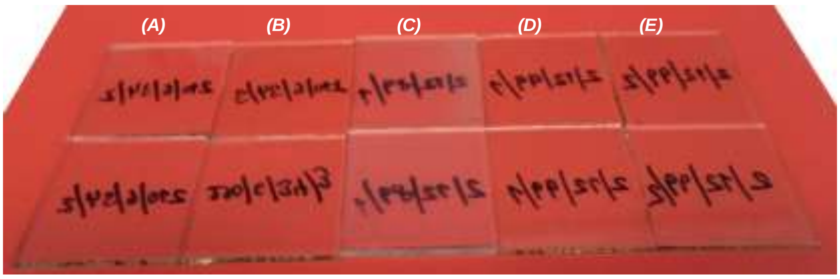

Fig. 3 Photos of functional transparent lacquers - (A) without ZnO, (B and C) with competitive nano ZnO (content 3 wt. %) and (D and E) with nano ZnO BOCHEMIE (content 3 and 1 wt. %)

Fig. 4 Photos of wood (spruce) with or without protection coating before (on the left side) and after 4 month UV-C exposition (on the right side)

ZnO is known as a universal wide-spectral inorganic UV filter. So a transparent lacquer with UV protection activity seems to be a very interesting application opportunity of this nanomaterial, e.g. protection film on wood. We have done an input test and prepared transparent coatings containing competitive nano ZnO and nano TiO_2. Unfortunately the UV protection activity was in both cases in-sufficient (**Fig. 4**). A possible reason of this negative finding could be a high photocatalytic effect of tested competitive nanomaterials.

3.3 Photocatalytic activity of nano ZnO

ZnO shows comparable photocatalytic properties as TiO_2, which is actually the most used photocatalyst (number one). Nevertheless photocatalytic activity of our nano ZnO samples is significantly lower compared to the other tested nanomaterials (**Fig. 5**). This property seems to be promising for application of our nano ZnO in UV protection lacquers. We plan to test this application opportunity of nano ZnO.

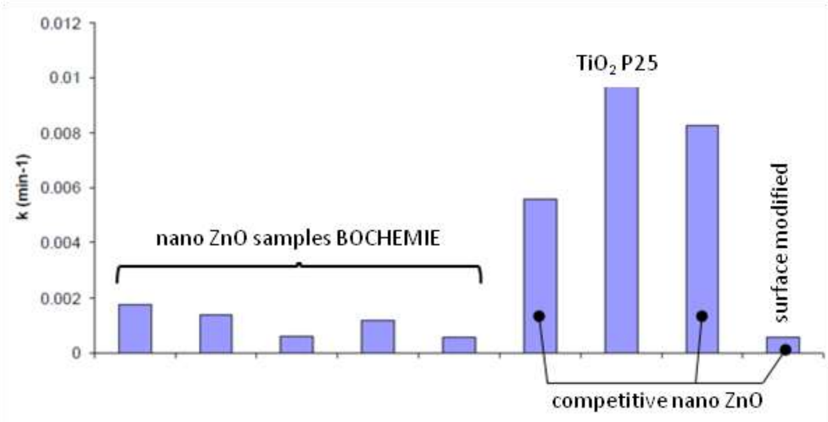

Fig. 5 A comparison of photocatalytic activity of samples BOCHEMIE with competitive nanomaterials

4. CONCLUSIONS

The main goal of this contribution is to present some application possibilities of nano ZnO. From the mentioned results seems to be that our nano ZnO is a very interesting material which shows better functional properties (especially vulcanizing and antimicrobial activity) than o-ZnO but also competitive nano ZnO products. The next very significant advantage of our nano ZnO will be its easy availability and thus its sale for a reasonable or even better a very interesting price, compared to actually available competitive nano ZnO products.

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