

# Application of zinc and magnesium oxides nanoparticles in crosslinking of carboxylated butadiene-acrylonitrile rubber.

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## ABSTRACT

In our work nanosized zinc oxides as well as magnesium oxide of different size and morphology for crosslinking of carboxylated butadiene-acrylonitrile rubber XNBR were applied. The relationship between the most important parameters influencing the activity during the ionic crosslinking process i.e specific surface area, particle size and morphology of oxides surface and the mechanical properties of obtained crosslinked materials were examined. The influence of used oxides on the curing kinetics, crosslink density of vulcanisates and the content of ionic crosslinks was determined. We conclude that zinc and magnesium oxides allowed to obtain vulcanisates with considerably better mechanical properties as compared to those crosslinked with 8 phr of commercially used microsized zinc oxide. Magnesium oxide nanoparticles showed higher activity in the crosslinking process and as a result vulcanisates with higher crosslink density and ionic crosslink content are achieved. Moreover, it was noticed that MgO nanoparticles have lower ability for agglomeration in the XNBR matrix and create smaller, well dispersed agglomerates.

**Keywords:** carboxylated butadiene-acrylonitrile rubber, nanoparticles, magnesium oxide, zinc oxide, ionic crosslinking

## 1 INTRODUCTION

Zinc oxide is one of the most important components of elastomer blends. It acts as an activator in sulphur vulcanization, additionally it can be used as a crosslinking substance of elastomers which contains reactive functional groups such as halogens or carboxyl groups<sup>1</sup>. Zinc oxide is a very effective crosslinking agent for carboxylated elastomers<sup>2-5</sup>. The reaction of carboxylic group presented in elastomer such as carboxylated butadiene-acrylonitrile rubber XNBR with metal oxides leads to salt formation<sup>6</sup>. Ionic crosslinks obtained this way are multifunctional, labile and able to form clusters or multiplets<sup>6</sup>. The presence of clusters causes the improvement of physical properties, even in case of unfilled ionic elastomers. Ionic elastomers show higher tensile strength, tear resistance, hardness and hysteresis as compared to those crosslinked with sulphur

and accelerators. These advantages result from their higher ability for stress relaxation. Moreover, ionic elastomers demonstrate thermoplastic properties and can be processed in a molten state<sup>7</sup>.

## 2 EXPERIMENTAL

### 2.1 Materials and characterization

In our work to prepare rubber mixtures carboxylated butadiene-acrylonitrile rubber XNBR (Krynac X7.50) containing 27 wt% acrylonitrile and 6.7 wt% carboxylic groups produced by Bayer AG was used. As a crosslinking agents were applied:

- magnesium oxide MgO – nanopowder (Sigma – Aldrich with surface area 130 m<sup>2</sup>/g
- zinc oxide ZnO A – nanopowder (Qinetiq Nanomaterials Ltd) with surface area 35 m<sup>2</sup>/g
- zinc oxide ZnO B – nanopowder (Sigma – Aldrich) with surface area 20 m<sup>2</sup>/g

The specific surface area of oxides was measured using low-temperature nitrogen adsorption method with Sorptomatic 1900 (Fisons Instruments). The size of oxides aggregates was determined using a Zetasizer NanoS90 apparatus (Malvern). The size of particles in water dispersions (0.2g/dm<sup>3</sup>) was measured based on the dynamic light scattering DLS method. The zeta potential of the oxides water dispersions (0.2g/dm<sup>3</sup>) was determined by Zetsizer 2000 (Malvern). The morphology and the surface structure of the oxides was determined from scanning electron microscope images by using LEO 1530 microscope (Zeiss). Samples with graphite coated structure were used in these investigation.

### 2.2 Preparation and characterization of rubber vulcanisates

Rubber mixtures were made by a laboratory two-roll mill at a temperature of approximately 35°C. The conditions of vulcanization were determined by oscillating disc rheometer. The samples were vulcanized at 160°C for the time necessary for a torque increase of moment of the rheometer by 90% ( $\tau_{0.9}$ ). The crosslink density of the vulcanisates was calculated from equilibrium swelling in toluene using Flory-Rehner equation<sup>8</sup>. In order to determine the content of ionic crosslinks in the elastomer network

samples were swollen in toluene in a desiccator with saturated ammonia vapour (25% aqueous solution). The mechanical properties of the vulcanisates were determined according to ISO-37 using a ZWICK 1435 universal machine. The dispersion of oxides in rubber matrix were estimated using scanning electron microscopy LEO 1530 (Zeiss). The surfaces formed after liquid-nitrogen fracture were examined. Samples with graphite coated structure were used in these investigation. The following magnification were used: 2000, 10 000, 20 000, 50 000.

### 3 RESULTS AND DISCUSSION

The particle sizes of used oxides were investigated (table 1).

oxides	Aggregate size, nm	Size of the aggregate main fraction, nm	Number, %
MgO	165-233	185	39
ZnO A	116-417	165	20
ZnO B	295-664	372	33

Table 1: Size of zinc and magnesium oxide aggregates.

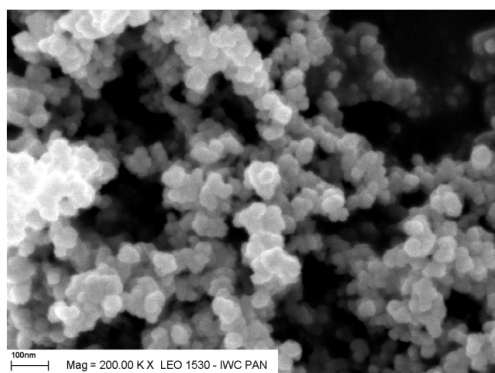


Fig 1: SEM image of MgO particles

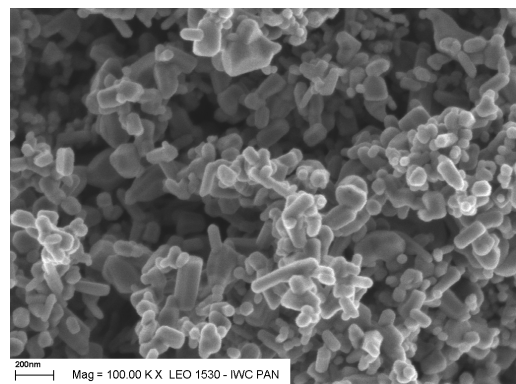


Fig 2: SEM image of ZnO B particles.

The sizes of aggregates determine the activity of the oxides during crosslinking. The reduction in size results in an increase in a specific surface area providing better contact between the particles and elastomer chains. Moreover it determines the size of the interphase between the surface and an elastomeric matrix. Both used zinc oxides showed high tendency to agglomerate and as a result formed aggregates with higher size than it was in case of magnesium oxide.

The morphologies of the zinc and magnesium particles were presented in figure 1-2. The ZnO B particles characterized elongated shape with sharp edges. In case of magnesium oxide the spherical morphological structure of particles was observed.

The zeta potential of oxides aqueous dispersions was also studied. The isoelectric point for magnesium dispersion occurred at pH = 5.7. For the dispersion of zinc oxide B the isoelectric point occurred at higher value of pH=6.5.

The influence of different amount of oxides on the vulcanization time was studied (table 2). Zinc oxide type A showed higher activity during crosslinking. The rubber mixtures crosslinked by ZnO A characterized the shortest vulcanization time  $\tau_{0.9}$ .

Amount of oxide used, phr	MgO	ZnO A	ZnO B
2	3235	2200	2488
3	2990	1611	1740
4	2644	1128	1418
5	1616	900	1105

Table 2: Vulcanization time  $\tau_{0.9}$  (s) for the XNBR mixtures crosslinked with different amount of zinc and magnesium oxides.

The mechanical properties of XNBR vulcanisates crosslinked using different amount of magnesium oxide and zinc oxide B were investigated. From the data compiled in table 3, it follows that the application of magnesium dioxide substantially increased the tensile strength TS of the vulcanisates as compared to those produced using zinc oxide (table 4, fig. 3). The 100% modulus  $SE_{100}$  of the vulcanisates increased with the amount of the mineral oxides in the composite. The influence of the amount of magnesium oxide on the elongation at break  $E_b$  was not observed.

Amount of MgO used, phr	$SE_{100}$ , MPa	TS, MPa	$E_b$ , %
2	1.89	29.03	691
3	2.72	29.91	619
4	3.40	45.84	640
5	3.48	40.34	691

Table 3: Mechanical properties of XNBR vulcanisates crosslinked using MgO.  $SE_{100}$  – 100% modulus, TS – tensile strength,  $E_b$  – elongation at break.

Amount of ZnO used, phr	SE <sub>100</sub> , MPa	TS, MPa	Eb, %
2	0.70	2.05	868
3	1.47	6.97	599
4	1.52	9.63	598
5	1.74	14.21	557

Table 4: Mechanical properties of XNBR vulcanisates crosslinked using ZnO B. SE<sub>100</sub> – 100% modulus, TS – tensile strength, Eb – elongation at break.

The zinc oxide A with higher surface area – 35 m<sup>2</sup>/g was more active crosslinking agent for XNBR than zinc oxide B (20 m<sup>2</sup>/g) as estimated based on the tensile properties of crosslinked vulcanisates (fig. 3).

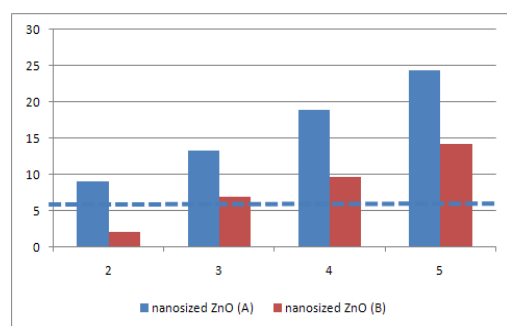


Fig. 3: Tensile strength (MPa) of XNBR vulcanisates crosslinked by different amount (phr) of nanosized ZnO. Index (A) ZnO surface area 35 m<sup>2</sup>/g, (B) ZnO surface area 20 m<sup>2</sup>/g, dotted line – the value of tensile strength of XNBR crosslinked with 8 phr micro-sized ZnO.

In tables 5-6 are presented the results of hysteresis measurements. The hysteresis of the vulcanisates increased with the amount of mineral oxide used.

Amount of MgO used, phr	W <sub>1</sub> , kJ/m <sup>2</sup>	W <sub>1</sub> - W <sub>5</sub>
2	8.51	5.30
3	20.62	14.86
4	28.43	22.27
5	34.21	28.15

Table 5: Hysteresis of XNBR. W<sub>1</sub> – hysteresis during 1<sup>st</sup> strain, W<sub>5</sub> – hysteresis during 5<sup>th</sup> strain.

Amount of ZnO used, phr	W <sub>1</sub>	W <sub>1</sub> - W <sub>5</sub>
2	6.17	4.67
3	6.59	4.48
4	11.13	7.36
5	13.46	9.02

Table 6: Hysteresis of XNBR. W<sub>1</sub> – hysteresis during 1<sup>st</sup> strain, W<sub>5</sub> – hysteresis during 5<sup>th</sup> strain.

Amount of oxide used, phr	MgO	Δv, %
2	7.13	24.54
3	9.43	24.92
4	6.47	25.97
5	7.36	32.88

Table 7: Crosslink density  $\nu \cdot 10^5$  (mol/cm<sup>3</sup>) of XNBR vulcanisates containing different amount of MgO.

We observed the increase in ionic crosslink content in the elastomer network ( $\Delta v$ ) due to amount of MgO used. The presence of multifunctional labile ionic clusters resulted in the higher ability of vulcanisates for stress relaxation and as a consequence led to an improvement of mechanical properties. The crosslink density of vulcanisates  $\nu$  increased with the amount of oxide used. The presented results of crosslink density (fig. 4) prove that as we supposed the activity of zinc oxides in the crosslinking process rises with the specific surface area

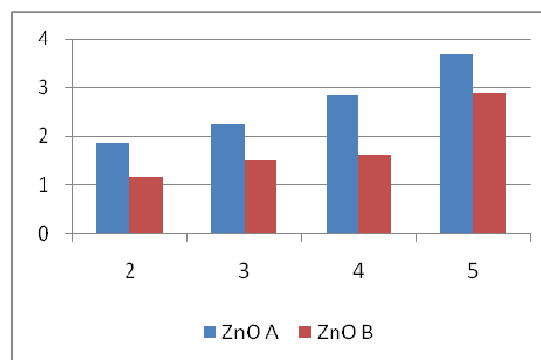


Fig 4: Crosslink density  $\nu \cdot 10^5$  (mol/cm<sup>3</sup>) of XNBR vulcanisates containing different amount of ZnO.

In order to improve the properties of blends and vulcanisates of carboxylated butadiene - acrylonitrile rubber XNBR different types of silica (20 phr) were added to rubber mixtures. For this purpose precipitated silica traditionally used in the rubber industry (Zeosil MP 175 - 175 m<sup>2</sup> / g) and nano-sized fumed silica (Aerosil 380 MP - 7 nm, 380 m<sup>2</sup> / g) were used.

Addition of silica to vulcanisates XNBR crosslinked using 2 phr of MgO resulted in improved mechanical properties only when micrometer silica Zeosil 175MP was used. Addition of nanometric silica did not affect significantly the properties of XNBR vulcanisates (Table 7).

In table 8 are presented the mechanical properties of XNBR vulcanisates crosslinked with 4 phr of ZnO B. Addition of silica to rubber mixtures affected significantly the tensile strength TS of vulcanisates in comparison to unfilled one.

We also studied the influence of silica application on the hysteresis of the vulcanisates (table 9).

Amount of MgO used, 2 phr	SE <sub>100</sub> , MPa	TS, MPa	Eb, %
Zeosil 175	5.48	40.40	541
Aerosil 380	3.35	24.73	635

Table 7: Mechanical properties of XNBR vulcanisates crosslinked using 2 phr MgO and containing 20 phr of silica.

Amount of ZnO used, 4 phr	SE <sub>100</sub> , MPa	TS, MPa	Eb, %
Zeosil 175	3.53	28.87	597
Aerosil 380	3.30	28.92	554

Table 8: Mechanical properties of XNBR vulcanisates crosslinked using 4 phr ZnO B and containing 20 phr of silica.

Silica used	MgO, 2phr		ZnO, 4 phr	
	W <sub>1</sub> , kJ/m <sup>2</sup>	W <sub>1</sub> - W <sub>5</sub>	W <sub>1</sub> , kJ/m <sup>2</sup>	W <sub>1</sub> - W <sub>5</sub>
Zeosil 175	61.94	51.19	36.40	28.96
Aerosil 380	26.10	19.47	32.36	25.27

Table 9: Hysteresis of XNBR containing different silicas. W<sub>1</sub> – hysteresis during 1<sup>st</sup> strain, W<sub>5</sub> – hysteresis during 5<sup>th</sup> strain.

Analysis of SEM images of MgO vulcanisates crosslinked with MgO and ZnO showed that magnesium oxide agglomerated in lesser extent than the ZnO and formed the agglomerates of a size not exceeding 800 nm (Fig. 6). Dispersion of MgO in elastomer matrix was homogeneous and uniform (fig 5.).

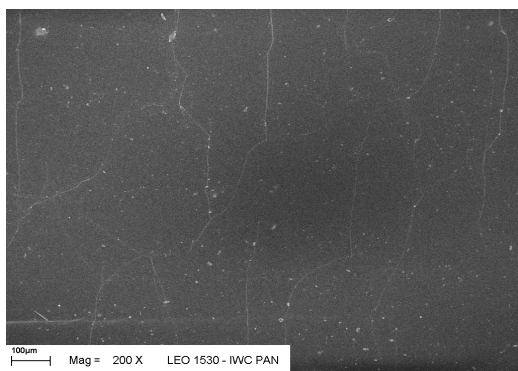


Fig 5: SEM image of XNBR vulcanisate crosslinked with 5 phr of MgO.

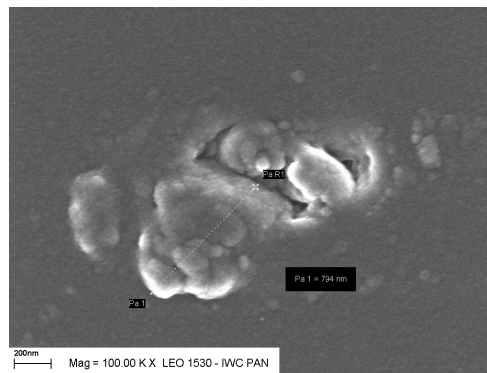


Fig 6: SEM image of MgO agglomerate.

## 4 CONCLUSIONS

Magnesium and zinc oxides with different surface area and particles size were used as crosslinking agents of carboxylated butadiene-acrylonitrile rubber XNBR.

The application of magnesium and zinc nanoparticles allowed to obtain vulcanisates with considerably better mechanical properties as compared to vulcanisates crosslinked with microsized ZnO. As a result of magnesium oxide application the vulcanisates with higher crosslink density and ionic crosslink content are achieved. These vulcanisates characterized the best mechanical properties (TS about 40 MPa). Magnesium oxide exhibited higher activity in crosslinking reactions than used zinc oxides. Moreover MgO nanoparticles had lower ability for agglomeration in the elastomer matrix and created smaller agglomerates as compared to the large agglomerates formed by zinc oxides.

The morphology and the size of zinc oxide particles influenced on the activity in the crosslinking process. The higher activity was observed for zinc oxide A with higher surface area and smaller particles size than in case of zinc oxide B. As a result the vulcanisates with higher crosslink density and better mechanical properties were achieved.

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