

The effect of zinc oxide nanoparticle morphology on activity in crosslinking of carboxylated nitrile elastomer

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Received 27 April 2009; accepted in revised form 9 June 2009

Abstract. The aim of this work was to study the activity of several nanosized zinc oxides in the crosslinking of carboxylated nitrile elastomer (XNBR). In this article, we discuss the effect of zinc oxide nanoparticles with respect to their specific surface area, particle size and morphology (spheres, whiskers, and snowflakes) on the crosslinking density and mechanical properties of vulcanisates.

The morphology of nanoparticles considerably influences the activity of zinc oxide towards carboxylated nitrile rubber. As a crosslinking agent, zinc oxide with snowflake particles seems to be the most active. The application of nanosized zinc oxide allows the amount of ZnO to be reduced by almost 40%, as compared to vulcanisates containing microsized particles. Moreover, vulcanisates crosslinked with zinc oxide nanoparticles exhibit thermoplastic properties that enable this material to be recycled, which is very important from an ecological point of view.

Keywords: *nanocomposites, rubber, mechanical properties, zinc oxide, carboxylated nitrile elastomer*

1. Introduction

Carboxylated nitrile rubber (XNBR) can be crosslinked by sulphur with accelerators; however, the most relevant method is the application of bivalent metal oxides, especially zinc oxide (ZnO) [1, 2]. The crosslinking of elastomer occurs via the reaction of its carboxylic groups with zinc oxide, resulting in the formation of carboxylic salts, considered to be ionic crosslinks. In contrast to the covalent crosslinks formed during conventional vulcanisation with sulphur/accelerator systems or peroxides, ionic crosslinks are multifunctional and labile [3]. Carboxylic salts group together, forming clusters or multiplets [4]. According to Ibarra and Alzoriz [2], multiplets consist of six to eight dipole ions associated to form larger multiplets, which disperse in the elastomer matrix without forming a separate phase. These multiplets have a considerable impact on the glass transition temperature of

the elastomer and its sensitivity to water. Clusters are considered as ionic aggregates, in separate ion-pair-rich regions, immersed in an elastomer matrix [1]. The presence of ionic clusters is responsible for the improved physical properties of ionic elastomers, even without filler addition, as compared to those conventionally crosslinked with sulphur and accelerators [5, 6]. The proportion of ionic crosslinks present in the form of multiplets or clusters in the elastomer network depends on the nature and structure of the elastomer macromolecule as well as the chemical nature and concentration of the carboxylic salt groups [2, 7]. According to Eisenberg and King [8], clusters are formed by the association of multiplets. This association is caused by electrostatic interactions between multiplets and is impaired by the retractive elastic forces of the backbone chains. The restricted elastomer chain mobility in the proximity of ionic clusters results in the

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formation of a hard phase. The presence of a hard phase in ionic elastomers or ionomers has been confirmed by measurements of dynamic mechanical properties, demonstrating the occurrence of a biphasic transition in XNBR/zinc oxide composites [9, 10]. Apart from the low glass transition temperature of elastomers, there is a high transition temperature due to the formation of a hard phase arising from the ionic clusters. Mandal *et al.* [5] confirmed the relationship between the high temperature transition and the presence of ionic aggregates in elastomer networks. Treatment of crosslinked samples with ammonia vapour caused the disappearance of the high temperature transition in the dynamic mechanical spectra. Ammonia acts as a plasticiser for the ionic aggregates, forming coordinating bonds with zinc ions of carboxylic salts or solvating the carboxylic ions. As a result, the ionic clusters are resolved, and the vulcanisate mechanical properties deteriorate.

Zinc oxide is a very effective and commonly used crosslinking agent for carboxylated elastomers [5, 10–13]. It can be used to produce vulcanisates with high tensile strength, tear resistance, hardness and hysteresis. The improved mechanical properties of ionic elastomers mainly result from their high ability for stress relaxation, due to elastomer chain slippage on the ionic cluster surface and reformation of ionic bonds upon external deformation of the sample. Moreover, ionic elastomers possess a thermoplastic character and can be processed in a molten state as a thermoplastic polymer [14]. However, there are some disadvantages to zinc-oxide-crosslinked carboxylic elastomers. The most important are the scorchiness, poor flex properties and high compression set [13]. In order to prevent scorchiness, carboxylated nitrile elastomers are crosslinked with zinc peroxide [2] or zinc peroxide/zinc oxide systems [13]. The vulcanisation of XNBR with zinc peroxide mainly leads to the formation of ionic crosslinks; covalent links are also formed between elastomer chains due to the peroxide action. However, higher vulcanisation times are required to achieve vulcanisates with a tensile strength and crosslink density comparable to that of vulcanisates crosslinked with zinc oxide [2]. In the case of XNBR vulcanisation with zinc peroxide/zinc oxide systems, the curing is the sum of at least three processes: a very fast formation of ionic crosslinks due to the initial zinc oxide present, per-

oxide crosslinking that leads to the formation of covalent links (peroxide action) and ionic crosslinking due to the production of zinc oxide from peroxide decomposition. The last process, which decays with vulcanisation time, is most likely related to the formation of ionic species [13]. The achieved vulcanisation times are considerably higher, as compared to those of XNBR crosslinking with zinc oxide. Therefore, apart from the scorch problems, zinc oxide is still commonly used as a crosslinking agent of carboxylated nitrile rubbers. Taking into account the fact that, during the crosslinking process, zinc oxide reacts with carboxylic groups of elastomer, which leads to the formation of carboxylic salts (ionic crosslinks), the most important parameters influencing zinc oxide activity are its specific surface area, particle size and morphology. These parameters determine the size of the interphase between the crosslinking agent and elastomer chains.

The influence of zinc oxide particle size on the curing of carboxylated rubbers was reported by Hamed and Hua [15]. However, there are still some important aspects, which should be clarified. The effect of zinc oxide particle morphology on the crosslinking process and vulcanisate properties has not yet been reported.

In this work, we applied zinc oxides with different specific surface areas, particle sizes and morphologies (spheres, whiskers, snowflakes) as crosslinking agents of carboxylated nitrile elastomer, in order to determine the relationship between zinc oxide characteristics and activity in the crosslinking process.

2. Experimental section

2.1. Materials

Carboxylated nitrile elastomer XNBR (Krynac X7.50) containing 27 wt% acrylonitrile and 6.7 wt% carboxylic groups was obtained from Bayer C.O. The Mooney viscosity was (ML1+4 (100°C):47). Zinc oxides with different specific surface areas, particle sizes and morphologies were applied as crosslinking agents. Didodecyltrimethylammonium bromide (DDAB, Fluka) was used to improve the dispersion of the zinc oxide particles in the elastomer matrix.

The physical characteristics of the zinc oxides applied are given in Table 1.

Table 1. Characteristics of zinc oxides

Symbol	Specific surface area [m ² /g]	Particle morphology	Producer
ZnO 10	10.00	spheres and rods	Sigma-Aldrich
ZnO 15	15–25	whiskers	Sigma-Aldrich
ZnO 24	24.43	snowflakes	Institute of High Pressure Physics, Polish Academy of Science
ZnO 40	40.86	spheres	Institute of High Pressure Physics, Polish Academy of Science
ZnO 42	42.50	spheres	Qinetiq Nanomaterials Limited
ZnO 50	50.00	spheres	Nanostructured & Amorphous Materials, Inc.

2.2. Zinc oxide specific surface area

The specific surface area of zinc oxide was measured using low-temperature nitrogen adsorption (78 K) method with Sorptomatic 1900 (Fisons Instruments) apparatus. The specific surface area was determined with BET method based on the first section of nitrogen adsorption isotherm for $P/P_0 = 0.05\text{--}0.35$. Before the measurement zinc oxide was vacuum out-gassed in the temperature 373 K for 24 h.

2.3. Zinc oxide aggregate size

The size of the zinc oxide aggregates was determined using a Zetasizer Nano Series S90 (Malvern Instruments) apparatus. The size of the zinc oxide particles in water suspensions was measured based on the DLS (Dynamic Light Scattering) method. The concentration of the suspensions was 0.05 g/l.

2.4. Preparation and characterisation of rubber compounds

Rubber compounds with the formulation given in Table 2 were prepared using a laboratory two-roll mill. The samples were cured at 160°C until they developed a 90% increase in torque, measured by an oscillating disc rheometer.

The crosslink density (ν_T) of the vulcanisates was determined by equilibrium swelling in toluene, based on the Flory-Rehner equation [16]. The Huggins parameter of the elastomer-solvent interaction χ was calculated from Equation (1) [12]:

$$\chi = 0.487 + 0.228V_r \tag{1}$$

Table 2. Composition of the XNBR-based rubber compounds [phr]

XNBR	100	100	100	100
ZnO	3	5	6	8
DDAB	1	1	1	1

where V_r is the volume fraction of elastomer in the swollen gel. In order to determine the content of ionic crosslinks in the elastomer network, samples were swollen in toluene in a dessicator with saturated ammonia vapour (25% aqueous solution). The content of ionic crosslinks (Δv) was calculated from Equation (2):

$$\Delta v = \frac{v_T - v_A}{v_T} \cdot 100\% \tag{2}$$

where v_A is the crosslink density determined for samples treated with ammonia vapour using the Huggins elastomer-solvent interaction parameter described by Equation (3) [17]:

$$\chi = 0.483 + 0.320V_r \tag{3}$$

The tensile properties of the vulcanisates were determined according to ISO-37, with a ZWICK 1435 universal machine.

2.5. Dynamic-mechanical analysis

Dynamic-mechanical measurements were carried out in the tension mode using a DMTA V visco-analyser (Rheometric Scientific). Measurements of the dynamic moduli were performed over the temperature range (–100–150°C) with a heating rate of 2°C/min, at a frequency of 1 Hz and a strain amplitude of 0.02%. The temperature of the elastomer glass transition was determined based on the maximum of $\tan\delta = f(T)$, where $\tan\delta$ is the loss factor and T is the measurement temperature.

2.6. Shrinkability measurements

In order to measure the shrinkability of the XNBR vulcanisates, the samples were stretched at ambient temperature until reaching an elongation of 300% at the time 48 h; they were then stabilised in the stretched form at (–7°C) for 8 h. Finally, the stretched samples were allowed to shrink at 70°C

for 48 h. The lengthwise shrinkage was calculated according to Equation (4) [18]:

$$S_h[\%] = \frac{L_{str} - L_{shr}}{L_{str}} \cdot 100 \quad (4)$$

where S_h is the percentage of shrinkability, L_{str} is the length of the sample after stretching, and L_{shr} is the length of the shrunk sample.

2.7. Scanning Electron Microscopy (SEM)

The morphology of the zinc oxide particles and their dispersion in the elastomer matrix were estimated using Scanning Electron Microscopy with a LEO 1530 SEM microscope. The XNBR vulcanisates were broken down in liquid nitrogen, and the fracture surfaces of the vulcanisate were examined. Prior to the measurements, the samples were coated with carbon.

3. Results and discussion

3.1. Zinc oxide particle size and morphology

The particle size of zinc oxide is a main parameter that has a great influence on the ZnO activity. A reduction in particle size results in an increase in the zinc oxide specific surface area, providing better contact between the crosslinking agent particles and the elastomer chains. Moreover, the morphology of the ZnO particles determines the size of the interphase between zinc oxide and the elastomer. The sizes of the zinc oxide aggregates are presented in Table 3. Figure 1 shows the distribution of particle sizes as a function of particle number.

The morphologies of the zinc oxide particles or aggregates are presented in Figure 2a–2f.

Agglomerates of micro-sized zinc oxide (Figure 2a) used commercially in XNBR crosslinking consisted of primary particles with a wide size distribution from several hundreds of nanometres to several micrometres. The ZnO 10 particles revealed

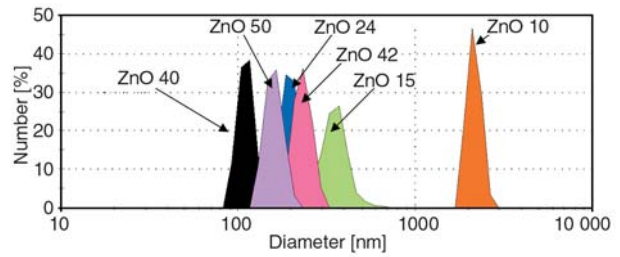


Figure 1. Zinc oxide particle size distribution by number

a variety of morphologies and irregular shapes (deformed spherical particles, elongated rods and blocks with sharp edges). The micro-sized ZnO agglomerates were broken down upon ultrasonic treatment. The aggregate size distribution determined in water dispersion ranged from 1.9–2.7 μm , with the main aggregate fraction at 2.1 μm (46%). The ZnO 15 particles were elongated whiskers with a length of 100–300 nm and a diameter below 100 nm (Figure 2b). The aggregate size, as determined in water, was within the range of 185–664 nm, with the size of the main number fraction being 371 nm (26%). However, in the case of elongated particles, the orientation of the whiskers in the field of laser radiation influenced the obtained data. Therefore, it could be supposed that the measured particle size was a combination of whisker diameter and length.

Interesting morphological structures were observed in the case of ZnO 24 (Figure 2c). Zinc oxide aggregates revealed a shape of snowflakes or three-dimensional flowers consisting of several wires and plates growing from a single core. The primary particles with a size of about 200 nm formed micro-sized aggregates. In water dispersion, the size of the zinc oxide aggregates was reduced upon ultrasonic treatment to 185 nm (35%) (Table 3).

Zinc oxides with specific surface areas of 40.86, 42.5 and 50 m^2/g were found to be spherical with a size of about 100 nm, which agglomerated, forming clusters 10–20 μm in size (Figure 2d–2f). Upon ultrasonic treatment, the ZnO agglomerates were reduced in the water dispersion to aggregates with sizes ranging from 92–131 nm (ZnO 40), 185–295 nm (ZnO 42) and 130–208 nm (ZnO 50) (Table 3).

Elastomers have a hydrophobic nature; therefore, the size of the zinc oxide particles was measured in a liquid hydrophobic medium–paraffin oil, which was chosen as the model for an elastomer matrix (Table 4). The aim of this study was to estimate the

Table 3. Zinc oxide aggregate size

Zinc oxide	Aggregate size [nm]	Size of the aggregate main fraction [nm]	Number [%]
ZnO 10	1886–2671	2118	46
ZnO 15	185–664	371	26
ZnO 24	147–262	185	35
ZnO 40	92–131	116	38
ZnO 42	185–295	234	36
ZnO 50	130–208	165	36

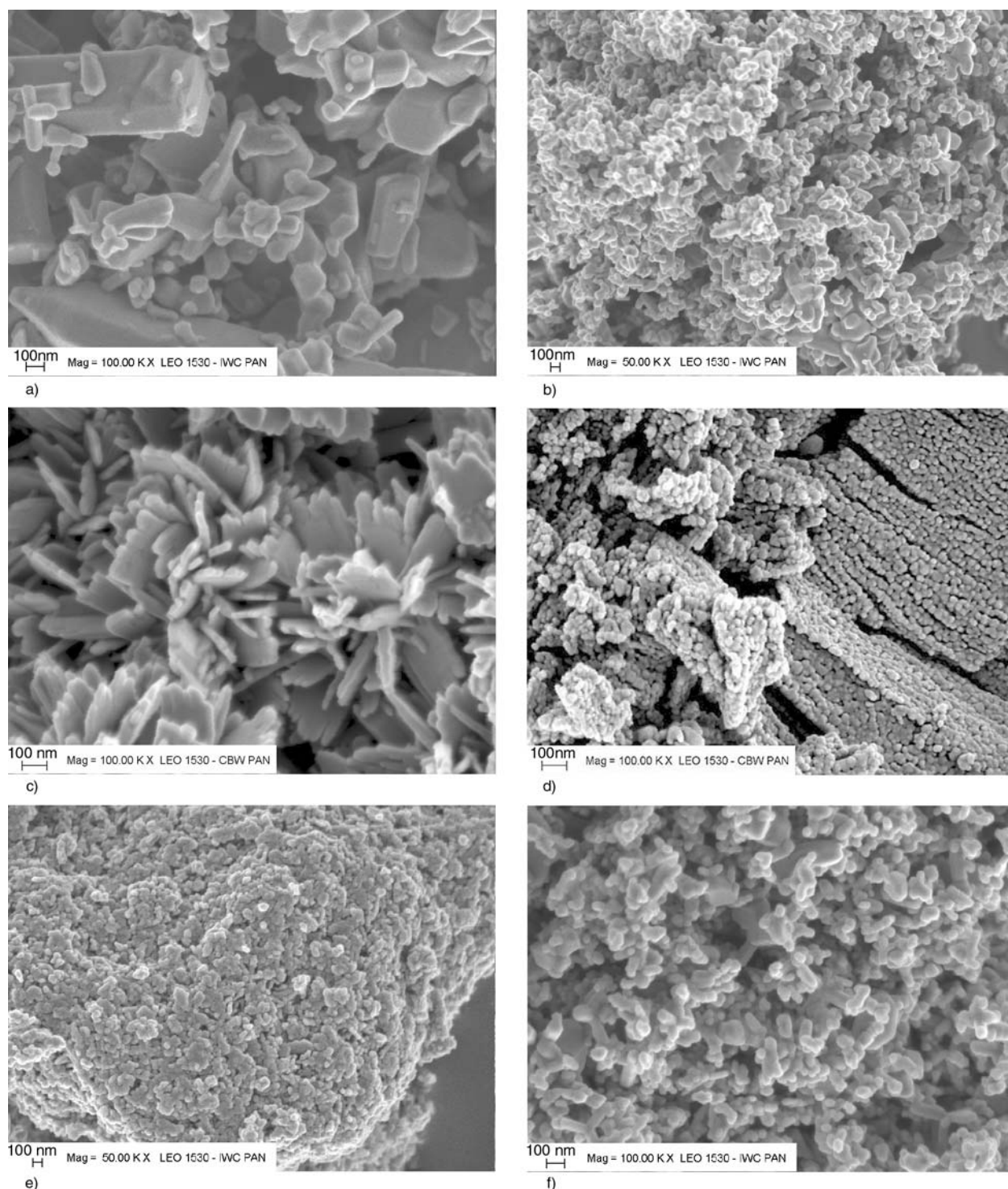


Figure 2. SEM images of zinc oxides: a) ZnO 10, b) ZnO 15, c) ZnO 24, d) ZnO 40, e) ZnO 42, f) ZnO 50

Table 4. Zinc oxide agglomerate size in paraffin oil

Zinc oxide	Agglomerate size [μm]
ZnO 10	10.0
ZnO 15	7.9
ZnO 24	7.9
ZnO 40	1.3
ZnO 42	9.3
ZnO 50	5.4

tendency of zinc oxide particles to agglomerate in elastomer. Unfortunately, zinc oxide particles exhibited a high ability for aggregation or agglomeration in paraffin oil. Primary particles formed microsized clusters with sizes ranging from 1.3 μm (ZnO 40) to 10 μm (ZnO 10).

3.2. Dispersion of zinc oxide particles in elastomer matrix

Assuming that zinc oxide particles diffuse through the elastomer matrix and react with carboxylic groups of elastomer chains, forming ionic crosslinks, the dispersion of ZnO particles in elastomer has a great importance as far as the activity of zinc oxides and their influence on vulcanisate

properties are concerned. The dispersion of nanoparticles in the elastomer was estimated based on the SEM images of vulcanisate surfaces (Figure 3a–3f).

The zinc oxide particles were poorly dispersed in the elastomer matrix and, therefore, were not homogeneously distributed (Figure 3a). They created microsized agglomerates with complex structures.

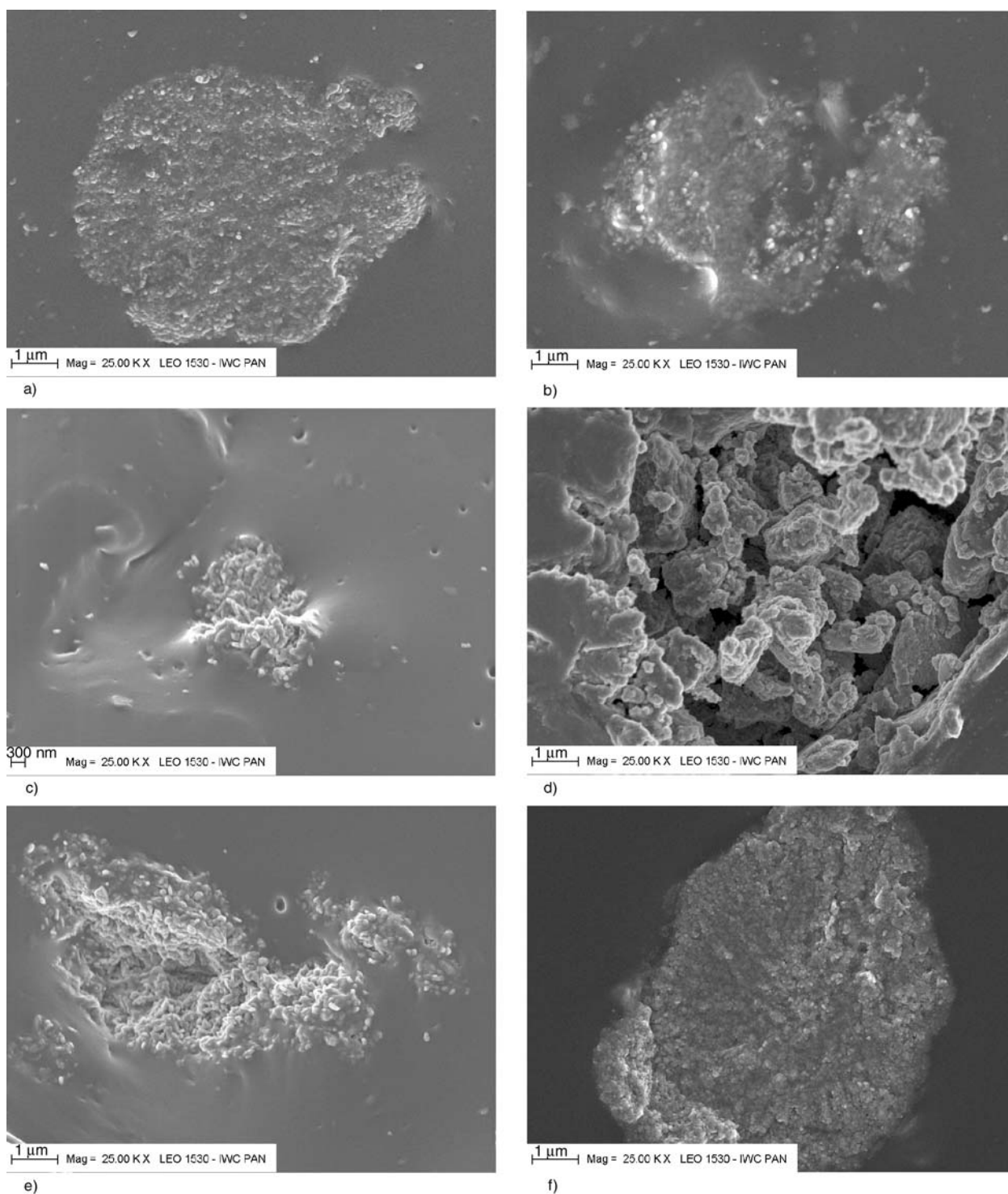


Figure 3. SEM images of XNBR vulcanisates with: a) ZnO 10, b) ZnO 15, c) ZnO 24, d) ZnO 40, e) ZnO 42, f) ZnO 50

The whisker particles of ZnO 15 (Figure 3b) created agglomerates several micrometres in size, which were surrounded by an elastomer film and were tightly bound to the elastomer matrix. It could be supposed that the wetting of ZnO 15 clusters with elastomer resulted in the good mechanical properties of the XNBR vulcanisates, despite the poor dispersion of the whiskers.

The ZnO 24 snowflake particles exhibited the weakest tendency to agglomerate. They created clusters about 3 μm in size (Figure 3c). The optimal dispersion of ZnO 24 in elastomer should lead to its high activity in the crosslinking process.

The spherical zinc oxide particles (ZnO 40, ZnO 42 and ZnO 50) were distributed very heterogeneously in the carboxylated nitrile rubber. The primary nanoparticles formed micro-sized agglomerates with irregular shapes, which displayed poor adhesion to the elastomer (Figure 3d–3f). Specifically, hollow structures were created by the ZnO 40 nanoparticles (Figure 3d). The strong tendency of ZnO nanoparticles to agglomerate arises from their high surface energy. The differences in the dispersed states of ZnO 40, ZnO 42 and ZnO 50 spherical nanoparticles in the elastomer resulted from different dispersive components of their surface energy and ability to undergo specific interactions. The influence of these parameters on the compatibility between zinc oxide particles and elastomer was thoroughly discussed [19]. The presence of impurities on ZnO 40 surface is probably the reason for its poor interfacial interaction with rubber. ZnO 40 was achieved by calcination of zinc oxalate, which was precipitated from hydrous solution of ammonium oxalate. Therefore, it contains some residues of hydroxyl groups, that remained after reaction. Moreover, the lowest content of crystalline phase (88%) compared to other zinc oxides (95–98%) as well as the presence of defects (oxygen vacancies) in the crystalline structure of ZnO 40 affect its activity towards XNBR elastomer.

3.3. Mechanical properties and crosslink density of vulcanisates

The influence of zinc oxide particle size and morphology on the activity in crosslinking of carboxylated nitrile elastomer was estimated based on the tensile properties and crosslink density of the vul-

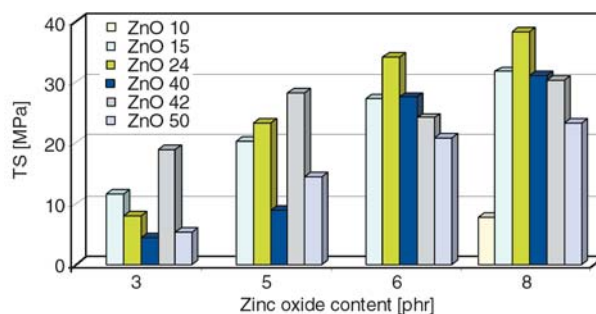


Figure 4. Tensile strength of XNBR vulcanisates

canisates. The results are given in Table 5 and Figure 4.

From the data presented in Figure 4, it follows that the application of zinc oxide nanoparticles considerably increased the tensile strength of the vulcanisates, as compared to those produced using conventional micro-sized ZnO 10. The tensile strength of the vulcanisates increased with the amount of zinc oxide in the composite. Moreover, the stress at a relative elongation of 300% increased, and the elongation at break decreased, due to an increase in the vulcanisate crosslink density (Table 5). The increment in vulcanisate tensile strength with the amount of zinc oxide arises from the increase in ionic crosslink content in the elastomer network (Δv). The presence of strong and multifunctional labile ionic clusters, which are able to move on the surface of the solid zinc oxide particles, resulted in the high ability of vulcanisates for stress relaxation, and as a consequence, an improvement in mechanical strength was achieved. Moreover, the considerable chain slippage and reformation of bonds in the elastomer network upon external stress contributed to the increase in vulcanisate tensile strength.

It could be supposed that the activity of zinc oxides in the crosslinking process will rise with the specific surface area. The presented results prove that the morphology of zinc oxide particles affects the vulcanisate crosslink density and mechanical properties more strongly than the specific surface area. The highest tensile strength (about 40 MPa) was achieved with a vulcanisate containing zinc oxide with three-dimensional snowflake particles (ZnO 24) (Figure 4). Moreover, the highest crosslink density and ionic crosslink content in the elastomer network (70%) were achieved for vulcanisates crosslinked with ZnO 24. Most likely, the high activity of this zinc oxide arises from a better contact between the surface of the crosslinking

Table 5. Mechanical properties and crosslink density of XNBR vulcanisates

Zinc oxide	ZnO content [phr]	SE300 [MPa]	EB [%]	$v_T \cdot 10^6$ [mol/cm ³]	Δv [%]
ZnO 10 (microsized)	8	3.6	426	24.1	29
ZnO 15 (whisker particles)	3	1.8	802	12.2	29
	5	2.4	740	14.1	27
	6	2.9	717	15.2	24
	8	3.2	709	20.9	42
ZnO 24 (snowflake particles)	3	1.6	871	27.0	45
	5	3.2	652	48.3	63
	6	4.8	617	62.9	70
	8	7.0	586	64.6	68
ZnO 40 (spherical particles)	3	1.6	705	8.9	28
	5	2.5	554	23.5	15
	6	3.3	580	29.1	17
	8	3.3	582	31.0	19
ZnO 42 (spherical particles)	3	2.5	579	17.1	16
	5	4.1	518	19.2	13
	6	4.8	576	23.6	11
	8	5.3	514	28.7	21
ZnO 50 (spherical particles)	3	1.2	861	20.0	49
	5	2.1	682	28.1	54
	6	2.9	620	30.6	67
	8	3.0	631	37.0	64

SE300 – stress at 300% relative elongation; TS – tensile strength; EB – elongation at break; v_T – vulcanisate crosslink density;

Δv – content of ionic crosslinks in elastomer network

agent particles and the elastomer chains (especially elastomer carboxylic groups), as compared to other zinc oxides. The specific shape and complex structure of ZnO 24 aggregates cause an increase in the size of the interphase between the elastomer and the snowflake particles, as compared to the spheres. Moreover, ZnO 24 nanoparticles exhibited the best dispersion in the elastomer matrix, which also contributed to the higher tensile strength and crosslink density in these vulcanisates, especially containing the high amount of ZnO (6; 8 phr). High tensile strength was also observed for the vulcanisates containing zinc oxide with whisker particles (ZnO 15).

Among the zinc oxides with spherical particles, the highest tensile strength was observed for vulcanisates with ZnO 42, especially with the small amount of zinc oxide (3; 5 phr). The weaker activity of the other zinc oxides was probably due to the poor dispersion of the particles in the elastomer matrix. Large and expanded agglomerates could act as critical sites, which may generate microcracks and initiate breaking of the sample under external stress. Moreover, the agglomeration of zinc oxide particles caused the surface area to decrease, followed by a decrease in the size of the interphase between the zinc oxide and the rubber chains. ZnO 40 was observed to be less efficient as a

crosslinking agent of carboxylated nitrile rubber, mainly due to the presence of hollow, large agglomerates with poor adhesion to the elastomer. Weak dispersion of ZnO 50 nanoparticles (Figure 3e) was also a reason for deterioration of vulcanisates tensile strength, despite the high content of ionic crosslinks.

It should be noticed that not only the size and morphology of ZnO nanoparticles or their tendency for agglomeration affect zinc oxide activity in elastomer crosslinking. The surface properties of ZnO and its ability to specific interactions, which were reported in our previous work [19], must be taken into account. Considering the zinc oxide acceptor-donor properties and the ability to undergo specific interactions, it was concluded that ZnO 15 and ZnO 24, which had strong interactions with donor solvents as well as ZnO 50, which strongly interacted with acetonitrile, are most prone to interactions with elastomers containing donor functional groups (e.g. nitrile groups $-C\equiv N$). From physico-chemical point of view, these oxides reveal the highest activity towards carboxylated acrylonitrile-butadiene elastomer. As a consequence, vulcanisates with high content of ionic crosslinks were achieved.

In previous work, we proved that it is possible to reduce the amount of zinc ions in acrylonitrile-

butadiene rubber [20]. It should be noted that the application of zinc oxide nanoparticles allowed the amount of ZnO to be reduced in XNBR compounds, without a detrimental effect on the vulcanisate properties. The highest reduction in the zinc oxide amount is possible in the case of ZnO 42, since the vulcanisates crosslinked with 3 phr of this oxide exhibited a tensile strength twice as great as that of vulcanisates produced with micro-sized zinc oxide, which is used commercially in crosslinking process. This is very important from an ecological point of view, because the European Union requires that the amount of zinc oxide be reduced as much as possible.

3.4. Dynamic-mechanical properties of vulcanisates

A dynamic-mechanical analysis was performed to confirm the existence of ionic clusters in the elastomer network. The loss factor $\tan\delta$, as a function of temperature, for the vulcanisates with micro-sized zinc oxide ZnO 10 and with zinc oxide ZnO 42 with spherical nanoparticles is presented as an example in Figure 5. The values of glass transition temperature T_g are given in Table 6.

The existence of two transitions can be observed. The first transition is the glass transition of the elastomer at low temperatures, with a maximum that represents T_g . The determined glass transition temperature for the vulcanisate with ZnO 10 was

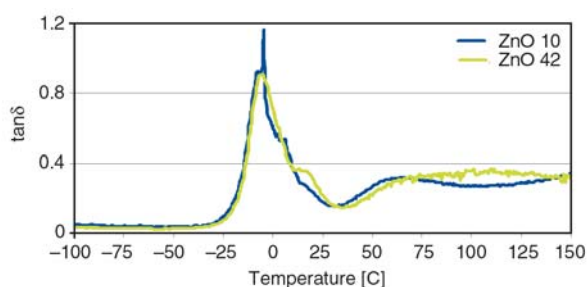


Figure 5. $\tan\delta$ versus temperature for XNBR vulcanisates containing zinc oxide

Table 6. Glass transition temperature of XNBR vulcanisates

Vulcanisate	T_g [°C]
XNBR/ZnO 10	−4.5
XNBR/ZnO 15	−5.1
XNBR/ZnO 24	−4.9
XNBR/ZnO 40	−5.5
XNBR/ZnO 42	−5.3
XNBR/ZnO 50	−5.1

(−4.5°C), whereas for vulcanisates with zinc oxide nanoparticles T_g values were within the range from (−4.9°C) to (−5.5°C). Therefore, it can be concluded that the zinc oxide particle size and morphology did not affect the elastomer T_g value considerably. The presence of additional maxima in the $\tan\delta$ plot at the temperatures 6°C (ZnO 10) and 17°C (ZnO 42) was probably due to the existence of differently immobilised elastomer phases on the ZnO particle surfaces.

The second transition is the ionic transition, occurring at high temperatures (50–100°C), resulting from the occurrence of a hard phase arising from ionic associations-ionic clusters or aggregates. Similar transitions were observed for all XNBR vulcanisates. This confirms the existence of a biphasic structure in the XNBR-ZnO system.

In the case of the vulcanisate containing ZnO 42, the considerable decrease in the $\tan\delta$ versus temperature maximum resulted from higher interactions between ZnO 42 and the elastomer, which prevented the rubber chains from a free relaxation at the glass transition temperature.

3.5. Shrinkability of XNBR vulcanisates

Heat-shrinkable polymers are widely used in packaging and in the cable industry; therefore, the shrinkability of XNBR vulcanisates crosslinked with zinc oxide is very important from a technological point of view. According to Mishra *et al.* [18], the shrinkage of polymer occurs due to an internal rearrangement of the structural elements within the stretched sample. The shrinkage driving force originates from oriented polymer chains of crystalline and amorphous phase. In the case of polyolefin/elastomer blends, the crosslinked elastomeric phase causes an enhancement in the blend shrinkability upon heating. It is believed that crosslinked points in the elastomer network serve as memory points, enhancing the heat shrinkability [21].

The examined samples were stretched above the glass transition temperature T_g until reaching an elongation of 300%; they were then stabilised in the stretched form at (−7°C) and shrunk above the ionic transition temperature at 70°C. The heat shrinkability values of the XNBR samples containing 8 phr of zinc oxide are presented in Table 7.

Vulcanisates of carboxylated nitrile elastomer crosslinked with zinc oxides exhibited heat shrink-

Table 7. Shrinkability of XNBR vulcanisates

Vulcanisate	L _{str} [cm]	L _{shr} [cm]	S _h [%]
XNBR/ZnO 10	11.2	3.9	65
XNBR/ZnO 15	11.2	3.5	69
XNBR/ZnO 24	11.2	2.7	76
XNBR/ZnO 40	11.2	3.5	69
XNBR/ZnO 42	11.2	2.7	76
XNBR/ZnO 50	11.2	2.6	77

ability. The highest shrinkage upon heating (76 and 77%) was achieved for vulcanisates containing ZnO 24 snowflake nanoparticles and spherical particles of ZnO 42 and ZnO 50. The lower shrinkability of the vulcanisates with the other zinc oxides (ZnO 10, ZnO 15 and ZnO 40) resulted from a lower crosslink density and ionic crosslink content in the elastomer network. Since the crosslinked points in the elastomer network serve as shape memory sites, a higher crosslink density improves the shrinkability of the vulcanisate. The stretched XNBR samples were shrunk upon heating above the temperature of the ionic transition, due to the occurrence of ionic multiplets in the elastomer network, which are multifunctional and labile crosslinks. Therefore, it can be concluded that the decomposition or rearrangement of the ionic clusters is one of the causes of heat shrinkability in XNBR vulcanisates containing zinc oxide.

4. Conclusions

Zinc oxides with different particle sizes and morphologies were used as crosslinking agents of carboxylated nitrile elastomer.

We conclude that the application of zinc oxide nanoparticles allowed for the realisation of vulcanisates with considerably better mechanical properties and higher crosslink density, as compared to vulcanisates crosslinked with micro-sized zinc oxide, which is used commercially as a crosslinking agent. Vulcanisates containing the same amount of zinc oxide nanoparticles exhibited a tensile strength about four times greater than that of vulcanisates with micro-sized particles. Moreover, 3 phr of nanosized ZnO 15, ZnO 24 or ZnO 42 is sufficient to obtain composites with comparable or even better tensile strengths, as compared to vulcanisates containing 8 phr of industrially used micro-sized ZnO. Therefore, the application of nanosized zinc oxide allows the amount of zinc

oxide to be reduced by almost 40%. This is a very important ecological goal, since zinc oxide is classified as toxic to aquatic species, and the European Union requires that the amount of zinc oxide in rubber compounds be reduced. Moreover, it should be noted that vulcanisates of carboxylated nitrile elastomer crosslinked with zinc oxide reveal heat shrinkability.

The morphology of zinc oxide particles mainly affects the activity in the crosslinking process. Particle size or zinc oxide specific surface area does not seem to have a considerable influence on the crosslinking agent efficiency. The highest activity was observed for zinc oxide with a specific surface area of 24.43 m²/g and three-dimensional snowflake particles (ZnO 24). The specific shape and complex structure of ZnO 24 aggregates, consisting of wires or plates growing from a single core, provide an increase in the size of the interphase between the elastomer carboxylic groups and the snowflake particles. As a result, vulcanisates with higher crosslink density and ionic crosslink content are achieved. These vulcanisates exhibit the best mechanical properties (TS about 40 MPa), mainly due to the high content of ionic clusters, which are multifunctional and labile crosslinks and can rearrange upon external stress, leading to stress relaxation. Moreover, ZnO 24 nanoparticles have the lowest ability for agglomeration in the elastomer matrix and create the smallest agglomerates, which concentrate the stresses during sample deformation to a smaller degree, as compared to the large agglomerates formed by other zinc oxides.

Acknowledgements

The authors wish to acknowledge the Polish Ministry of Science and Higher Education for supporting this research.

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