# Modified and unmodified zinc oxide as coagent in elastomer compounds

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The aim of this work was to study the activity of unmodified and modified ZnO in the peroxide crosslinking of hydrogenated acrylonitrile-butadiene elastomer (HNBR) and ethylene-propylene copolymer (EPM). In the first step, zinc oxide was obtained by emulsion precipitation. Maleic acid was introduced onto the surface of ZnO using an in situ method. The unmodified and modified zinc oxide was characterized using dispersive and morphological analysis, BET surface area analysis, and elemental, spectroscopic and thermal analysis. In the second stage of the research, the ZnO/MA systems were incorporated into the structure of elastomer compounds improving the kinetic and mechanical properties of vulcanizates. The proposed modification method had a favorable effect on the physicochemical properties of the zinc oxide and on the kinetic and mechanical properties of the vulcanizates. This study demonstrated that modification of zinc oxide by maleic acid is a promising technique.

**Keywords:** zinc oxide, maleic acid, emulsion precipitation, modification, elastomers, vulcanizates.

## INTRODUCTION

Global production of zinc oxide is about $10^5$ tonnes per year, and a major portion is consumed by the rubber industry to manufacture various different cross-linked rubber products[1]. The thermal conductivity of typical pure silicone rubber is relatively low; however, it can be improved by adding some thermal conductivity fillers, including metal powders, metal oxides and inorganic particles. Some kinds of thermal conductivity powders, such as $Al_2O_3$, MgO, $Al_2N_3$, $SiO_2$ and $ZnO^2$, etc. can improve the thermal properties of silicone rubber while retaining its high electrical resistance, making them promising candidates for high-performance engineering materials. The incorporation of nano-scale fillers can achieve high thermal conductivity even at a relatively low filling content[3–5]. However, the ZnO nanoparticles tend to aggregate together to form particles of large size in the polymer matrix due to the weak interaction between the surface of the nanoparticles and the polymer[6].

In order to solve the aforementioned problem, surface modification techniques have been applied to improve the interaction between the nanoparticles and the polymer. In Yuan et al.[7], in order to prepare a silicone rubber with high thermal conductivity, pristine and surface-modified ZnO nanoparticles containing the vinyl silane group are incorporated into the silicone rubber via a hydrosilylation reaction during the curing process. The corresponding structure, morphology and properties of the silicone rubber/ZnO (MPQ/ZnO) and silicone rubber/SiVi@ZnO (MPQ/SiVi@ZnO) nanocomposites are evaluated. Yuan et al. synthesized the ZnO nanoparticles (with an average size below 10 nm) by a sol-gel procedure. Next the silicone coupling agent VTES was successfully incorporated onto the surface of the nanoparticles. The MPQ/SiVi@ZnO nanocomposites displayed better mechanical properties and higher thermal conductivity, due to the formation of a cross-linking structure with the silicone rubber matrix and better dispersion.

Zinc oxide is a very effective and commonly used cross-linking agent for carboxylated elastomers[8, 9]. It can be used to produce vulcanizates with high tensile strength, tear resistance, hardness and hysteresis. The improved mechanical properties of ionic elastomers mainly result from their high propensity 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 are thermoplastic and can be processed in molten state as thermoplastic polymers[10, 11]. However, there are some disadvantages to zinc oxide-crosslinked carboxylic elastomers. The most important are the scorchiness, poor flex properties and high compression set. In order to prevent scorchiness, carboxylated nitrile elastomers are crosslinked with zinc peroxide or zinc peroxide/zinc oxide systems. The vulcanization 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's action. However, higher vulcanization times are required to achieve vulcanizates with a tensile strength and crosslink density comparable to those of vulcanizates crosslinked with zinc oxide. In the case of XNBR vulcanization with zinc peroxide/zinc oxide systems, the curing represents the sum of at least three processes: very fast formation of ionic crosslinks due to the initial zinc oxide present, peroxide crosslinking leading 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 vulcanization time, is most likely related to the formation of ionic species. The achieved vulcanization times are considerably higher than those for XNBR crosslinking with zinc oxide. Therefore, in spite of the scorch problems, zinc oxide is still commonly used as a crosslinking agent of carboxylated nitrile rubbers[12–17].

Taking into account the fact that, during the crosslinking process, zinc oxide reacts with carboxylic groups of the 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.

In this work, we prepared compounds consisting of zinc oxide and maleic acid (ZnO/MA) as coagent for the crosslinking of EPM and HNBR with dicumyl peroxide. Zinc oxide was obtained by the method of emulsion precipitation, with zinc acetate and potassium hydroxide. Additionally the obtained zinc oxide was modified with maleic acid. The influence of the ZnO/MA systems on the cure kinetics of rubber compounds and their crosslinking efficiency, vulcanizate crosslink density and tensile strength was investigated.

## EXPERIMENTAL SECTION

### Chemicals and materials

The precursor of zinc oxide was 10% solution of dihydrate zinc acetate $Zn(CH_3COO)_2 \cdot H_2O$ (Chempur). The precipitating agent was a 5% solution of potassium hydroxide KOH (Chempur). Also used in emulsion formation were cyclohexane (Chempur) as an organic phase, and polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether Trioton X-100 and X-114 (Sigma-Aldrich) as a mixture of emulsifiers. Maleic acid (MA) $C_2H_2(COOH)_2$, supplied by POCh SA, was used as modifier. All reagents were of analytical grade. Deionized water was used throughout the work. Ethanol (~96%) was used as a solvent of the modifying agent. Hydrogenated acrylonitrile-butadiene elastomer HNBR (Therban 3407) containing 34 wt% acrylonitrile and 0.9 wt% of residual double bonds after hydrogenation was obtained from Bayer C.O. Ethylene-propylene copolymer EPM (Dutral CO 034) containing 28% propylene was obtained from Polimeri Europa. The Mooney viscosity was (ML1+4 (100°C):70). It was vulcanized with dicumyl peroxide DCP (Aldrich).

### Emulsion precipitation

Appropriate quantities of the emulsifiers (Triton X-100 and X-114) were weighed and dissolved in the organic phase (cyclohexane), to which zinc acetate was added in the proper concentration. The mixture was homogenized for 30 minutes, after which the emulsion was ready for ZnO precipitation. Precipitation was carried out in a reactor of 500 cm³ capacity equipped with a homogenizer. The emulsion was placed in the reactor, into which a solution of KOH was dosed using an Ismatec ISM833A type peristaltic pump. The system was intensely stirred (9000 rpm). The system obtained as a result of the reaction taking place in the reactor (QVF Mini-Plant Pilot Tec) was subjected to destabilization at 80°C. Then the organic phase was separated by the vacuum evaporation technique, and the mixture obtained was filtered off under reduced pressure. Next the sample was washed with hot water and methanol to remove residues of the emulsifiers. The filtrate cake was then dried in a stationary drier at 120°C to obtain the final product ZnO.

### Modification process

Modification of zinc oxide with maleic acid was performed by an *in situ* method (during the precipitation stage). Appropriate quantities of maleic acid (MA) (1 or 5 g) were weighed and dissolved in an ethanol and water mixture with a volume ratio of 4:1. In the next step, this mixture was added in portion to the reactor (with the emulsion) during the dosing of potassium hydroxide. Further, the precipitation process of the modified zinc oxide was carried out in the same way as described above.

### Physicochemical Properties of Precipitated ZnO

Particle size distributions were determined using a Zetasizer Nano ZS (Malvern Instruments Ltd.), an analyzer based on the noninvasive back scattering method (NIBS). At the next stage, morphology and microstructure were investigated to obtain data on dispersion, grain morphology, structure of individual particles, and agglomeration types in the obtained zinc oxide. The study was performed using a Zeiss EVO40 scanning electron microscope. In order to characterize the adsorption properties, nitrogen adsorption/desorption isotherms at 77 K and parameters such as surface area, total volume, and mean size of pores were determined using an ASAP 2020 instrument (Micromeritics Instrument Co.). A thermogravimetric analyzer (TG, model Jupiter STA 449F3, made by Netzsch) was used to investigate the thermal decomposition behavior of the samples. In order to identify the characteristic groups present on the surface of the precipitated ZnO, the samples were subjected to FT-IR analysis using an IFS 66 v/s spectrophotometer (Bruker). Elemental composition of the products was established with the use of a Vario El Cube instrument made by Elementar (Germany), which gave the elemental contents of carbon, hydrogen, nitrogen and sulfur after high-temperature combustion of the analyzed samples.

### Preparation and Characterization of Rubber Compounds

Rubber compounds, with the formulation given in Table 1, were prepared using a laboratory two-roll mill at a temperature of about 40°C. The samples were cured at 160°C until they developed a 90% increase in torque, measured by an oscillating disc rheometer according to ASTMD 2084-81. The criterion for scorch time determination was 20% torque increase over the minimum torque value.

The crosslink density ($\nu_T$) of the vulcanizates was determined by equilibrium swelling in toluene, based on the Flory-Rehner equation[18]. The Huggins parameter of the elastomer-solvent interaction χ was calculated from the equation $\chi = 0.501 + 0.273V_r$    (1)[19] where $V_r$ is the volume fraction of elastomer in the swollen gel. To determine the quantity of ionic crosslinks in the elastomer network, samples were swollen in toluene in a desiccator with saturated ammonia vapor (25% aqueous solution). The content of ionic crosslinks ($\Delta\nu$) was calculated from equation (2), where $\nu_A$ is the crosslink density determined for samples treated with ammonia vapor.

$$\Delta\nu = \frac{\nu_T - \nu_A}{\nu_T} \cdot 100\%$$    (2)

**Table 1.** Composition of HNBR and EPM-based rubber compounds (phr)

| HNBR | 100 | 100 | EPM | 100 | 100 |
|---|---|---|---|---|---|
| Coagent | 0 | 5 | Coagent | 0 | 5 |
| DCP | 2 | 2 | DCP | 4 | 4 |

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

## RESULTS AND DISCUSSION

### Dispersive and morphological characterization of zinc oxide

During the studies three samples were obtained and labeled as: ZnO (ZnO unmodified), ZnO/MA1 (ZnO modified with 1 g maleic acid), and ZnO/MA5 (ZnO modified with 5 g maleic acid). Table 2 presents the dispersive parameters of precipitated zinc oxide. The low values of the dispersity index (ZnO – PdI = 0.348, ZnO/MA1 – PdI = 0.162, ZnO/MA5 – PdI = 0.378) imply that the particles have relatively high homogeneity and direct regular shapes (confirmed in the SEM images; see Figure 1). The sizes of the obtained zinc oxide particles (modified and unmodified) were in the range 255–825 nm, with the main fraction at 459–531 nm. Dispersive and morphological analysis showed that the modification process does not cause significant changes in the particle size of the zinc oxide.

### Characteristics of porous structure of modified and unmodified ZnO

As can be seen in Table 2, the ZnO samples obtained in the manner described above have large specific surface areas, the largest (31 $m^2$/g) being recorded for ZnO/MA5 (ZnO modified with 5 g maleic acid). The pore volume and mean pore diameter in this sample were 0.127 $cm^3$/g and 16.4 nm respectively. The smallest specific surface area (7.3 $m^2$/g) was found for unmodified ZnO, and the pore volume and mean pore diameter in this sample were 0.022 $cm^3$/g and 12.5 nm. The specific surface area of ZnO/MA1 (ZnO modified with 1 g maleic acid) was 8.1 $m^2$/g, while the pore volume was 0.038 $cm^3$/g and the mean pore diameter 19.2 nm. Porous structure analysis showed that with an increase in the amount of modification agent (maleic acid), the specific surface area of the resulting samples increases.

### Thermal stability

The ZnO samples obtained were subjected to thermogravimetric (TG) analysis, which provides information on the chemical and physical transformations taking place upon heating. The TG curves recorded are presented in Figure 2. The greatest mass loss, of about 55%, was observed for ZnO/MA5. In this sample the



(a)



(b)



(c)
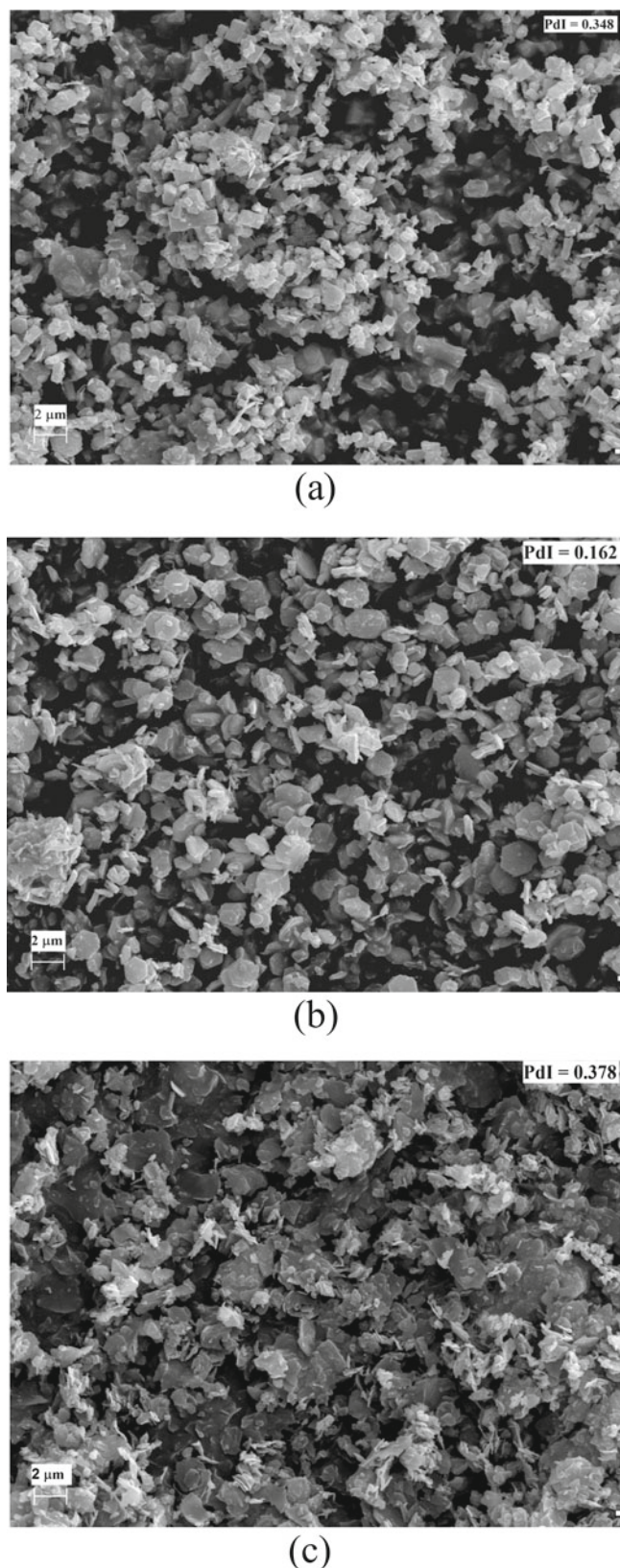
**Figure 1.** SEM images of zinc oxide structures: (a) ZnO, (b) ZnO/MA1 and (c) ZnO/MA5

**Table 2.** Dispersive parameters and characteristic of porous structure of ZnO

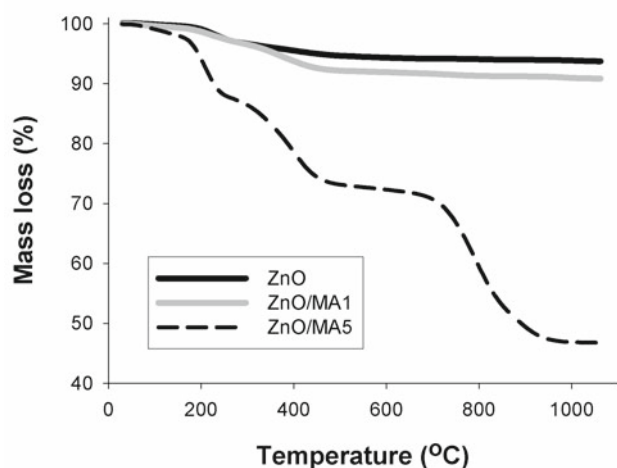| No of sample | Particle size [nm] | Size of the particle main fraction [nm] | Number [%] | Specific surface area [$m^2$/g] | Pore volume [$cm^3$/g] | Pore diameter [nm] |
|---|---|---|---|---|---|---|
| ZnO | 255–712 | 459 | 28 | 7.3 | 0.022 | 12.5 |
| ZnO/MA1 | 295–712 | 459 | 29 | 8.1 | 0.038 | 19.2 |
| ZnO/MA5 | 342–825 | 531 | 33 | 31.0 | 0.127 | 16.4 |

**Figure 2.** Thermal analysis curves for the obtained samples of zinc oxide

decrease occurred in three ranges: 20–200°C, 300–400°C and 400–800°C. The decrease observed in the range of 300–400°C and 400–800°C (for sample ZnO/MA5) is connected with decarboxylation of maleic acid to acetic acid and carbon dioxide. A smaller mass loss of about 10% in the range 20–400°C was noted for ZnO and ZnO/MA1. The mass loss is caused mainly by thermal decomposition related to water loss (water of crystallization and constitutional water).

**Spectroscopic and elemental analysis**

In order to identify the characteristic groups present on the surface of the ZnO samples that confirm the effectiveness of the modification process, the zinc oxides were subjected to spectroscopic analysis. The FT-IR spectra obtained for all samples are presented in Fig. 3. Surface modification of ZnO with maleic acid (ZnO/MA5) caused a significant increase in the intensity of
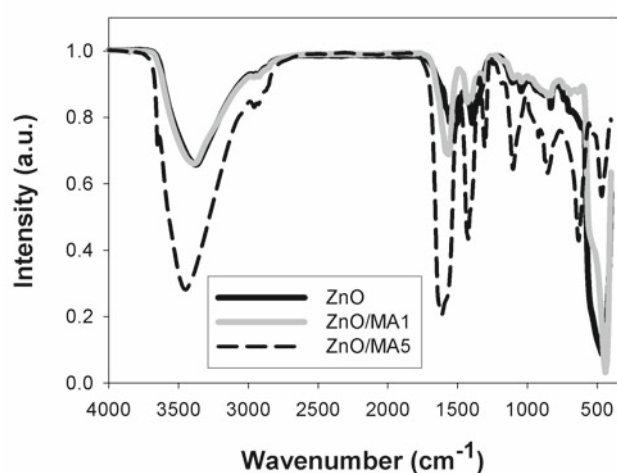


**Figure 3.** FT-IR spectra of unmodified and modified zinc oxide

the adsorption band for stretching vibrations of –OH groups (~3400 cm$^{-1}$). Additionally the peak (Figure 3) at ~1650 cm$^{-1}$ is due to C=O stretching, and that at ~2900 cm$^{-1}$ is due to C-H stretching vibrations of the maleic acid coating on the zinc oxide.

Based on the results of elemental analysis it was also found that the modification process was carried out effectively (the amount of carbon and hydrogen incre-

**Table 3.** Elemental content of obtained zinc oxide

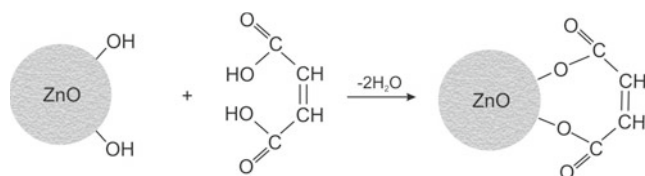| No of sample | Elemental content [%] | |
| --- | --- | --- |
| | C | H |
| ZnO | 0.76 | 0.46 |
| ZnO/MA1 | 1.95 | 0.70 |
| ZnO/MA5 | 8.92 | 2.35 |



**Figure 4.** Probable mechanism occurring during the surface modification of ZnO with maleic acid

ased) (Table 3). Probable mechanism occurring during the surface modification of ZnO with maleic acid was presented in Figure 4.

**Cure characteristics and crosslink density of vulcanizates**

The main goal of coagent application is improvement of the crosslinking efficiency and increased crosslink density of the vulcanizates. We believed that the application of coagents based on zinc oxide modified with maleic acid would result in the formation of additional crosslinks, which can be expected to improve the crosslink density of the vulcanizates.

To examine the activity of the coagents in the crosslinking process, the cure characteristics of the rubber compounds were determined. The results are presented in Table 4.

Additionally, the cure characteristic of the rubber compounds is presented by vulcanization curve (Fig. 5). In the case of EPM compounds, the increase in maximum torque was achieved when pure zinc oxide was used (Fig. 5a). However, application of ZnO/MA1 decreased the vulcanization time. The highest maximum torque was observed for the rubber compound containing ZnO/MA5. Considering the HNBR compounds, similar maximum torque was achieved for rubber compounds containing pure and modified zinc oxide. The amount of MA grafted to the ZnO surface had no considerable effect on the maximum torque (Fig. 5b).

The rubber compound crosslinked only with dicumyl peroxide and without the addition of coagent was characterized by an increase of torque during vulcanization by approximately 41 dNm (HNBR) and 37 dNm (EPM). The application of coagents caused a considerable increase in the torque increment as compared with the conventional rubber compound. The torque increment during vulcanization is an indirect measure of the degree of elastomer crosslinking. Therefore it can be concluded that the coagents are actively involved in the crosslinking process.

The active participation of zinc oxide in HNBR and EPM crosslinking was confirmed by the values of the vulcanizate crosslink density determined from their equilibrium swelling in toluene. Vulcanizates containing coagents exhibited crosslink densities higher than the pure peroxide-crosslinked vulcanizate. The crosslink density of vulcanizates was improved by the formation of additional ionic crosslinks in the presence of coagents. The vulcanizate without coagents exhibited a non-cova-

**Table 4.** Cure characteristics of HNBR and EPM compounds

| Vulcanizate | ΔG [dNm] | $t_{90}$ [min] | $t_{02}$ [s] | $\upsilon_T \cdot 10^{-5}$ [mol/cm$^3$] | Δυ [%] |
|---|---|---|---|---|---|
| HNBR/DCP | 40.6 | 50 | 174 | 2.95 | 3.3 |
| HNBR/ZnO | 60.1 | 38 | 120 | 3.55 | 8.0 |
| HNBR/ZnO/MA1 | 56.9 | 33 | 133 | 3.66 | 13.9 |
| HNBR/ZnO/MA5 | 58.5 | 32 | 135 | 3.76 | 24.8 |
| EPM/DCP | 36.9 | 20 | 102 | 1.00 | 10.6 |
| EPM/ZnO | 108.9 | 17 | 130 | 5.21 | 32.1 |
| EPM/ZnO/MA1 | 110.0 | 16 | 120 | 6.34 | 28.9 |
| EPM/ZnO/MA5 | 136.0 | 16 | 110 | 13.28 | 31.9 |
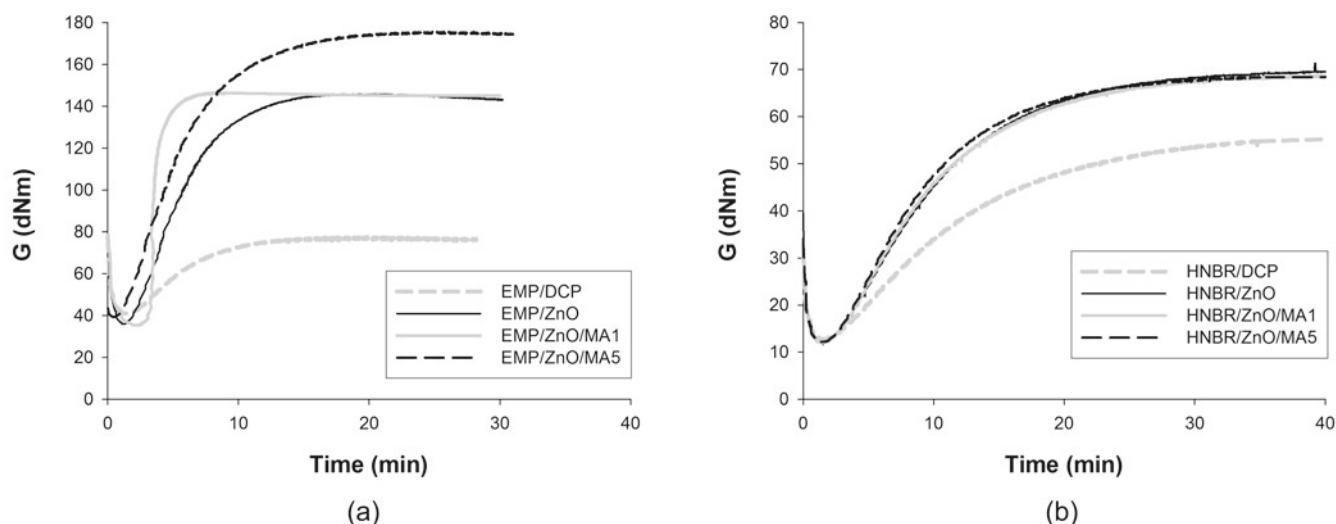


**Figure 5.** Vulcanization curve for: (a) EMP and (b) HNBR

lent link content of approximately 3.3% (HNBR) and 10.6% (EPM). These crosslinks are probably labile ionic crosslinks. The highest content of ionic crosslinks in the elastomer network was achieved for vulcanizates crosslinked with zinc oxide containing 5 g of MA (more than 24% for HNBR and 31% for EPM compounds), because of the higher quantity of coagent functional groups that can take part in the formation of the compounds.

The effect of coagents on the vulcanization and scorch time of rubber compounds was also examined. Application of coagents reduced the vulcanization time by almost 20 minutes for HNBR and 5 minutes for EPM compounds. Moreover, coagents with HNBR led to a shortening of scorch time by approximately 30 seconds from the time observed for the peroxide-crosslinked

**Table 5.** Mechanical properties of HNBR and EPM vulcanizates

| Vulcanizate | TS [MPa] | EB [%] |
|---|---|---|
| HNBR/DCP | 10.3 | 556 |
| HNBR/ZnO | 10.8 | 537 |
| HNBR/ZnO/MA1 | 13.3 | 554 |
| HNBR/ZnO/MA5 | 14.4 | 549 |
| EPM/DCP | 11.9 | 799 |
| EPM/ZnO | 17.7 | 554 |
| EPM/ZnO/MA1 | 17.5 | 531 |
| EPM/ZnO/MA5 | 13.5 | 406 |

composite. On the other hand, coagents with EPM led to an extension of scorch time by approximately 20 seconds.

One of the most important parameters determining the potential application of elastomeric materials is their tensile strength (Table 5). Coagents improved the tensile strength of the HNBR and EPM vulcanizates in comparison with the tensile strength of the peroxide-

-crosslinked vulcanizate. The highest tensile strength was exhibited by vulcanizates containing HNBR/ZnO/MA5 (approximately 15 MPa) or EPM/ZnO (approximately 18 MPa). No considerable effect of coagents was observed for the elongation at break for HNBR compounds; however for EPM vulcanizates this parameter decreases, reaching 406% (for EPM/ZnO/MA5 samples). The improvement of the tensile strength of the vulcanizates may be partially caused by the increase in their stress relaxation ability. The considerable chain slippage and reformation of ionic bonds in the elastomer network under external stress contribute to the increase in the vulcanizates' tensile strength. These results confirm that the applied coagents participated in the formation of ionic crosslinks which improved the mechanical properties of the vulcanizates.

## CONCLUSION

The investigated process of modification of zinc oxide with maleic acid had a significant effect on the particle diameter, and improved significantly the properties of the porous structure of the modified ZnO. In this case the product had a specific surface area of 31 m$^2$/g. Spectroscopic analysis of the product showed that the modified zinc oxide has characteristic COO-Zn groups (a wavenumber of about 1600 cm$^{-1}$), which confirms that the modification process has occurred.

We conclude that the application of coagents makes it possible to create vulcanizates with considerably improved mechanical properties and higher crosslink density compared with vulcanizates crosslinked only with peroxide. In the case of hydrogenated acrylonitrile-buta-

diene rubber (HNBR) the zinc oxide containing maleic acid turned out to be an active peroxide vulcanization coagent. Confirmation of the activity of oxides used in the vulcanization process of HNBR is given by the increase in non-covalent crosslink content and in the cross-link density of the vulcanizates. As a result of the increase in the cross-link density of HNBR and the presence of labile ionic aggregates in the structure of the vulcanizates, the tensile strength was increased to 14 MPa. The vulcanization time of HNBR decreased with an increase in the quantity of maleic acid used.

The application of modified and unmodified zinc oxide in EPM (ethylene-propylene copolymer) caused an increase in the degree of elastomer crosslinking. The cross-link density and tensile strength of EPM vulcanizates also increased (with increasing quantity of maleic acid in the coagent). A reduction in the vulcanization time of ethylene-propylene copolymer (EPM) was also observed. There are no significant effects of the investigated coagents for EPM scorch time.

## NOMENCLATURE

| | |
|---|---|
| $\Delta G$ | – increment of torque in the rubber compound during vulcanization |
| $t_{90}$ | – optimal vulcanization time |
| $t_{02}$ | – scorch time |
| $\upsilon_T \cdot 10^{-5}$ | – cross-link density of vulcanizates |
| $\Delta\upsilon$ | – non-covalent crosslink content |
| TS | – tensile strength |
| EB | – elongation at break |

## ACKNOWLEDGMENT

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