

Effect of Ionic Liquids and Surfactants on Zinc Oxide Nanoparticle Activity in Crosslinking of Acrylonitrile Butadiene Elastomer

Magdalena Przybyszewska, Marian Zaborski

Department of Chemistry, Institute of Polymer and Dye Technology, Technical University of Lodz, Stefanowskiego Street 12116, 90-924 Lodz, Poland

Received 7 July 2009; accepted 28 September 2009

DOI 10.1002/app.31519

Published online 23 November 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The goal of this work was to study the influence of several ionic liquids and cationic surfactants on zinc oxide nanoparticle activity in sulfur vulcanization of acrylonitrile butadiene elastomer (NBR). In this article, we discuss the effect of ionic liquids and surfactants on the cure characteristics, crosslink density, and distribution in the elastomer network as well as on mechanical properties of the acrylonitrile butadiene rubber. Ionic liquids (alkylimidazolium salts) and cationic surfactants (alkylammonium bromides) decrease the vulcanization time of rubber compounds. Their application results in the increase of

vulcanizate crosslink density as well as of the heterogeneity of elastomer network. The influence of ionic liquids on the acrylonitrile butadiene elastomer properties depends on the anion present in the molecule and on the length of alkyl chains attached to the imidazolium ring. The most active ionic liquids seem to be the ones with the 1-butyl-3-methylimidazolium cation or the BF_4^- anion. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 155–164, 2010

Key words: composites; crosslinking; elastomers; nanoheterogeneity; vulcanization

INTRODUCTION

Zinc oxide is widely used as an activator in sulfur vulcanization of unsaturated elastomers by sulfur or sulfur donors.¹ As a result, the amount of bound sulfur and the efficiency of crosslinking system increase.² Moreover, zinc oxide reduces the vulcanization time of rubber compounds, improves their processing and the physical properties of vulcanizates. The role of zinc oxide during sulfur vulcanization of elastomers is well known.^{3–5} It reacts with accelerators to form highly active zinc complexes, which are believed to be more reactive than the free accelerator. Next, sulfur is incorporated into these complexes, and active sulfurating agents are formed. This reactive species reacts with allylic hydrogen atoms of elastomer unsaturation to form crosslink precursors. The crosslink precursor reacts with another rubber chain to generate crosslinks, which contain rather large amounts of sulfur atoms in the bridge.⁶ Next, crosslink shortening, usually accompanied by side reactions, such as crosslinks degradation or modification of the elastomer macromolecules, results in the final elastomer network. Ghosh et al.⁷ divided the reaction taking place during the

vulcanization process into three reaction groups: reactions resulting in the formation of active sulfurating agent (accelerator chemistry); reactions leading to crosslink formation (crosslinking chemistry), and reactions that cause crosslink shortening and degradation (post-crosslinking chemistry). Heideman et al.⁶ studied the role of zinc oxide during different stages of vulcanization based on model compound studies using squalene and 2,3-dimethyl-2-butene as the model compounds. It was reported that zinc oxide activates the breakdown of the accelerator (*N*-cyclohexyl-2-benzothiazolesulfenamide or 2-mercaptobenzothiazole) in squalene. The breakdown of the accelerator begins at shorter reaction times. Moreover, in the presence of ZnO, more sulfur is incorporated into the accelerator in the initial stage of the reaction. According to Chapman and Porter,⁸ zinc oxide has a great influence on natural rubber (NR) vulcanization. When zinc oxide is present, sulfuration is caused by substituting allylic hydrogen atoms rather than by combining substitution and addition to the C=C double bonds. As a result, shortening of crosslinks is catalyzed, and a network with a greater proportion of mono- and di-sulphidic crosslinks is formed. The presence of zinc oxide also leads to a small increase in scorch safety and crosslinking efficiency.

Despite the important role of zinc oxide in sulfur vulcanization of elastomers, its amount in rubber compounds, especially used in aquatic areas, must be reduced at least to below 2.5%, as zinc oxide was

Correspondence to: M. Przybyszewska (magdalena.przybyszewska@p.lodz.pl).

classified as toxic to aquatic species.⁹ Methods to reduce the amount of zinc oxide in elastomers have been widely studied. Chapman and Johnson⁹ proved that zinc oxide content in NR or EPDM compounds can be reduced to 2 phr without affecting vulcanizate properties. However, further reduction requires the use of anti-reversion agents.

Heideman et al.¹⁰ studied the possibilities to reduce ZnO amount by incorporating zinc with higher chemical activity in the form of reactive zinc complexes. Due to the crystalline structure of ZnO, some ions are within crystals and have limited accessibility. The availability of zinc ions in a complex molecule is higher than in ZnO crystals. It appeared that zinc m-glycerolate is a good substitute for ZnO as an activator for ethylene-propylene-diene elastomer and butadiene-styrene rubber sulfur vulcanization, without detrimental effect on the cure characteristics and physical properties of vulcanizates. Zinc 2-ethylhexanoate can also be applied as the activator in the SBR vulcanization process. Przybyszewska et al.¹¹ used zinc chelates with 1,3-diketones as activators for sulfur vulcanization of acrylonitrile butadiene elastomer. The most effective activators seemed to be zinc 1,3-diphenylpropane-1,3-dione and zinc 1-(4'-t-butylphenyl)-3-phenylpropane-1,3-dione. Application of zinc chelates allowed a reduction of the amount of zinc ions in rubber compounds by 40% compared to zinc oxide without deterioration of the crosslinking rate or vulcanizate properties. Heideman et al.¹² reported that zinc loaded clay can also be regarded as an alternative for zinc oxide commonly used in sulfur vulcanization. However, slightly shorter scorch time was achieved.

According to Nieuwenhuizen,¹³ the ZnO surface acts as a catalytic reaction template by activating and joining reactants. Particles of accelerators, sulfur and fatty acids diffuse through the elastomer matrix and are adsorbed onto the ZnO surface, forming intermediate reactive complexes. Therefore, the contact between ZnO particles and accelerators in the elastomer matrix should be maximized to enhance the efficiency of zinc oxide during vulcanization. This contact depends on the ZnO particle shape, size, and specific surface area. However, the dispersion of zinc oxide particles in the elastomer is also very important for the activation of sulfur vulcanization. The complex of zinc, accelerator, and fatty acid formed during vulcanization includes a central zinc cation, two stearyl anions, and accelerator residues. This complex and other components of the crosslinking system are strongly polar and reveal the tendency for agglomeration in the elastomer. The crosslinking route and efficiency depend on zinc ion mobility in the complex molecule and on the diffusion rate of the remaining components of the crosslinking system.¹⁴ Therefore, the application of

ligands with higher solvation power towards zinc cations than towards stearyl anions should improve the dispersion of the active sulfurating agent as well as of the crosslinking system components in the elastomer matrix. As a result, the crosslinking rate and efficiency should increase.

In recent years, ionic liquids (ILs) have been promoted as "green solvents" and applied in many fields of chemistry and industry due to their chemical and thermal stability, low vapor pressure, and high ionic conductivity properties. ILs have been widely used in polymer science as polymerization media, solvents for organic synthesis and catalysis, as well as media for extraction processes.¹⁵

In this work, we applied ionic liquids and cationic surfactants to improve the activity of nanosized zinc oxide in sulfur crosslinking of acrylonitrile butadiene rubber. Ionic liquids and surfactants are believed to catalyze the interface reactions.¹⁶ Moreover, it is supposed that zinc oxide nanoparticles can be dispersed more easily and homogeneously in the elastomer matrix when ILs or surfactants are present. Therefore, their accessibility in reactions with accelerator and sulfur is higher.

EXPERIMENTAL

Materials

Acrylonitrile butadiene rubber NBR (Nipol DN 4050) containing 40 wt % of acrylonitrile was obtained from Zeon-Europe GmbH. Its Mooney viscosity was ML1+4 (100°C): 46–60. It was cured with sulfur in the presence of 2-mercaptobenzothiazole (MBT). Nanosized zinc oxide with a specific surface area of 42.5 m²/g and an average particle size of 234 nm (Qinetiq Nanomaterials Limited, Hampshire), together with stearic acid (Sigma-Aldrich), was applied as the standard activator. Ionic liquids and cationic surfactants given in Table I were provided by Fluka.

Preparation and characterisation of rubber compounds

Rubber compounds with the general formulations given in Table II were prepared using a laboratory two-roll mill. Each of the samples contained one of the ionic liquids or one of the surfactants. The samples were cured at 160°C until they developed a 90% increase of torque (measured using an oscillating disk rheometer produced by Zach Metalchem). The tensile properties of vulcanizates were determined according to ISO-37 with a universal machine Zwick 1435. The crosslink density of vulcanizates was determined by equilibrium swelling in toluene, based on the Flory-Rehner equation¹⁷ using the Huggins parameter of elastomer-solvent interaction $\mu = 0.381 + 0.671V_r$ [eq. (1)].

TABLE I
Ionic Liquids and Cationic Surfactants Used as Dispersing Agents

Dispersing agent	Molecular formula
1-ethyl-3-methylimidazolium chloride	C ₆ H ₁₁ ClN ₂
1-butyl-3-methylimidazolium chloride	C ₈ H ₁₅ ClN ₂
1-hexyl-3-methylimidazolium chloride	C ₁₀ H ₁₉ ClN ₂
1-methyl-3-octylimidazolium chloride	C ₁₂ H ₂₃ ClN ₂
1-ethyl-3-methylimidazolium bromide	C ₆ H ₁₁ BrN ₂
1-butyl-3-methylimidazolium bromide	C ₈ H ₁₅ BrN ₂
1-ethyl-3-methylimidazolium hexafluorophosphate	C ₆ H ₁₁ F ₆ N ₂ P
1-butyl-3-methylimidazolium hexafluorophosphate	C ₈ H ₁₅ F ₆ N ₂ P
1-methyl-3-octylimidazolium hexafluorophosphate	C ₁₂ H ₂₃ F ₆ N ₂ P
1-ethyl-3-methylimidazolium tetrafluoroborate	C ₆ H ₁₁ BF ₄ N ₂
1-butyl-3-methylimidazolium tetrafluoroborate	C ₈ H ₁₅ BF ₄ N ₂
1-methyl-3-octylimidazolium tetrafluoroborate	C ₁₂ H ₂₃ BF ₄ N ₂
Tetrabutylphosphonium bromide	(CH ₃ CH ₂ CH ₂ CH ₂) ₄ P(Br)
Tetrabutylammonium bromide	(CH ₃ CH ₂ CH ₂ CH ₂) ₄ N(Br)
Tetrahexylammonium bromide	[CH ₃ (CH ₂) ₅] ₄ N(Br)
Tetraoctylammonium bromide	[CH ₃ (CH ₂) ₇] ₄ N(Br)
Didodecyldimethylammonium bromide	[CH ₃ (CH ₂) ₁₁] ₂ N(CH ₃) ₂ Br

$$v_e = -\frac{\ln(1 - V_r) + V_r + \mu V_r^2}{V_o \left(V_r^{1/3} - \frac{V_r}{2} \right)} \quad (1)$$

where: v_e - crosslink density, V_r - volume fraction of elastomer in swollen gel, V_o - molar volume of solvent [mol/cm³].

Heterogeneity of elastomer network

The distribution of crosslinks in the elastomer network was estimated based on solvent freezing point depression of the solvent confined in the polymer gel. Thermograms of solidification were recorded on a Differential Scanning Calorimetry (DSC) instrument (Perkin-Elmer DSC 7) by decreasing the temperature from 30 to -90°C at a rate of 10°C/min. Before this measurement, samples were swollen in benzene for 24 h.¹⁸⁻²¹

Dispersion of zinc oxide in elastomer matrix

The distribution of zinc oxide nanoparticles was estimated using Scanning Electron Microscopy with an SEM microscope LEO 1530.

RESULTS AND DISCUSSION

Cure characteristics and crosslink density of vulcanizates

The influence of ionic liquids (alkylimidazolium salts) and cationic surfactants (alkylphosphonium and alkylammonium bromides) was estimated based on rheometer measurements. The cure characteristics of NBR compounds and crosslink densities of vulcanizates are given in Table III.

Applying ionic liquids (alkylimidazolium salts) resulted in a considerably shorter vulcanization time of rubber compounds compared to the conventional ZnO system. It confirmed that ILs act as catalysts of interface reactions. The optimal vulcanization time decreased with the length of alkyl chains attached to the imidazolium ring in ionic liquid molecule. The influence of the anion present in the alkylimidazolium salt was also observed. The shortest cure times were exhibited by rubber compounds containing alkylimidazolium chlorides or bromides, whereas the longest vulcanization times were observed for rubber compounds with alkylimidazolium hexafluorophosphates. The length of alkyl chains in the ionic liquid molecule did not significantly affect the torque increment of rubber compounds during vulcanization; only a slight decrease of ΔG values was observed for elastomer composites containing ionic liquids with longer alkyl chains. The anion type of the ionic liquid seemed to have a higher impact on the torque increment. The highest ΔG values were exhibited by elastomer compounds with alkylimidazolium hexafluorophosphates and chlorides.

From the presented data, it follows that the application of some ILs increased the crosslink density of

TABLE II
General Composition of the NBR-Based Rubber Compounds, phr

Compound	M1	M2	M3
NBR	100	100	100
Sulfur	2	2	2
Accelerator (MBT)	2	2	2
nano ZnO	2	2	2
Stearic acid	2	-	-
Ionic liquid	-	1	-
Surfactant	-	-	1

TABLE III
Cure Characteristics of NBR Compounds and Crosslink Densities of Vulcanizates

Dispersing agent	ΔG (dNm)	t_{90} (min)	$v_e \cdot 10^5$ (mol/cm ³)
-	68.0	70	11.7
1-ethyl-3-methylimidazolium chloride	84.1	35	9.6
1-butyl-3-methylimidazolium chloride	81.3	30	9.2
1-hexyl-3-methylimidazolium chloride	77.8	25	10.4
1-methyl-3-octylimidazolium chloride	76.1	25	12.1
1-ethyl-3-methylimidazolium bromide	61.2	38	12.4
1-butyl-3-methylimidazolium bromide	66.2	30	14.3
1-ethyl-3-methylimidazolium hexafluorophosphate	109.6	50	13.0
1-butyl-3-methylimidazolium hexafluorophosphate	98.5	48	12.9
1-methyl-3-octylimidazolium hexafluorophosphate	97.1	45	15.0
1-ethyl-3-methylimidazolium tetrafluoroborate	73.8	55	11.5
1-butyl-3-methylimidazolium tetrafluoroborate	73.2	48	13.7
1-methyl-3-octylimidazolium tetrafluoroborate	71.5	35	12.8
Tetrabutylphosphonium bromide	41.1	15	12.7
Tetrabutylammonium bromide	55.2	20	13.4
Tetrahexylammonium bromide	59.1	25	14.7
Tetraoctylammonium bromide	61.0	30	15.3
Didodecyldimethylammonium bromide	76.5	35	12.8

ΔG , increment of torque in the rubber compound during vulcanization; t_{90} , optimal vulcanization time; v_e – crosslink density of vulcanizate.

NBR vulcanizates due to the catalytic effect of alkylimidazolium salt on the efficiency of the interface crosslinking reactions. However, some exceptions were observed for chlorides with ethyl, butyl, and hexyl-3-methylimidazolium cations or 1-ethyl-3-methylimidazolium tetrafluoroborate, probably as a result of weaker dispersion of zinc oxide nanoparticles in the elastomer. Crosslink density of vulcanizates usually increased with increasing length of alkyl chains attached to the imidazolium ring. Considering the anion of the ionic liquid, the lowest crosslink densities were achieved for vulcanizates containing alkylimidazolium chlorides.

The catalytic influence on the crosslinking reactions was particularly evident in the case of cationic surfactants, alkylammonium, or alkylphosphonium bromides. Vulcanization time of NBR compounds decreased to as little as 15 min when tetrabutylphosphonium bromide was present. For rubber compounds containing tetraalkylammonium bromides, vulcanization time was within the range of 20–35 minutes and increased with increasing length of surfactant alkyl chain from C4 to C10. Cationic surfactants caused the increase of crosslink density compared to the conventional ZnO system. Crosslink density increased with the length of alkyl chains of tetraalkylammonium bromides.

Crosslinks distribution in the elastomer network

Apart from crosslink density, the spatial arrangement (distribution) of crosslinks and the presence of defects in the elastomer network are highly impor-

tant for mechanical properties of vulcanizates. Heterogeneous distribution of crosslinks in the elastomer network is believed to have a detrimental effect on vulcanizate mechanical properties, as the densely crosslinked domains of the network can concentrate stresses and initiate breaking of the sample upon external strain. Therefore, vulcanizates with a homogenous crosslink distribution exhibit higher tensile strength.²² On the other hand, Vilgis and Heinrich²³ postulated that the distribution of stress in a crosslinked sample can be more effective in a less crosslinked part of the network due to the stress relaxation process. The microcrack propagation within these areas could be hindered, and microcracks can occur only under higher stresses or deformations. As a result, the tensile strength and elongation at the break of a vulcanizate increase. Therefore, heterogeneous distribution of crosslinks in the elastomer network improves material mechanical properties. The positive effect of network heterogeneity on tensile properties of vulcanizates was confirmed by Przybyszewska et al.¹¹ in the case of NBR vulcanizates crosslinked with sulfur and containing zinc chelates with 1,3-diketones as activators.

We analyzed the influence of different dispersing agents (ionic liquids and cationic surfactants) on crosslink spatial arrangement in the elastomer network. The distribution of crosslinks in an NBR matrix was estimated using the DSC method based on the freezing point depression of solvent confined in polymer gel. This method was proposed by Baba et al.^{18–21} to determine the structure of the network in rubber composites. The freezing point depends on

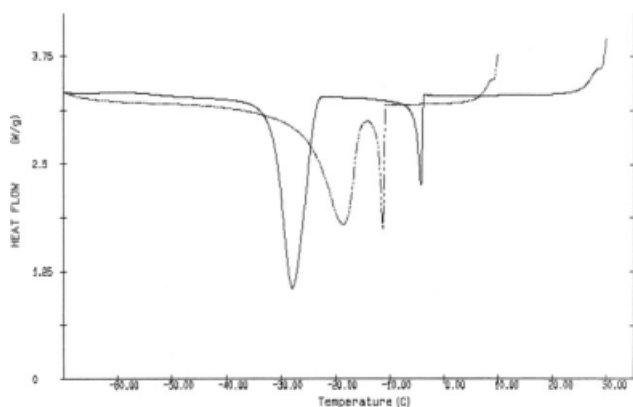


Figure 1 DSC thermogram of swollen NBR vulcanizates: without ionic liquid (continuous line), with 1-butyl-3-methylimidazolium bromide (broken line).

the conditions required for the formation of crystalline nuclei, which are limited by elastomer network restrictions and limitations in movement of polymer chains.

DSC thermograms of NBR vulcanizates swollen in benzene are presented in Figures 1–4. The freezing point depression of solvent in a swollen elastomer network depends on the crosslink structure. Two peaks were observed on the DSC curves. The first, detected at (-6°C), is due to the crystallization of free benzene. The other corresponds to the crystallization of benzene entrapped in the swollen gel, the position of which depends on the crosslink density. The peak of the confined solvent is shifted towards a lower temperature compared to the free benzene peak. In the case of vulcanizates crosslinked in the presence of ionic liquids (alkylimidazolium salts) or cationic surfactants (alkylammonium salts), the peak of benzene entrapped in the swollen network is shifted towards higher temperatures compared to a vulcanizate without dispersing agent. In the case of vulcanizates containing ionic liquids (Figs. 1 and 2),

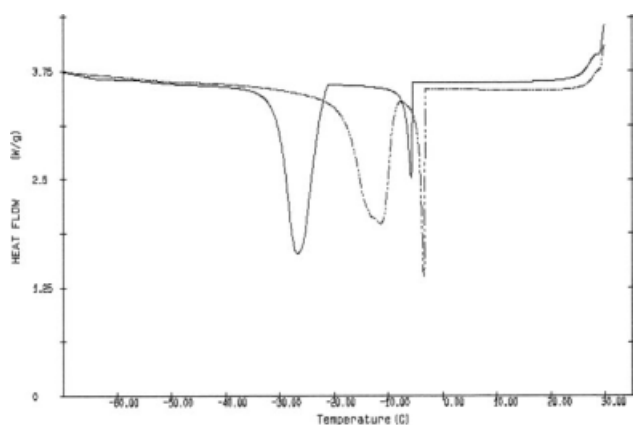


Figure 2 DSC thermogram of swollen NBR vulcanizates: without ionic liquid (continuous line), with 1-butyl-3-methylimidazolium tetrafluoroborate (broken line).

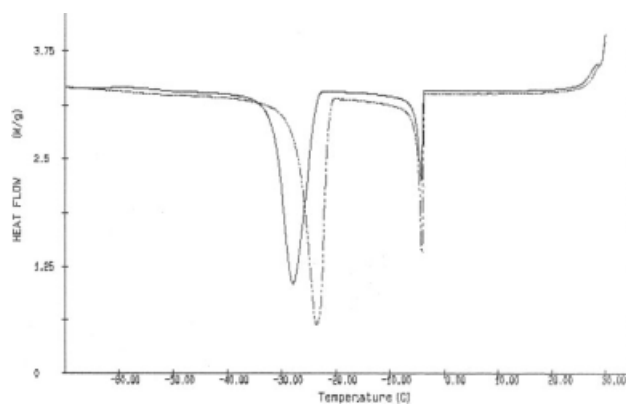


Figure 3 DSC thermogram of swollen NBR vulcanizates: without cationic surfactant (continuous line), with tetrabutylammonium bromide (broken line).

the broadening of the solidification peaks suggests a broadening of the distribution of mesh sizes in the elastomer network. Considering the shape and width of the entrapped benzene peaks obtained for vulcanizates with cationic surfactants (Figs. 3 and 4), it could be concluded that alkylammonium salts did not affect the crosslink distribution in the elastomer network.

According to Baba,¹⁸ the peak position of the solvent confined in the polymer gel is directly related to the radius of the mesh (R_p) by the following relationship [eq. (2)]:

$$R_p = \frac{-A}{\Delta T} + B \quad (2)$$

where $\Delta T = T_0 - T$; T_0 is the triple point temperature of solvent, A and B are constants depending on the solvent.

The radius of the mesh is proportional to the molecular weight of the network between crosslinks M_c . Therefore, to analyze the vulcanizate structures,

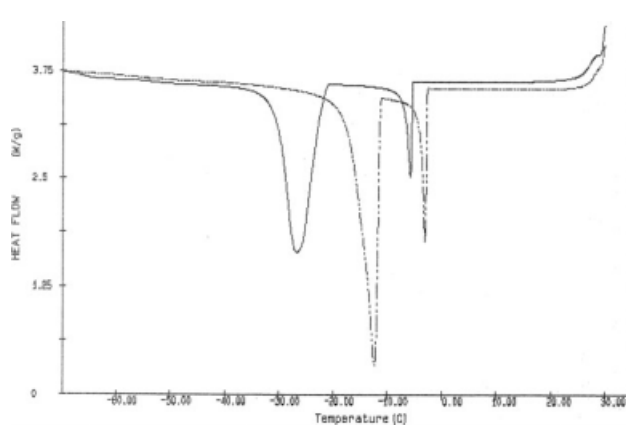


Figure 4 DSC thermogram of swollen NBR vulcanizates: without cationic surfactant (continuous line), with didodecylmethylammonium bromide (broken line).

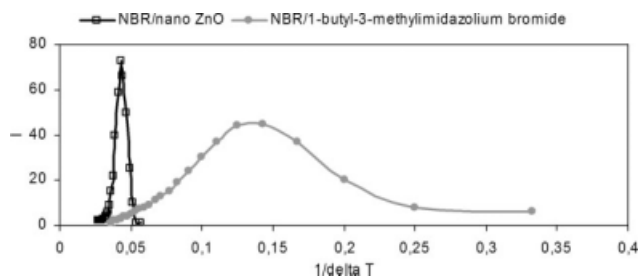


Figure 5 Distribution of molecular weights (I) between network crosslinks in NBR vulcanizate with 1-butyl-3-methylimidazolium bromide.

the distribution of molecular weights between crosslinks was estimated. Results are shown in Figures 5–8. Parameter I corresponds to the molecular weight of the network between crosslinks and was estimated based on the peak intensity of benzene confined in a swollen gel.

The data presented in Figures 5–8 indicate that the distribution of crosslinks in the elastomer network resembles a Gaussian distribution. However, broadening of the crosslink distribution was observed for vulcanizates containing ILs, especially 1-butyl-3-methylimidazolium bromide. Therefore, it can be concluded that elastomer networks obtained using alkylimidazolium salts are more heterogeneous than those formed without addition of ionic liquid. Conversely, the crosslink distribution in vulcanizates with cationic surfactants was similar to that obtained without alkylammonium salt or even narrower in the case of didodecyldimethylammonium bromide. This is probably due to the better dispersion of zinc oxide nanoparticles in the elastomer in the presence of surfactants. Assuming that crosslinking takes place around the activator particles, on which other components of the crosslinking system are adsorbed, more homogeneous dispersion of ZnO results in the formation of a polymer network with homogeneous crosslink distribution. It is worth noting that vulcanizates with heterogeneous networks exhibited higher tensile strength (results in Table IV). Therefore, the heterogeneity of the network contributes to the improvement of vulcanizate mechanical properties.

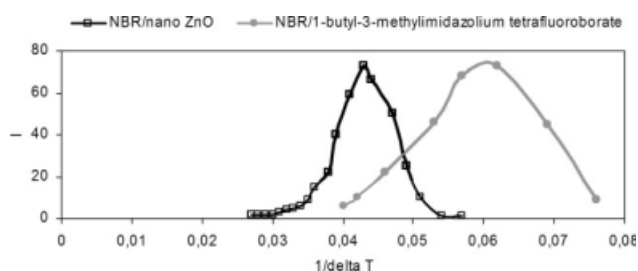


Figure 6 Distribution of molecular weights (I) between network crosslinks in NBR vulcanizate with 1-butyl-3-methylimidazolium tetrafluoroborate.

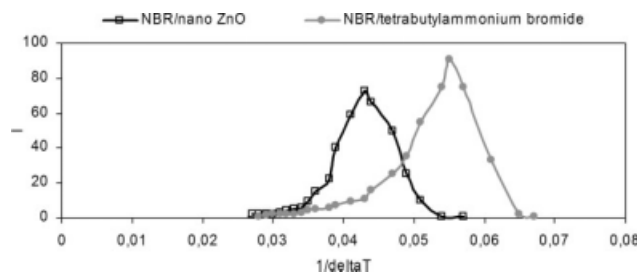


Figure 7 Distribution of molecular weights (I) between network crosslinks in NBR vulcanizate with tetrabutylammonium bromide.

To confirm that application of alkylimidazolium salts leads to heterogeneous distribution of crosslinks in the elastomer network, we examined the kinetics of vulcanizate swelling in toluene. The kinetics of vulcanizate swelling is related to the diffusion of solvent in the elastomer network and depends on the crosslink density and distribution in the polymer matrix. Results are shown in Figure 9. Vulcanizates containing ILs swelled much quicker, especially in the case of vulcanizates with 1-butyl-3-methylimidazolium tetrafluoroborate. This proved the heterogeneous distribution of network crosslinks in these vulcanizates and confirmed the results obtained by the DSC method. The swelling curves of vulcanizates with cationic surfactant were very similar to those determined for vulcanizates without dispersing agents. Therefore, alkylammonium bromides had no influence on the crosslink distribution in the elastomer network.

Mechanical properties of vulcanizates

Having established the influence of ILs and cationic surfactants on the vulcanization process and crosslink distribution in the elastomer network, we then examined the mechanical properties of NBR vulcanizates. Results are given in Table IV.

During the first stage of the studies, we examined the rubber compounds and vulcanizates made according to the formulation given in the experimental section of this article. Unfortunately, vulcanizates

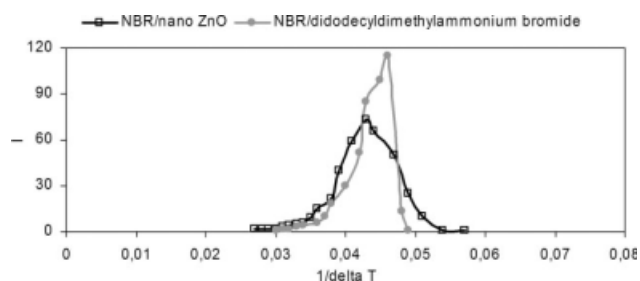


Figure 8 Distribution of molecular weights (I) between network crosslinks in NBR vulcanizate with didodecyldimethylammonium bromide.

TABLE IV
Mechanical Properties of NBR Vulcanizates

Dispersing agent	SE ₃₀₀ , MPa	TS, MPa	EB, %
-	2.4	6.9	571
1-ethyl-3-methylimidazolium chloride*	1.7	6.5	509
1-butyl-3-methylimidazolium chloride*	2.0	7.2	517
1-hexyl-3-methylimidazolium chloride*	2.4	5.3	488
1-methyl-3-octylimidazolium chloride*	2.3	5.2	497
1-ethyl-3-methylimidazolium bromide	2.7	5.3	422
1-butyl-3-methylimidazolium bromide	2.9	8.4	368
1-ethyl-3-methylimidazolium hexafluorophosphate	1.9	5.6	580
1-butyl-3-methylimidazolium hexafluorophosphate	2.3	6.2	503
1-methyl-3-octylimidazolium hexafluorophosphate	2.0	5.5	565
1-ethyl-3-methylimidazolium tetrafluoroborate	2.6	6.6	449
1-butyl-3-methylimidazolium tetrafluoroborate	2.7	12.1	518
1-methyl-3-octylimidazolium tetrafluoroborate	2.5	7.1	462
Tetrabutylphosphonium bromide*	3.8	5.4	353
Tetrabutylammonium bromide*	3.7	5.5	391
Tetrahexylammonium bromide*	3.3	5.4	470
Tetraoctylammonium bromide*	2.3	5.2	473
Didodecyldimethylammonium bromide	3.3	6.6	416

*Vulcanizates containing 1.3 phr of sulfur; 1.3 phr of 2-mercaptobenzothiazole; 1.3 phr of Nano ZnO, and 0.6 phr of dispersing agent.

containing alkyliimidazolium chlorides and tetraalkylammonium bromides exhibited a very high modulus at a relative elongation of 300% (3.8 MPa), elongation at break below 300% and, as a consequence, very low tensile strength (below 4.6 MPa). It resulted from their very high crosslink density. Therefore, it was necessary to reduce the amount of crosslinking system components to obtain vulcanizates with optimal crosslink density and elongation at break about 500%. It was found that the content of nanosized zinc oxide, sulfur, and 2-mercaptobenzothiazole should be reduced to 1.3 phr and the dispersing agent to 0.6 phr. Therefore, results presented in Table IV concern the properties of vulcanizates with an optimized contents of the crosslinking system and dispersing agents. However, it should be noted that the reduction of zinc or sulfur compound contents in the elastomer is very important from an ecological point of view. Reduction of sulfur, ZnO nanoparticle, accelerator, and dispersing agent amounts increased the vulcanization time of rubber compounds. Small decrease of torque increment during vulcanization was also observed as a result of crosslink density decrease.

Applying ionic liquids had no considerable effect on the modulus at 300% relative elongation of vulcanizates. The effect of ionic liquids on the tensile strength of NBR vulcanizates was dependent on the length of the alkyl chain attached to the imidazolium ring in the cation as well as the anion of the alkyliimidazolium salt. The tensile strength of vulcanizates containing ionic liquids increased with the increase of the length of alkyl chain attached to the imidazolium ring in the ILs molecule from C2 to C4. Further

increase of ILs alkyl chain length led to a deterioration of the vulcanizate tensile strength. The highest tensile strengths were achieved for vulcanizates containing ionic liquids with 1-butyl-3-methylimidazolium cation.

Considering the effect of the anion, the most effective ones seemed to be tetrafluoroborates. The vulcanizate with 1-butyl-3-methylimidazolium tetrafluoroborate exhibited a tensile strength almost twice that of the vulcanizate without ionic liquid. Chlorides, bromides, and hexafluorophosphates had no significant influence on TS values. However, their application reduced vulcanizate elongation at break due to the increase of their crosslink density.

From the data compiled in Table IV, it follows that the length of alkyl chains in ammonium bromide did not affect the tensile strength of vulcanizates. However, a slight decrease of elongation at break could be observed. Among cationic

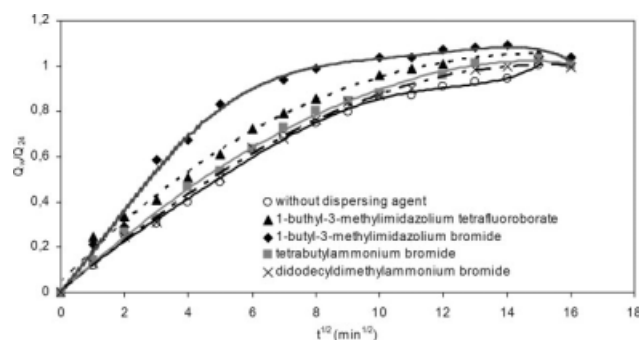


Figure 9 Swelling kinetics of NBR vulcanizates in toluene.

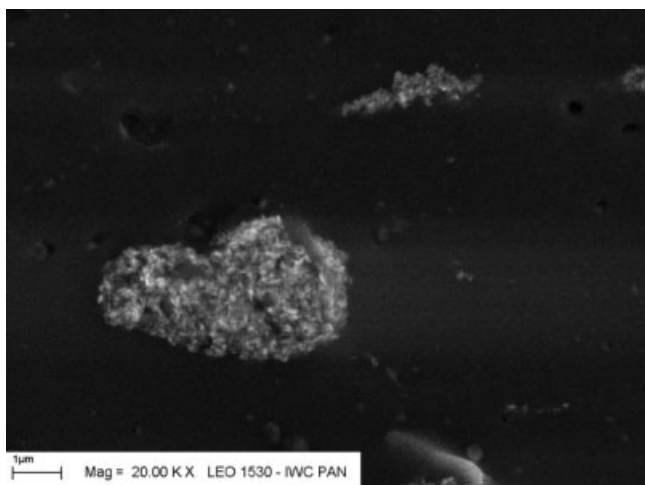


Figure 10 SEM image of NBR vulcanizate without dispersing agent.

surfactants, the highest tensile strength was achieved for vulcanizates containing didodecyldimethylammonium bromide.

Dispersion of zinc oxide nanoparticles in the elastomer

The dispersion of zinc oxide nanoparticles in the elastomer matrix is very important to the activation of sulfur vulcanization. Homogeneous dispersion of ZnO nanoparticles provides better contact between the activator and other components of the crosslinking system. SEM images were taken to estimate the dispersion of zinc oxide nanoparticles in the elastomer in the presence of ionic liquids and cationic surfactants (Figs. 10–14).

Zinc oxide nanoparticles (Fig. 10) are not homogeneously distributed in the elastomer matrix. They create microsized agglomerates with different

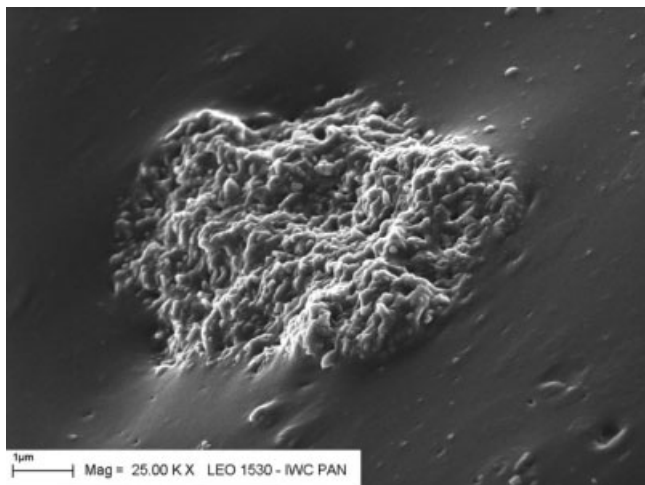


Figure 11 SEM image of NBR vulcanizate with 1-butyl-3-methylimidazolium bromide.

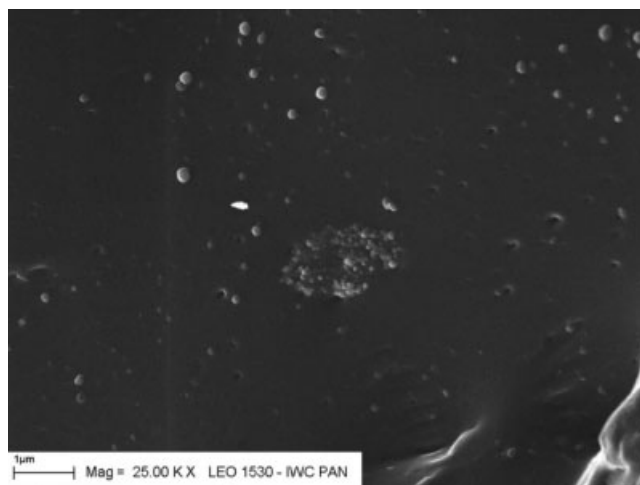


Figure 12 SEM image of NBR vulcanizate with 1-butyl-3-methylimidazolium tetrafluoroborate.

shapes. The high tendency of ZnO nanoparticles for agglomeration results from their high surface energy and ability for specific interactions.²⁴ The agglomeration of zinc oxide nanoparticles causes their surface area to decrease, followed by a decrease of the interface between the zinc oxide and other components of the crosslinking system. As a result, the efficiency of elastomer crosslinking decreases. Moreover, agglomerates of zinc oxide nanoparticles may be responsible for local increases in crosslink density of vulcanizates and formation of densely crosslinked domains with low elasticity, which may initiate breaking of the sample under external stress.

The improvement of zinc oxide nanoparticles dispersion in the vulcanizate containing 1-butyl-3-methylimidazolium tetrafluoroborate (Fig. 12) is one of the reasons for the enhancement of vulcanizate tensile properties. Nanoparticles are more homogeneously distributed in the elastomer and create only

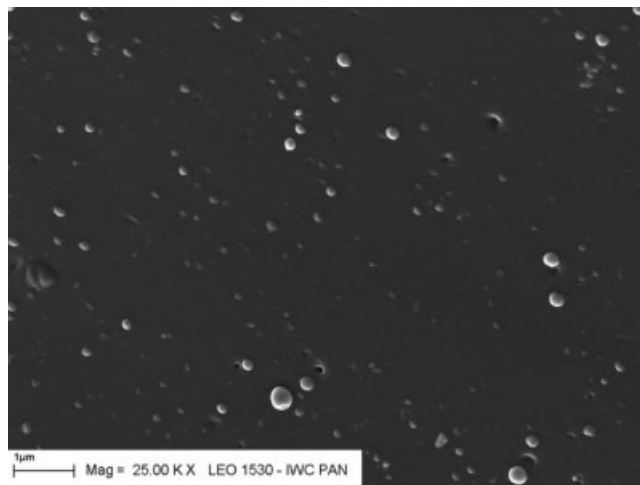


Figure 13 SEM image of NBR vulcanizate with tetrabutylammonium bromide.

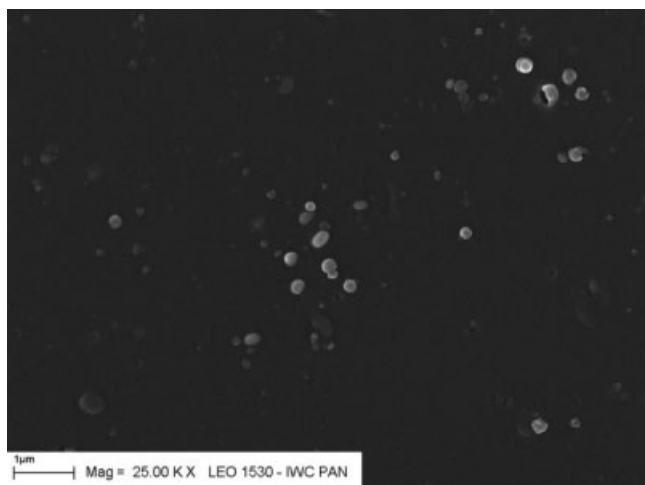


Figure 14 SEM image of NBR vulcanizate with didodecyldimethylammonium bromide.

small agglomerates approximately 1–2 μm in size. This ionic liquid seemed to be one of the best dispersing agents, which effectively prevented ZnO nanoparticles from agglomeration. 1-butyl-3-methylimidazolium bromide exhibited considerably lower efficiency as a dispersing agent compared to tetrafluoroborate. Clusters of zinc oxide nanoparticles several microns in size could be seen in the SEM image (Fig. 11). Similar agglomerates were observed in the case of vulcanizates containing the other examined ionic liquids.

Cationic surfactants (alkylammonium bromides) improved the dispersion of nanosized zinc oxide in the elastomer matrix (Figs. 13–14). Nanoparticles were homogeneously distributed in the elastomer and did not exhibit the tendency for agglomeration. This resulted in a homogeneous distribution of crosslinks in the elastomer network. Despite the uniform dispersion of ZnO nanoparticles and distribution of crosslinks, vulcanizates with alkylammonium salts displayed lower tensile strength than those containing 1-butyl-3-methylimidazolium tetrafluoroborate or bromide. This observation confirmed that the heterogeneity of the elastomer network helps improve mechanical properties of vulcanizates.

CONCLUSIONS

Ionic liquids (alkylimidazolium salts) and cationic surfactants (alkylphosphonium and alkylammonium salts) were used to improve the dispersion of zinc oxide nanoparticles in elastomer and its activity in sulfur vulcanization of NBR.

We conclude that alkylimidazolium and alkylammonium salts catalyze the interface crosslinking reactions. As a consequence, the vulcanization time of rubber compounds significantly decreased, and the crosslink density of vulcanizates increased. The

structure of ionic liquid or cationic surfactant is very important for their activity. The cure rate and crosslink density of NBR vulcanizates increased with the length of alkyl chains present in the alkylimidazolium or alkylammonium salt. The effect of the anion was also observed. Higher cure rate was exhibited by rubber compounds containing alkylimidazolium chlorides and bromides, whereas the longest vulcanization times were observed for rubber compounds with alkylimidazolium hexafluorophosphates. Considering mechanical properties of vulcanizates, the most effective ones were ILs with 1-butyl-3-methylimidazolium cation, especially 1-butyl-3-methylimidazolium tetrafluoroborate and bromide.

ILs increased the heterogeneity of the elastomer network, which improves the tensile strength of vulcanizates. Cationic surfactant did not considerably affect the distribution of crosslinks in the elastomer network.

Alkylammonium salts allow the achievement of homogeneous distribution of zinc oxide nanoparticles in the elastomer matrix. Among ILs, only 1-butyl-3-methylimidazolium tetrafluoroborate improved the dispersion of nanosized zinc oxide in the elastomer.

Applying alkylimidazolium chlorides and tetraalkylammonium bromides enables to obtain vulcanizates with the amount of zinc oxide, sulfur, and 2-mercaptobenzothiazole reduced to 1.3 phr, which exhibit the tensile strength comparable to vulcanizates without dispersing agent. This is an important ecological goal, as zinc oxide and sulfur compounds are believed to be harmful for the environment.

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

References

1. Abi, S. A.; Kuruvilla, J.; Sabu, T. *Rubber Chem Technol* 2005, 78, 458.
2. Heideman, G.; Datta, R. N.; Noordermeer, J. W. M. *Rubber Chem Technol* 2004, 77, 512.
3. Gradwell, M. H. S.; Mc Gill, W. J. *J Appl Polym Sci* 1996, 61, 1515.
4. Gradwell, M. H. S.; Mc Gill, W. J. *J Appl Polym Sci* 1996, 61, 1131.
5. Coran, A. Y. *J Appl Polym Sci* 2003, 87, 24.
6. Heideman, G.; Datta, R. N.; Noordermeer, J. W. M.; Van Baarle, B. *J Appl Polym Sci* 2005, 95, 1388.
7. Ghosh, P.; Katare, S.; Patkar, P.; Caruthers, J. M.; Venkatasubramanian, V.; Walker, K. A. *Rubber Chem Technol* 2003, 76, 592.
8. Chapman, A. V.; Porter, M. In *Natural Rubber Science and Technology*; Roberts, A. D., Ed.; Oxford University Press: Oxford, 1988; p 511.
9. Chapman, A.; Johnson, T. *Kautsch Gummi Kunstst* 2005, 58, 358.
10. Heideman, G.; Noordermeer, J. W. M.; Datta, R. N. *Rubber Chem Technol* 2005, 78, 245.

11. Przybyszewska, M.; Zaborski, M.; Zawadiak, J.; Jakubowski, B. *Express Polym Lett* 2009, 3, 256.
12. Heideman, G.; Noordermeer, J. W. M.; Datta, R. N.; Van Baarle, B. *Rubber Chem Technol* 2004, 77, 336.
13. Nieuwenhuizen, P. J. *Appl Catal A Gen* 2001, 207, 55.
14. Kleps, T.; Piaskiewicz, M.; Parasiewicz, W.; Parys, T.; Ślusarski, L. *Elastomery* 2003, 7, 38.
15. Lu, J.; Yan, F.; Texter, J. *Prog Polym Sci* 2009, 34, 431.
16. Parvulescu, V. I.; Hardacre, C. *Chem Rev* 2007, 107, 2615.
17. Flory, P. J.; Rehner, J. *J Chem Phys* 1943, 11, 521.
18. Baba, M.; Gardette, J. L.; Lacoste, J. *Polym Degrad Stab* 1999, 63, 121.
19. Baba, M.; Gardette, J. L.; Lacoste, J. *Polym Degrad Stab* 1999, 65, 415.
20. Baba, M.; Lacoste, J.; Gardette, J. L. *Polym Degrad Stab* 1999, 65, 421.
21. Baba, M.; Nedelec, J. M.; Lacoste, J.; Gardette, J. L.; Morel, M. *Polym Degrad Stab* 2003, 80, 305.
22. Hernandez, L. G.; Diaz, A. R.; De Benito Gonzales, J. L.; Orosa, I. F.; Fernandez, A. M. *Kautsch Gummi Kunstst* 1992, 45, 1033.
23. Vilgis, T. A.; Heinrich, G. *Kautsch Gummi Kunstst* 1992, 45, 1006.
24. Przybyszewska, M.; Krzywania, A.; Zaborski, M.; Szyrkowska, M. I. *J Chromatogr A* 2009, 1216, 5284.