

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

185,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Ionic Liquids in the Vulcanization of Elastomers

Magdalena Maciejewska and Filip Walkiewicz

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/59064>

1. Introduction

Vulcanization is the basic process used in elastomer technology. The first patent for the sulfur vulcanization of natural rubber was issued to Charles Goodyear in 1839. The most important disadvantage of sulfur vulcanization at its creation was the long process time of several hours. In 1906, Oenslager discovered the accelerating effect of aniline on sulfur vulcanization [1]. This discovery was followed by the introduction of guanidines. Other organic vulcanization accelerators, such as thiazole and sulfenamide, were developed in 1930 [2]. In later years, thiurames and dithiocarbamates were applied. Although vulcanization is one of the oldest and best known processes, thiazoles, sulfenamides and dithiocarbamates were the last significant accelerator classes to be introduced in industry. Soon afterward, it was discovered that zinc oxide could activate the sulfur vulcanization process. Zinc oxide reacts with accelerators to form zinc complexes, which are more reactive than free accelerators. Sulfur is then incorporated into these complexes, and active sulfating agents are formed that react with the allylic hydrogen atoms of unsaturated elastomers to form crosslink precursors. These precursors then react with other rubber chains to generate crosslinks that contain large amounts of sulfur atoms in their bridges. In the next step of the vulcanization process, crosslink shortening, usually accompanied by side reactions, produces the final elastomer network [3].

It is commonly postulated that acceleration of sulfur vulcanization results from homogeneous catalysis by zinc complexes or zinc salts [3]. Traditionally, stearic acid is used together with zinc oxide to activate sulfur vulcanization. In this way, a complex composed of zinc, an accelerator, and stearic acid is formed during vulcanization and includes a central zinc cation, two stearyl anions, and accelerator residues. This complex and other components of the crosslinking system are strongly polar and also reveal a tendency for agglomeration in the elastomer, resulting in the reduction of vulcanization efficiency [4]. Therefore, the application

of novel ionic liquids (ILs)-the derivatives of 2-mercaptobenzothiazole-as accelerators for the vulcanization process seems to be reasonable. Because of their catalytic activity [5], ILs increase the rates of interfacial crosslinking reactions. Moreover, because of their ionic character, ILs should be able to form salts or complexes with zinc ions, similarly to standard accelerators; however, these complexes are more reactive than zinc-accelerator complexes. Additionally, the application of ligands with higher solvation power towards zinc cations than stearyl anions should improve the dispersion degree of the active sulfurating agent as well as of the crosslinking system components in the elastomer. As a result, the crosslinking rate and efficiency should increase considerably.

Recently, IL research has been one of the most rapidly growing fields in chemistry and industry, mainly due to the many unique properties of ionic liquids, such as chemical, electrochemical and thermal stability, low vapor pressure and high ionic conductivity [6]. ILs are generally defined as salts with melting temperatures lower than 100 °C and commonly consist of an asymmetric, organic cation and a rather weakly coordinating organic or inorganic anion [6,7]. Most ILs have good miscibility with organic solvents or monomers, are able to solvate a large variety of organic polar and nonpolar compounds, and show potentially “environmentally-friendly” characteristics due to their negligible vapor pressure and flammability [8]. ILs are nonvolatile compounds; thus, the chance for fugitive emissions during their use in technology is limited. Due to their ionic character, ILs are highly polar but non-coordinating, so they may affect the course of ionic reactions [9]. Therefore, ILs can be used as solvents for electrochemical processes [6,10], and their chemical and physical properties can be tailored by varying the cations and anions for a wide range of potential applications. In recent years, ILs have been widely used in polymer science, mainly as solvents in different types of polymerizations (e.g., free radical polymerization [11], atom transfer radical polymerization [12] or ionic polymerization [13]). Wang et al. used room-temperature ILs such as triethylamine hydrochloride-aluminum chloride ($\text{Et}_3\text{NHCl-AlCl}_3$) as an initiator for the cationic copolymerization of 1,3-pentadiene with styrene [14]. The best results were obtained for AlCl_3 content of 60 wt%. The reaction produced a high-molecular-weight copolymer with a smaller molecular weight distribution than that produced when using an organic solvent. Increasing the concentration of IL led to an increase of copolymerization yield. Moreover, as the concentration of ionic liquid increased, more crosslinked products were achieved as a result of the higher concentration of macromolecular chains in the reaction medium, which favored the intermolecular reaction of carbocations with the copolymer. The cationic ring-opening polymerization of 3,3-bis(chloromethyl)oxacyclobutane was carried out in 1-butyl-3-methylimidazolium tetrafluoroborate and hexafluorophosphate [15]. The polymerization process proceeded to high conversions, although polymer molecular weights were limited, similar to polymerization in organic solvents. ILs were able to be separated from other reagents and reused. The moisture-stable ionic liquid composed of choline chloride and zinc chloride was applied to the radiation-induced copolymerization of vinyl monomers – styrene and methyl methacrylate. The mechanism of copolymerization was the same as in conventional organic solvents at room temperature, and the copolymer was produced with

high efficiency [16]. The IL 1-butyl-3-methylimidazolium hexafluorophosphate was also used as a solvent in the radical polymerization of methyl methacrylate [17]. A considerable increase in the rate constant of propagation was observed that was related to increasing polarity of the polymerization medium that favored a transition state involving charge transfer or complex formation between IL and either monomer or radical. The rate of polymerization was approximately 10 times higher than in traditionally used benzene. The molecular weights of polymers were also considerably higher, indicating a decrease in the rate of termination. This ionic liquid can be successfully used for synthesis of styrene and methyl methacrylate block copolymers [18]. The IL 1-butylpyridinium tetrafluoroborate was used in the radical polymerization of 2-hydroxyethyl methacrylate [19]. Transparent and highly conductive polymer electrolytes were obtained and characterized with high mechanical strength. ILs can serve as solvents for the organotellurium-mediated living radical polymerization (TERP) of methyl methacrylate (MMA), methyl acrylate (MA), and styrene [20]. The reaction rate of MMA and MA polymerization significantly increased, and the controllability of the polydispersity index (PDI) was also improved. The TERP of MMA yielded poly(methyl methacrylates) with PDI less than 1.1. The improved control of polymerization was ascribed to a faster degenerative chain transfer reaction that is a key parameter in the control of PDI for TERP. Moreover, facile separation of polymers from ILs and the possibility of IL recycling were described.

ILs can also be polymerized to form ionic gels [21-23]; 1-(8-(acryloyloxy)octyl)-3-methylimidazolium chloride was reported to photopolymerize and form a hydrogel through self-assembly [24]. This hydrogel was physically crosslinked and possessed an ordered lamellar structure that enabled reversible swelling in water up to 200 times its original volume.

ILs can be used to dissolve polymers such as cellulose [25], starch [26], or silk fibroin [27] and have shown great potential as effective wood preservatives. Hydrophobic ammonium-based ILs, which are air- and moisture-stable, possess anti-bacterial and anti-fungal activity [28]. The ability to dissolve cellulose was described for 1-butyl-3-methylimidazolium chloride, acetate and formate [29]. Pernak et al. reported the possibility of dissolving cellulose using ILs with 4-benzyl-4-methylmorpholinium and alkyl(cyclohexyl)dimethylammonium cations [30,31]. Alkylimidazolium 1,2,4-triazolates and benzotriazolates were tested for fungistatic activity against strains of *Aspergillus* and *Penicillium* molds. The highest antifungal activity was demonstrated by 1-dodecyl-methylimidazolium 1,2,4-triazolate, which effectively protected paper against molds [32].

ILs are used for filler modification to increase the interactions between a filler and an elastomer matrix and to improve the dispersion of filler particles in the elastomer, especially in the case of silica, clays, carbon black and carbon nanotubes [33-35]. ILs such as 1-butyl-3-methylimidazolium chloride, tetrafluoroborate and hexafluorophosphate were used to improve the dispersion degree of magnetic fillers in an ethylene-octene copolymer [36]. ILs increased the magnetorheological effect of composites due to the homogeneous distribution of magnetic filler nanoparticles in the polymer. A significant improvement of the mechanical properties of composites, such as tensile strength, was achieved.

Due to very high ionic conductivity below their decomposition temperature, ILs can have an important role in electrolyte matrices. The application of ILs provides the polymer electrolyte with high tensile strength and elasticity by giving conductivity to elastomers. Conductive butadiene-acrylonitrile elastomer (NBR) composites with an ionic conductivity of $2.54 \times 10^{-4} \text{ S cm}^{-1}$ have previously been prepared using 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [37]. The use of ILs resulted in the development of conductive polychloroprene rubber containing a low concentration of multi-walled carbon nanotubes [38]. Stable polymer electrolytes with an ionic conductivity of over $10^{-4} \text{ S cm}^{-1}$ were obtained from polymerizable ionic liquids with an imidazolium cation [39].

Despite the wide applications of ionic liquids in polymer and elastomer science, their use as accelerators for the sulfur vulcanization of unsaturated elastomers has not yet been reported, with the exception of our previous publications [40,41]. Thus, this chapter represents an innovative and original solution.

For our studies, we believe that the application of ILs will result in the development of new eco-friendly accelerators for elastomer sulfur vulcanization. The most popular accelerator (MBT) is an allergenic agent. Like guanidines, sulfenamides are amine derivatives with different amine moiety contents. Therefore, their application in technology should be limited because of toxicity. The proposed ILs are derived from conventional accelerators, but due to their greater activity, the amount of crosslinking system components (sulfur, zinc oxide, accelerator) in rubber products can be reduced. Moreover, because of the application of ILs, conductive elastomer composites should be possible. Preliminary studies have confirmed that mercaptobenzothiazolate or dithiocarbamate anions could be successfully incorporated into IL structures [40]. The proposed solution could make an original contribution to both the synthesis of novel ionic liquids and their application as well as provide for the development of new, environmentally friendly accelerators for elastomer vulcanization. Traditional accelerators have been applied in the rubber industry for years. However, severe European Union directives regarding environmental protection require the reduction of sulfur and zinc oxide contents in rubber products and modification of recipes for producing elastomer composites. Novel vulcanization accelerators based on ILs may allow the requirements of EU legislation to be met and improve the properties of the obtained rubber products.

Because of their catalytic activity, ILs can accelerate the process of elastomer crosslinking and increase the efficiency of sulfur consumption. As a result, reduction in the sulfur content of rubber products should be achieved for ecological reasons. Moreover, ILs may act as dispersants, improving the dispersion of crosslinking system components (sulfur or activator) in elastomers. The dispersion degree of zinc oxide, sulfur, and accelerator is very important for the activation of sulfur vulcanization. Our preliminary studies confirmed the high activity of synthesized ILs with 2-mercaptobenzothiazolate in the vulcanization of elastomers [40,41]. This result was most likely due to the more homogeneous dispersion of crosslinking agents in the elastomer. SEM images showed that, in the case of a standard NBR vulcanizate with 2-mercaptobenzothiazole (MBT), zinc oxide particles were not homogeneously distributed in the elastomer matrix. The agglomeration of zinc oxide particles caused the particle surface area

to decrease, which was followed by a reduction in the interfacial area between crosslinking system components. As a result, the efficiency of elastomer crosslinking decreased. In the case of vulcanizates produced with the prepared ILs, more homogeneously dispersed crosslinking agent particles were observed. The application of ILs increased the crosslink density of the vulcanizates. Therefore, the application of appropriately structured ILs as vulcanization accelerators seems to be reasonable.

In these studies, ILs such as alkylimidazolium and alkylammonium salts of 2-mercaptobenzothiazole as well as nanosized zinc oxide were used to successfully form pro-ecological elastomer composites with reduced amounts of vulcanization accelerators and activators. Several aspects were analyzed, including crosslink density, static and dynamic mechanical properties of the vulcanizates, as well as their thermal stability and resistance to UV and thermo-oxidative aging.

Pro-ecological composites based on NBR and SBR elastomers containing ILs as vulcanization accelerators were manufactured and studied. Elastomers were vulcanized with sulfur and nanosized zinc oxide in the presence of ILs as accelerators, alternatively to standard 2-mercaptobenzothiazole (MBT) and N-cyclohexyl-2-benzothiazolesulfenamide (CBS). As accelerators, the salts of 2-mercaptobenzothiazole with the following cations were used: dioctyldimethylammonium (C8DM), didecyldimethylammonium (C10DM), dodecyltrimethylammonium (C12TMA), 1-butyl-3-methylimidazolium (C4mim), 1-methyl-3-octylimidazolium (C8mim), and 1-dodecyl-3-methylimidazolium (C12mim).

2. Experimental section

2.1. Materials

The acrylonitrile-butadiene elastomer (EUROPREN N3960) containing 39 wt % acrylonitrile was obtained from Polimeri Europa (Rome, Italy). The Mooney viscosity was (ML1+4 (100°C): 60). This elastomer was vulcanized with sulfur (Siarkopol, Poland) with micro-sized zinc oxide as the activator (ZnO, Aldrich, Germany).

The butadiene-styrene elastomer (KER 1500) containing 22-25 wt % styrene was obtained from Synthos Dwory, Oswiecim (Poland). The Mooney viscosity was (ML1+4 (100°C): 46-54). This elastomer was vulcanized with sulfur (Siarkopol Tarnobrzeg, Poland) with micro-sized zinc oxide as the standard activator (ZnO, Aldrich, Germany). Accelerators included 2-mercaptobenzothiazole (MBT, Aldrich, Germany) and N-cyclohexyl-2-benzothiazolesulfenamide (CBS, Aldrich, Germany).

To reduce the number of zinc ions in rubber compounds, nanosized zinc oxide (nZnO, Nanostructured & Amorphous Materials, Inc., USA) was used as an alternative to micro-sized ZnO. Silica with a specific surface area of 380 m²/g (Aerosil 380, Evonic Industries, Germany) was used as a filler. The ionic liquids listed in Table 1 were synthesized at the Poznan University of Technology, according to a procedure described elsewhere [40,41].

Ionic Liquid	Symbol
Diocetyltrimethylammonium 2-mercaptobenzothiazolate	C8DMA
Didecyltrimethylammonium 2-mercaptobenzothiazolate	C10DMA
Dodecyltrimethylammonium 2-mercaptobenzothiazolate	C12TMA
1-Butyl-3-methylimidazolium 2-mercaptobenzothiazolate	C4mim
1-Methyl-3-octylimidazolium 2-mercaptobenzothiazolate	C8mim
1-Dodecyl-3-methylimidazolium 2-mercaptobenzothiazolate	C12mim

Table 1. Ionic liquids used in this study

2.2. Preparation and characterization of rubber compounds

Rubber compounds with the formulations 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, as measured by an oscillating disc rheometer (Monsanto).

SBR (phr)			NBR (phr)		
Without IL (reference sample)		With IL	Without IL (reference sample)		With IL
Elastomer	100	100	Elastomer	100	100
Sulfur	2	2	Sulfur	2	2
*ZnO	5	2	*ZnO	5	2
MBT	1	-	MBT	2	-
CBS	1	-	Silica	30	30
Silica	30	30	Ionic liquid	-	2.5
Ionic liquid	-	3			

Table 2. Composition of SBR-and NBR-based rubber compounds (*2 phr of nanosized zinc oxide was used alternatively with 5 phr of standard activator)

The kinetics of rubber compound vulcanization was studied using a DSC1 (Mettler Toledo) analyzer by decreasing the temperature from 25 to-100 °C at a rate of 10 °C/min and then heating to 250 °C with the same heating rate.

The crosslink densities (v_T) of the vulcanizates were determined by their equilibrium swelling in toluene, based on the Flory-Rehner equation [42]. The Huggins parameter of the SBR-solvent

interaction (χ) was calculated from the equation $\chi=0.3700+0.5600V_r$ (Equation 1), where V_r is the volume fraction of elastomer in the swollen gel, and $\chi=0.3809+0.6707V_r$ for NBR-solvent interaction (Equation 2).

The tensile properties of the vulcanizates were measured according to ISO-37 standard procedures using a ZWICK 1435 universal machine.

2.3. Dynamic-mechanical analysis

Dynamic-mechanical measurements were carried out in tension mode using a DMA/SDTA861^e analyzer (Mettler Toledo). Measurements of the dynamic moduli were performed between -80 and 100 °C with a heating rate of 2 °C/min, a frequency of 1 Hz and a strain amplitude of 4 μ m. The temperature of the elastomer glass transition was determined from the maximum of $\tan \delta=f(T)$, where $\tan \delta$ is the loss factor and T is the measurement temperature.

2.4. Scanning Electron Microscopy (SEM)

The dispersion degree of zinc oxide and filler nanoparticles in the elastomer matrix was estimated using scanning electron microscopy with an LEO 1530 SEM. The vulcanizates were broken down in liquid nitrogen, and the surfaces of the vulcanizate fractures were examined. Prior to measurements, the samples were coated with carbon.

2.5. Thermogravimetry analysis

The thermal stability of the vulcanizates was studied using a TGA/DSC1 (Mettler Toledo) analyzer. Samples were heated from 25 °C to 700 °C in an argon atmosphere (60 ml/min) with a heating rate of 10 °C/min. Decomposition temperatures at weight losses of 2% (T_{02}), 5% (T_{05}), 50% (T_{50}) and total weight loss during decomposition of vulcanizates were determined.

2.6. Thermo-oxidative and UV aging

The thermo-oxidative degradation of the vulcanizates was performed at a temperature of 100 °C for 240 h. The UV degradation of the vulcanizates was carried out for 120 h using a UV 2000 (Atlas) machine in two alternating segments: a day segment (irradiation 0.7 W/m², temperature 60 °C, time 8 h) and a night segment (without UV radiation, temperature 50 °C, time 4 h).

To estimate the resistance of the samples to aging, their mechanical properties and crosslink densities after aging were determined and compared with the values obtained for vulcanizates before the aging process. The aging factor (S) was calculated as the numerical change in the mechanical properties of the samples upon aging (Equation 3) [43], where TS is the tensile strength of the vulcanizate, and EB is the elongation at break:

$$S = (TS \cdot EB)_{after\ aging} / (TS \cdot EB)_{before\ aging} \quad (1)$$

3. Results and discussion

3.1. SBR composites containing ILs

3.1.1. Curing characteristics and crosslink densities of SBR vulcanizates

The activity of novel ILs as accelerators in the sulfur vulcanization of SBR was estimated based on rheometry measurements. The curing characteristics of the SBR compounds and the crosslink densities of the vulcanizates are given in Table 3. To reduce the amount of vulcanization activator, nanosized zinc oxide was applied (2 phr) alternatively with the normally used microsized ZnO (5 phr).

SBR	ΔG (dNm)	t_{90} (min)	t_p (min)	$v_T \cdot 10^4$ (mol/cm ³)
ZnO	53.3	60	3.7	15.4
nZnO	59.3	50	3.3	16.5
C8DMA	72.3	30	2.1	19.9
C10DMA	64.1	30	2.5	18.3
C12TMA	60.5	30	2.0	17.5
C4mim	72.9	35	2.6	20.8
C8mim	69.2	35	2.8	18.3
C12mim	67.8	35	2.5	17.3

Table 3. Curing characteristics and crosslink densities of SBR vulcanizates (ΔG -increment of torque in the rubber compound during vulcanization; t_{90} -optimal vulcanization time; t_p -scorch time, v_T – crosslink density of vulcanizates).

Nanosized zinc oxide seems to be very active in SBR vulcanization. Despite the reduced amount of vulcanization activator, an increase in the crosslink density of vulcanizates is observed, and, as a consequence, the torque increment during vulcanization is comparable to that of the reference rubber compound with microsized ZnO. Moreover, a reduction of vulcanization time by 10 min was achieved. The nanosized zinc oxide does not influence the scorch time of rubber compounds. Applying ILs as vulcanization accelerators results in a further increase in torque increment during the vulcanization process because of the increase in vulcanizate crosslink densities. Alkylammonium and alkylimidazolium salts of MBT seem to catalyze the interface crosslinking reactions, which is evident from the considerable reduction of vulcanization time (approximately 25-30 min) and scorch time (approximately 1.5 min) compared to conventionally crosslinked SBR compounds. Alkylammonium and alkylimidazoilum ILs have comparable activity in the vulcanization of SBR. However, the crosslink density of vulcanizates decreases slightly with the increase of alkyl chain length in the ammonium or imidazolium cation of ILs.

The most important parameters of the vulcanization process are temperature and energetic effect. The influence of nanosized zinc oxide and novel ILs on these parameters is given in Table 4.

SBR	Vulcanization temperature range (°C)	Energetic effect of vulcanization (J/g)
ZnO	175-231	10.0
nZnO	173-226	9.1
C8DMA	156-236	4.9
C10DMA	152-234	4.4
C12TMA	150-237	8.8
C4mim	147-235	9.8
C8mim	148-237	8.6
C12mim	149-236	8.0

Table 4. Temperatures and energetic effects of SBR vulcanization measured by DSC

Nanosized zinc oxide has no significant influence on the temperature and heat of vulcanization in comparison with SBR compounds containing a micro-sized activator. Vulcanization is an exothermic process that occurs in a temperature range of 173-226 °C, with an energetic effect of 9 J/g. 2-Mercaptobenzothiazolate ILs, especially alkylimidazolium salts, decrease considerably the onset temperature of vulcanization. The vulcanization process begins in the temperature range of 150-156 °C for SBR compounds containing alkylammonium ILs and 147-149 °C in the case of alkylimidazolium salts. This result confirms the catalytic effect of ILs on interfacial crosslinking reactions. The energetic effect of vulcanization ranges from 8.0 J/g to 9.8 J/g and decreases with alkyl chain length for rubber compounds with alkylimidazolium salts. A considerable reduction in the heat of vulcanization is achieved for alkyl dimethylammonium ILs, indicating a decrease in the efficiency of the vulcanization process and confirming that the structure of the accelerator (ILs) affects vulcanization efficiency.

3.1.2. Dispersion degree of crosslinking system particles in SBR

Having concluded that the novel ILs catalyze interfacial crosslinking reactions and influence the efficiency of vulcanization, we then examined their effect on the dispersion degree of crosslinking system components in the SBR elastomer. The homogeneous distribution of ZnO, sulfur and accelerator particles is very important for the activation of sulfur vulcanization. Sulfur and accelerator diffuse inside the elastomer matrix and are adsorbed on the zinc oxide surface during vulcanization.

For the vulcanizate with MBT, crosslinking system particles are not homogeneously distributed in the elastomer matrix (Figure 1). Micro-sized agglomerates (several micrometers in size) are created. The agglomeration of particles causes their surface area to decrease, followed by

a reduction of the interface between zinc oxide, sulfur, and the accelerator. As a result, the efficiency of elastomer crosslinking decreases.

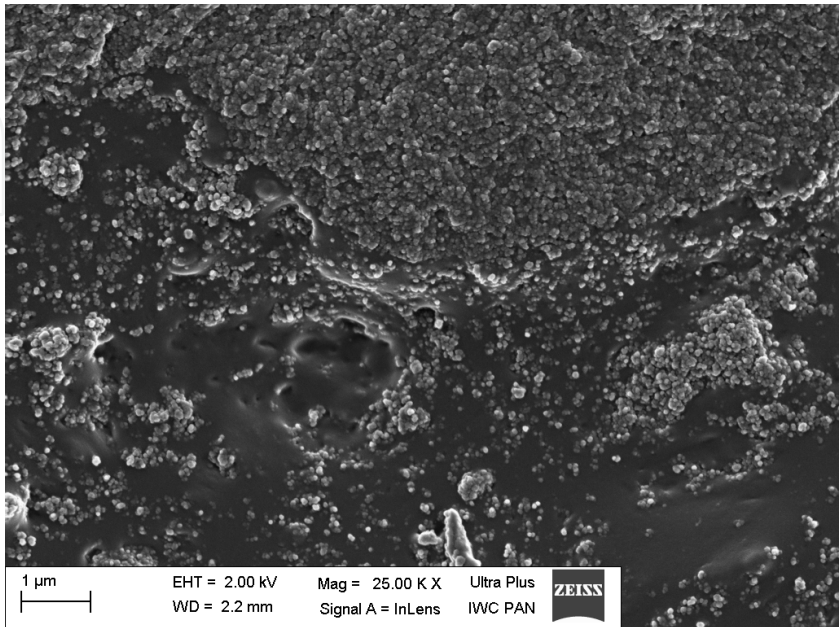


Figure 1. SEM images of SBR vulcanizates containing nZnO without IL

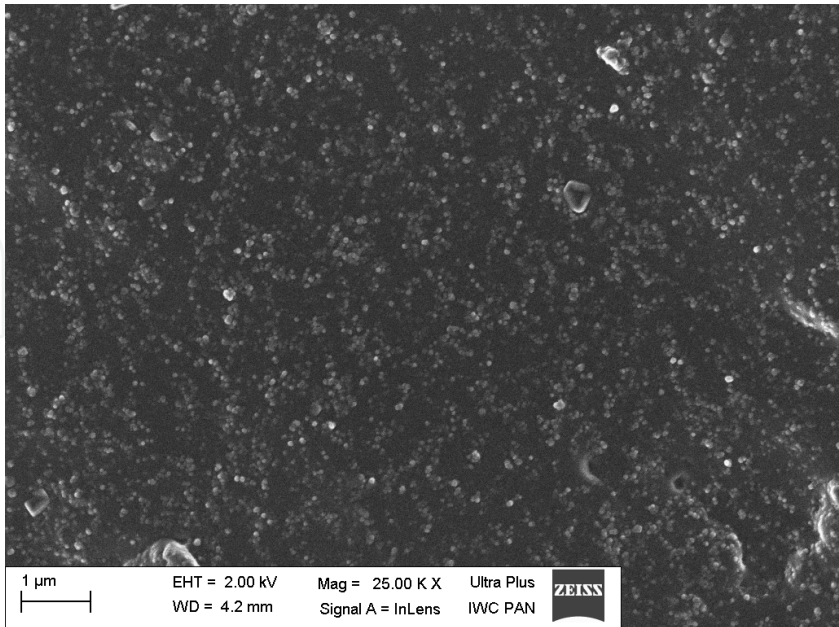


Figure 2. SEM images of SBR vulcanizates containing nZnO with C8DMA

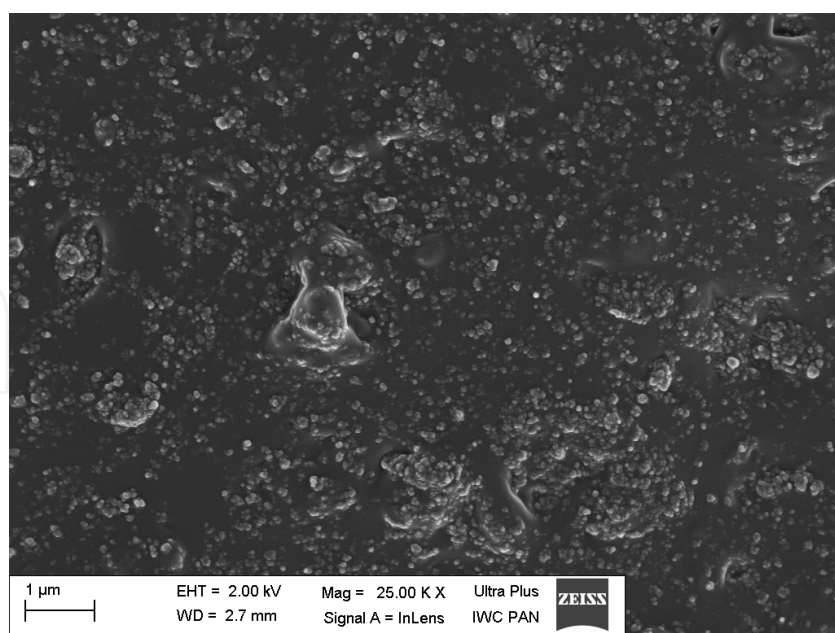


Figure 3. SEM images of SBR vulcanizates containing nZnO with C10DMA

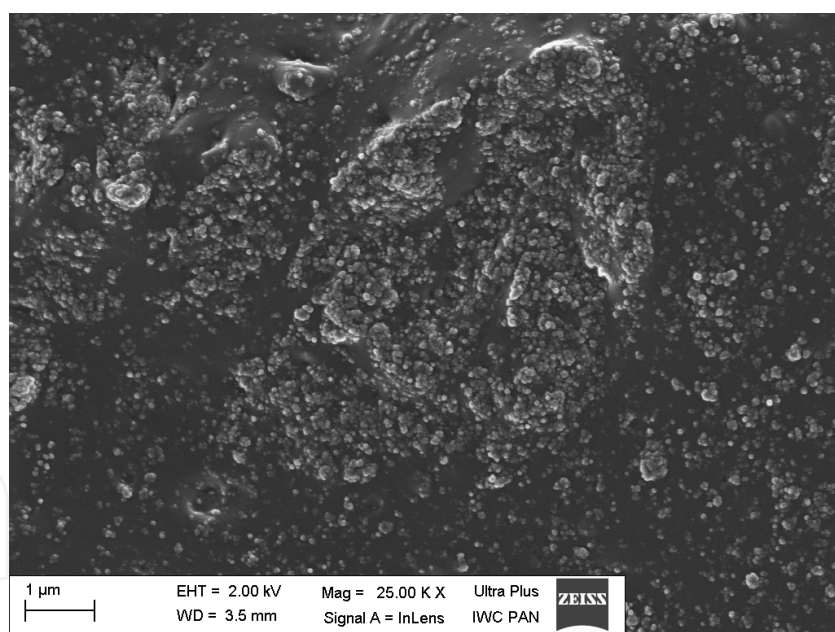


Figure 4. SEM images of SBR vulcanizates containing nZnO with C12TMA

In the case of vulcanizates with novel ILs, a more homogeneous distribution of crosslinking agent particles in SBR is observed (Figures 2-6). The dispersion degree depends on the IL structure and improves with the decrease in the ammonium or imidazolium cation alkyl chain length. In the case of ILs with C8 chains in the cation, particles of the crosslinking system are homogeneously distributed in the elastomer, and no agglomeration is observed. For ILs with C12 chains, some agglomerates can be observed in the SEM images but with a smaller size

than conventionally crosslinked SBR vulcanizates. Therefore, it can be concluded that, apart from accelerating action, ILs act as dispersing agents that prevent crosslinking system particles from agglomeration. The homogeneous dispersion of particles provides better contact between the activator and other components of the crosslinking system, resulting in higher vulcanization efficiency.

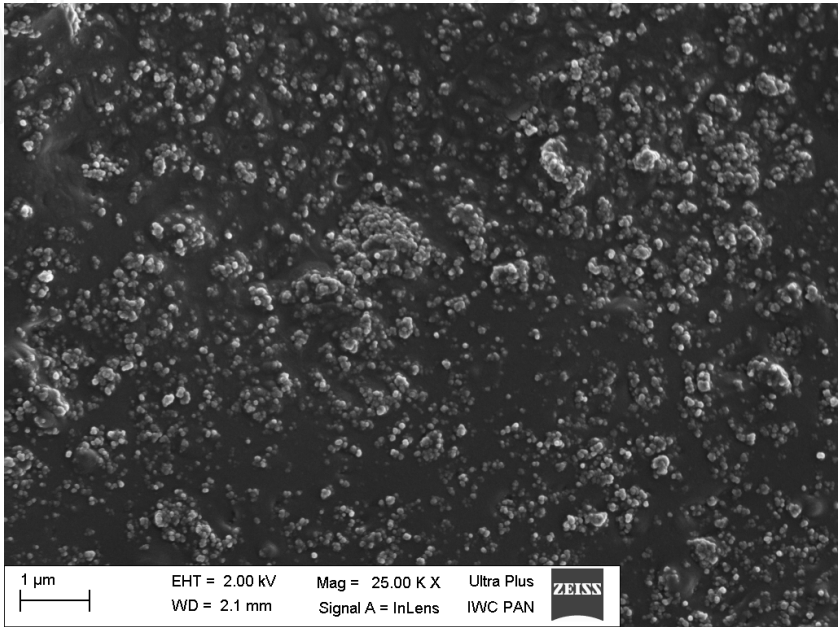


Figure 5. SEM images of SBR vulcanizates containing nZnO with C8mim

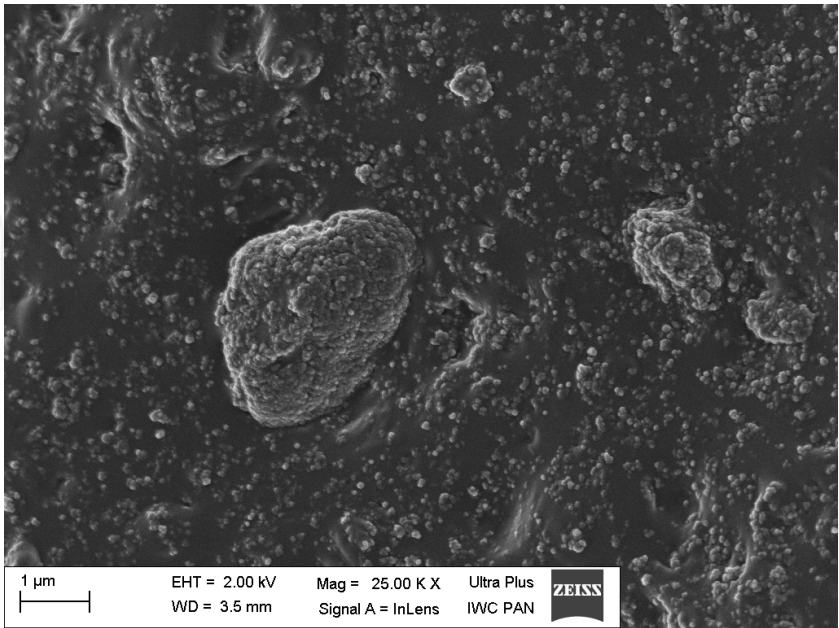


Figure 6. SEM images of SBR vulcanizates containing nZnO with C12mim

3.1.3. Mechanical properties of SBR vulcanizates

Having established the influence of ILs on the vulcanization process and on the crosslink density of vulcanizates, we then examined their mechanical properties. The results are given in Table 5.

SBR	TS (MPa)	EB (%)
ZnO	18.3	777
nZnO	22.4	781
C8DMA	32.0	634
C10DMA	25.5	635
C12TMA	24.2	580
C4mim	28.2	607
C8mim	27.2	651
C12mim	26.0	665

Table 5. Tensile strength (TS) and elongation at break (EB) of SBR vulcanizates

Despite the reduced amount of zinc oxide, vulcanizates containing nanosized ZnO exhibit approximately 4 MPa higher tensile strength than the reference sample. The elongation at break is similar in both vulcanizates. Applying ILs increases the tensile strength of SBR by 10 MPa in the case of C8DMA as a result of the improved dispersion degree of crosslinking system and filler particles in the SBR. The tensile strength decreases with the increase in IL alkyl chain length, as the dispersion degree of crosslinking system particles deteriorates. The elongation at break is reduced by 100 – 150% due to the increase in the crosslink density of the vulcanizates.

For technological applications of SBR, dynamic mechanical properties are very important. Rubber products must meet requirements of rigidity and strength so that their stability during use is sufficient. Even more important is their ability to dampen vibrations. Using DMA, the influence of ILs on the loss factor ($\tan \delta$) was determined. The loss factor, $\tan \delta$, as a function of temperature for the vulcanizates containing ILs is presented in Figure 7 and Table 6.

The existence of one transition can be observed (Figure 7), the glass transition of SBR, with a maximum that represents T_g . Applying nanosized zinc oxide alternatively with micro-sized activator does not influence the glass transition temperature of SBR, which is approximately 41.0 °C. Vulcanizates containing ILs exhibit higher glass transition temperatures than the reference samples because of their higher crosslink density. A greater number of crosslinks in the elastomer network results in greater restriction of mobility of the elastomer chains and, as a consequence, higher T_g . As expected, the highest T_g values occur for vulcanizates with the highest crosslink densities.

Nanosized zinc oxide or ILs have no significant effect on the $\tan \delta$ values of SBR vulcanizates (Table 6). Only a slight increase in the $\tan \delta$ at glass transition temperature is observed for IL-

containing vulcanizates. The loss factor is practically unchanged in the temperature range of 25-100 °C. Therefore, it could be concluded that SBR vulcanizates exhibit stable dynamic mechanical properties at application temperatures. It is worth noting that ILs applied as novel vulcanization activators alternatively to standard MBT and CBS do not deteriorate the dynamic mechanical properties of SBR and its ability for vibration damping, which is very important for technological reasons.

SBR	T _g (°C)	tan δ at T _g (-)	tan δ at 25 °C (-)	tan δ at 100 °C (-)
ZnO	-40.9	0.58	0.13	0.09
nZnO	-40.1	0.63	0.13	0.09
C8DMA	-33.4	0.71	0.09	0.07
C10DMA	-36.1	0.73	0.12	0.11
C12TMA	-38.0	0.69	0.12	0.11
C4mim	-36.8	0.68	0.12	0.09
C8mim	-38.8	0.71	0.13	0.12
C12mim	-38.9	0.68	0.11	0.09

Table 6. Glass transition temperature (T_g) and loss factor (tan δ) of SBR vulcanizates

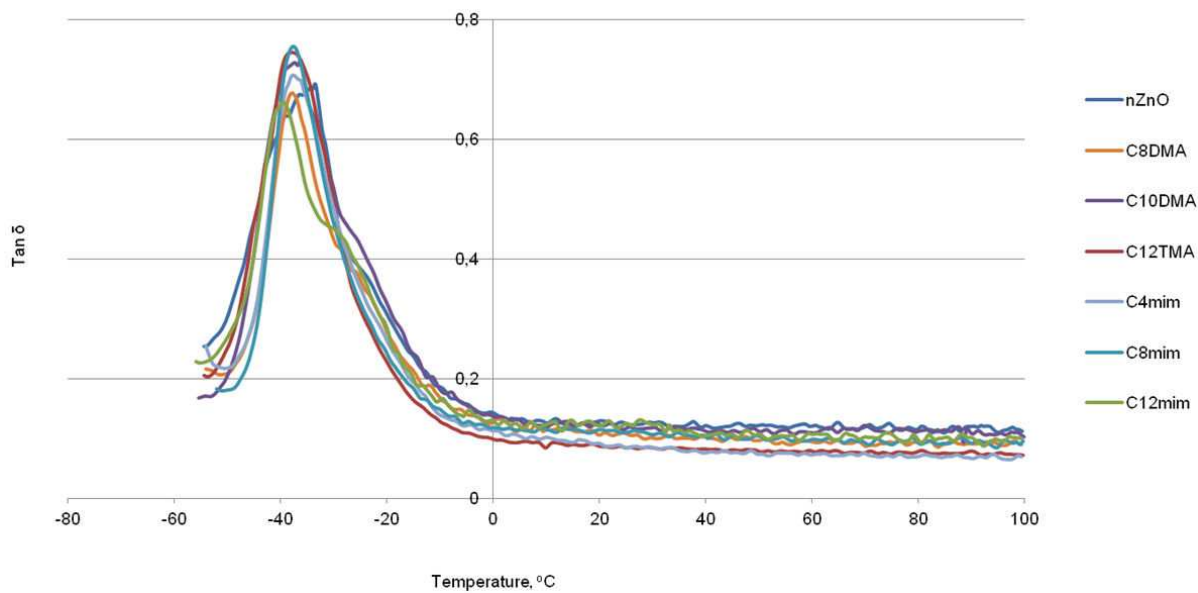


Figure 7. Loss factor (tan δ) versus temperature for SBR vulcanizates

3.1.4. Thermal stability and aging resistance of SBR vulcanizates

Rubber products often work at elevated temperatures. Therefore, novel vulcanization accelerators must not reduce the thermal stability of vulcanizates. Using TGA analysis, the effect of ILs on the thermal stability of SBR vulcanizates was determined (Table 7).

Nanosized zinc oxide increases the onset decomposition temperature of SBR (T_{02}) by 15 °C. Most likely, the network created by the zinc oxide and filler nanoparticles is a barrier for the transport of gases and volatile pyrolysis products during the decomposition process, thus increasing the thermal stability of the elastomer. ILs result in a further increase in the onset decomposition temperature of SBR, likely due to the improved dispersion degree of the nanoparticles in the elastomer matrix. The T_{02} for IL-containing vulcanizates is in the range of 363–365 °C. No influence of nanosized ZnO and ILs is achieved for T_{05} and T_{50} temperatures as well as for the total weight loss during decomposition (approximately 76%).

SBR	T_{02} (°C)	T_{05} (°C)	T_{50} (°C)	Total weight loss (%)
ZnO	288	362	442	74.2
nZnO	303	360	442	76.9
C8DMA	325	364	445	75.9
C10DMA	324	365	445	76.3
C12TMA	322	363	445	75.8
C4mim	326	365	444	76.3
C8mim	324	364	444	75.9
C12mim	325	364	444	76.4

Table 7. Decomposition temperatures at weight losses of 2% (T_{02}), 5% (T_{05}), 50% (T_{50}) and total weight loss during the decomposition of SBR vulcanizates

Having established the effects of nanosized zinc oxide and ILs on thermal stability, we then examined SBR resistance to thermo-oxidative and UV aging. The influence of ILs on aging resistance was studied through changes in mechanical properties and the crosslink density of the vulcanizates (Figures 8–10).

Thermo-oxidative and UV aging significantly increase the crosslink densities of SBR vulcanizates (Figure 8). This change is most evident in the case of thermo-oxidative degradation, where an almost threefold increase in the number of crosslinks is determined. Prolonged exposure to elevated temperatures results in further crosslinking of SBR. However, the increase in crosslink density is slightly smaller in the case of vulcanizates containing ILs. The elongation at break is reduced by 300–400% in comparison with vulcanizates before the aging process. This change is due to the large increase in the crosslink density of vulcanizates (Figure 9). In most cases, thermo-oxidative and especially UV aging deteriorate the tensile strength of vulcanizates with ILs, as in the case of vulcanizates with standard accelerators (Figure 10).

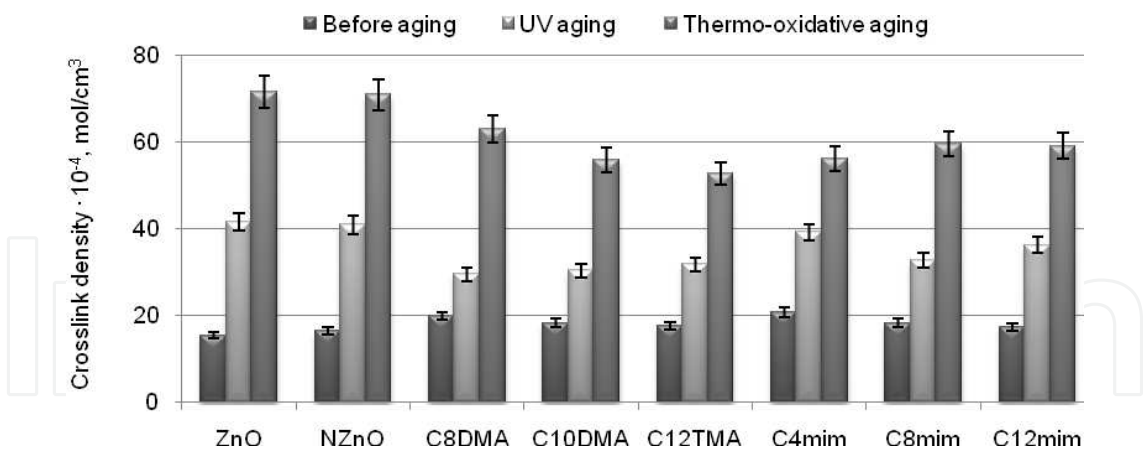


Figure 8. Crosslink density of SBR vulcanizates after aging

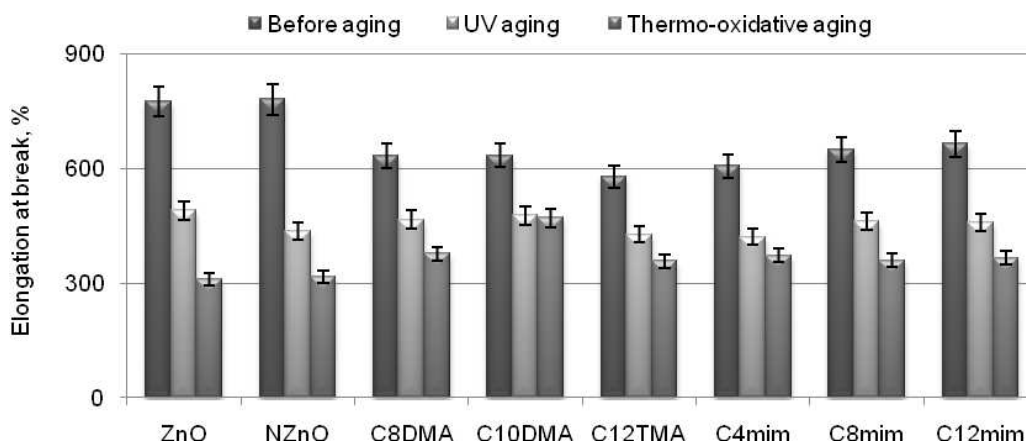


Figure 9. Elongation at break of SBR vulcanizates after aging

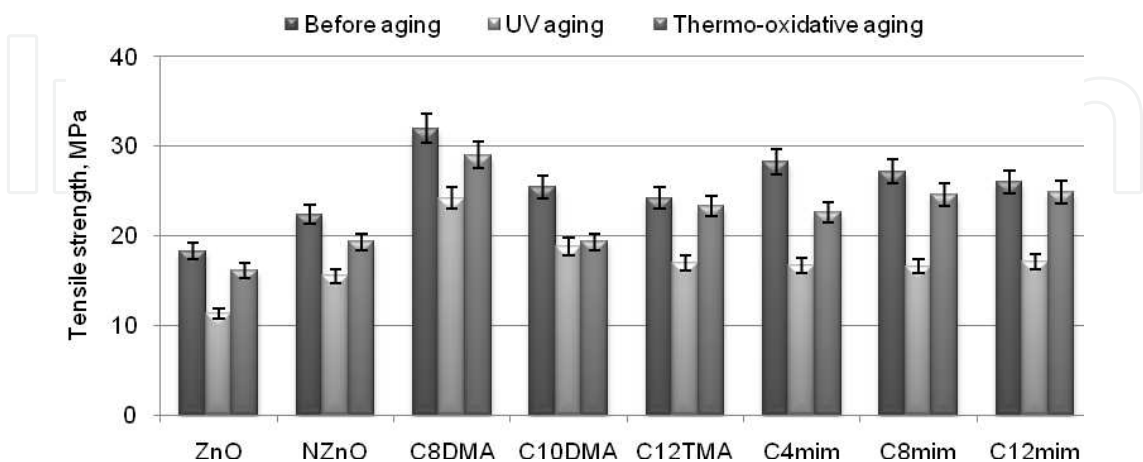


Figure 10. Tensile strength of SBR vulcanizates after aging

The aging factor S was calculated to quantitatively estimate the change in mechanical properties of vulcanizates. This factor is the change in the sample deformation energy under the aging process (Table 8).

Nanosized zinc oxide used as an alternative to the micro-sized ZnO does not influence the resistance of vulcanizates to aging. ILs, mainly alkylammonium salts, improve the resistance of SBR vulcanizates to thermo-oxidative and UV aging, most likely due to the limitation of the increase in vulcanizate crosslink density. An increase in the S_T and S_{UV} values of 0.2 is achieved for alkylammonium salts.

SBR	$S_{UV} (-)$	$S_T (-)$
ZnO	0.39	0.35
NZnO	0.39	0.35
C8DMA	0.54	0.56
C10DMA	0.56	0.55
C12TMA	0.59	0.52
C4mim	0.49	0.41
C8mim	0.50	0.43
C12mim	0.53	0.45

Table 8. Thermo-oxidative and UV aging factors for SBR vulcanizates

3.2. NBR composites containing ILs

Acrylonitrile-butadiene elastomer (NBR) is characterized by high resistance to oil, petrol and aliphatic hydrocarbons. As a result, NBR is widely applied to the manufacture of seals, inner tubes, hoses for liquid fuels and oils as well as elements used for damping vibration. Therefore, the use of novel ILs as accelerators for sulfur vulcanization of NBR was studied. To reduce the amount of zinc oxide in NBR compounds, nanosized ZnO was applied (2 phr) alternatively with traditionally used micro-sized activator (5 phr).

3.2.1. Curing characteristics and crosslink densities of NBR vulcanizates

Based on rheometric measurements, the effect of nanosized zinc oxide and ILs on the curing characteristics of NBR compounds was examined. Results are given in Table 9.

Nanosized zinc oxide increases the torque increment during vulcanization by approximately 20 dNm compared with the reference NBR compound containing micro-sized ZnO due to the increase in crosslink density of the vulcanizate. The amount of nanosized ZnO is 60% lower than for the micro-sized activator. Therefore, nanosized zinc oxide effectively activates the sulfur vulcanization of NBR. Zinc oxide particle size does not appear to affect vulcanization time or scorch time. Applying ILs causes a threefold increase in the torque increment during vulcanization compared to the rubber compound with micro-sized ZnO and a twofold increase

in ΔG in comparison with nanosized ZnO-containing NBR. These results occur because of the considerable increase in the crosslink density of vulcanizates. Moreover, ILs reduce the vulcanization time of NBR compounds by 10-20 min, whereas no influence is observed for scorch time. Higher activity in the vulcanization process is observed for alkylimidazolium salts of MBT. The length of alkyl chains in the imidazolium or ammonium cations of ILs does not seem to affect their activity in vulcanization.

NBR	ΔG (dNm)	t_{90} (min)	t_p (s)	$v_T \cdot 10^5$ (mol/cm ³)
ZnO	44.5	50	2.2	19.8
nZnO	67.8	50	2.9	20.4
C8DMA	113.1	40	2.9	25.4
C10DMA	122.2	40	3.0	24.8
C12TMA	122.9	35	2.8	24.5
C4mim	127.6	30	2.6	26.3
C8mim	127.0	35	2.5	26.0
C12mim	127.2	35	2.4	25.1

Table 9. Curing characteristics and crosslink densities of NBR vulcanizates (ΔG -increment of torque in the rubber compound during vulcanization; t_{90} -optimal vulcanization time; t_p -scorch time, v_T – crosslink density of vulcanizates)

Having established the effect of nanosized zinc oxide and ILs on the vulcanization time and crosslink density of vulcanizates, we then examined their influence on vulcanization temperature and energetic effect (Table 10).

NBR	Vulcanization temperature range (°C)	Energetic effect of vulcanization (J/g)
ZnO	163-240	10.1
nZnO	165-231	14.6
C8DMA	144-232	6.1
C10DMA	148-231	5.5
C12TMA	143-220	13.5
C4mim	141-220	12.8
C8mim	142-220	9.7
C12mim	143-220	10.4

Table 10. Temperatures and energetic effects of NBR vulcanization measured by DSC

Despite the reduced amount of ZnO, nanosized zinc oxide has no significant influence on vulcanization temperature. Moreover, the heat of vulcanization is higher in comparison with

the NBR compound containing micro-sized ZnO, so the vulcanization is most likely more effective. Vulcanization is an exothermic process that occurs in a temperature range of 165–231 °C, with an energetic effect of 14.6 J/g. Therefore, nanosized ZnO can be applied as an activator for NBR without detrimental effects on vulcanization characteristics. ILs decrease the vulcanization temperature by 17–24 °C. Alkylammonium ILs, especially dioctyl- and didecyl-dimethylammonium salts decrease the energetic effect of vulcanization. Alkylimidazolium salts also reduce the amount of heat generated during vulcanization but to a smaller degree than in the case of alkylammonium ILs.

The reduction of vulcanization time and temperature as well as the increase in the crosslink densities of vulcanizates could be due to the catalytic action of ILs during NBR crosslinking, similar to the SBR vulcanization process. However, the dispersion degree of crosslinking system components in the elastomer should be taken into account.

3.2.2. Dispersion degree of crosslinking system particles in NBR

Assuming that particles of accelerators, sulfur, and fatty acids diffuse through the polymer matrix and are adsorbed on the surface of zinc oxide to form intermediate complexes, the dispersion of zinc oxide nanoparticles in the elastomer matrix has great importance to the activation of sulfur vulcanization. SEM images of the vulcanizate surfaces were collected to estimate the dispersion degree of activator particles and other components of crosslinking system in the NBR elastomer (Figures 11–16).

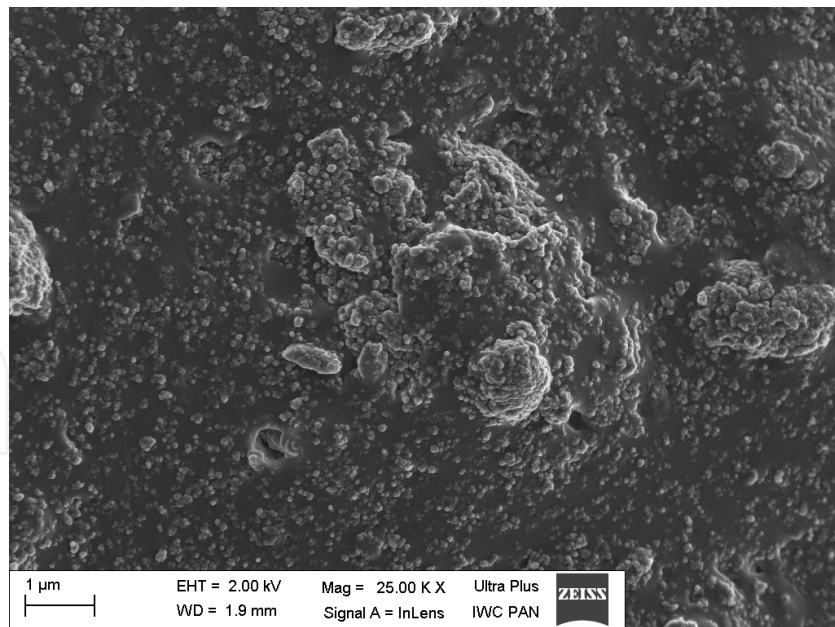


Figure 11. SEM images of NBR vulcanizates containing nZnO without IL

ZnO nanoparticles are poorly dispersed in the elastomer matrix (Figure 11), creating micro-sized clusters of particles with complex structures. The agglomeration of zinc oxide nanoparticles decreases the efficiency of vulcanization. However, in IL-containing vulcanizates,

particles are homogenously distributed in the elastomer (Figures 12-16). The estimated size of crosslinking system particles seems to be in the nanometer range, which makes their surfaces available for interactions. Thus, the interactions of these particles with sulfur and accelerators are more efficient. Furthermore, filler nanoparticles are also homogeneously distributed in the elastomer.

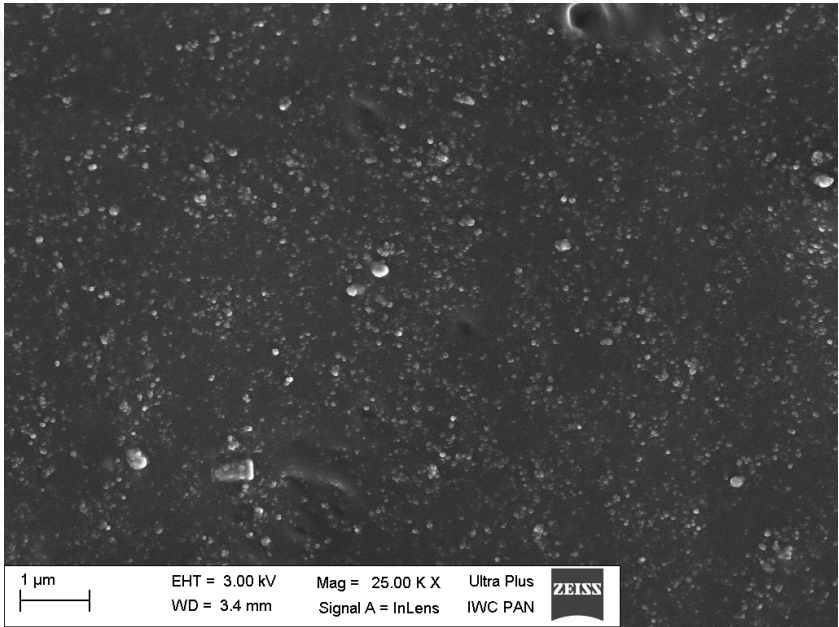


Figure 12. SEM images of NBR vulcanizates containing nZnO with C8DMA

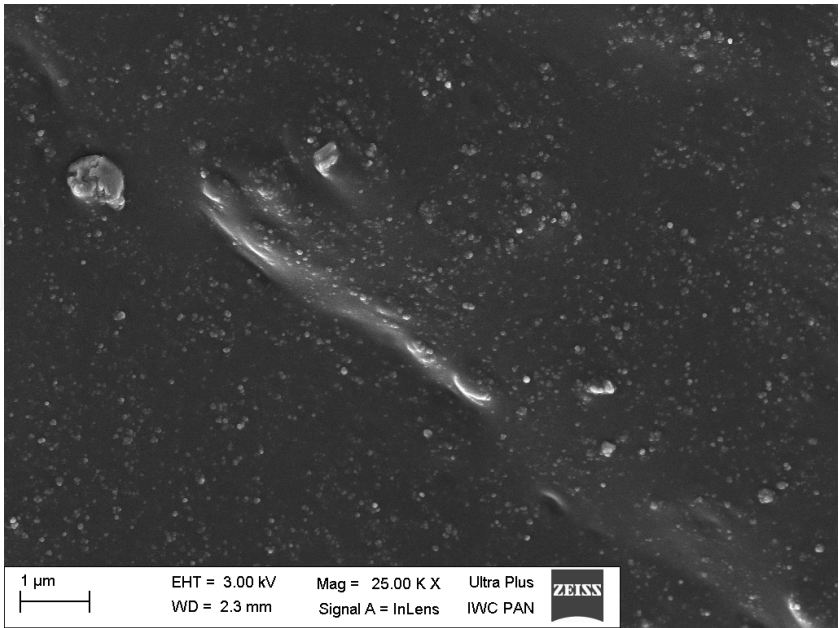


Figure 13. SEM images of NBR vulcanizates containing nZnO with C10DMA

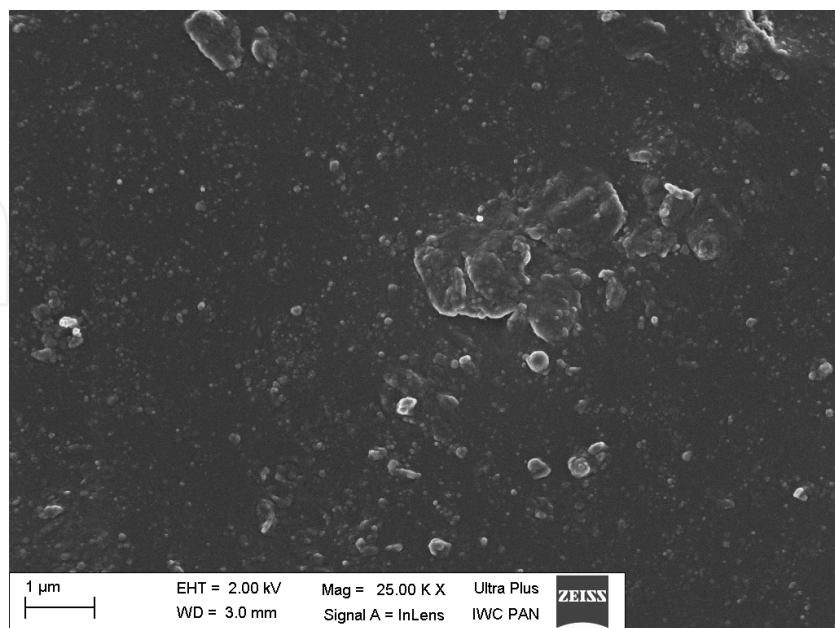


Figure 14. SEM images of NBR vulcanizates containing nZnO with C12TMA

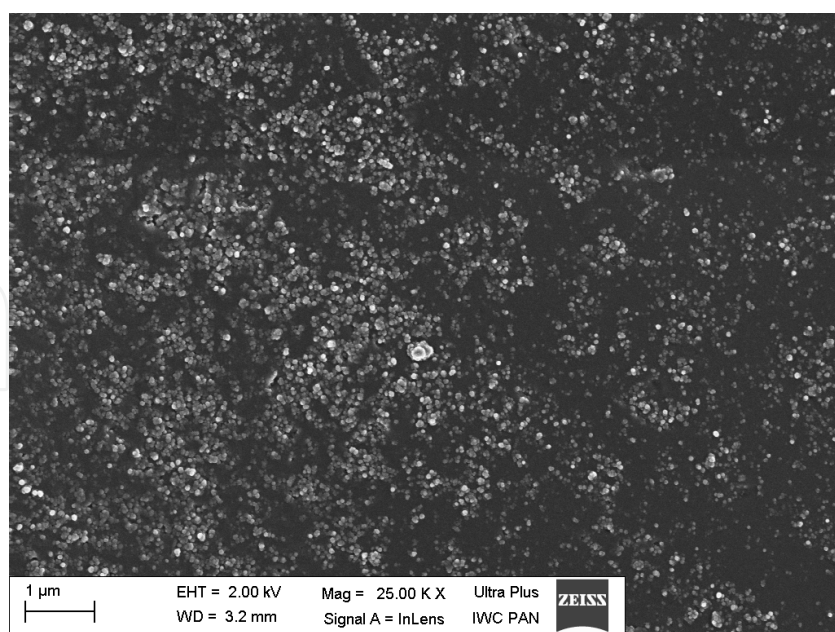


Figure 15. SEM images of NBR vulcanizates containing nZnO with C8mim

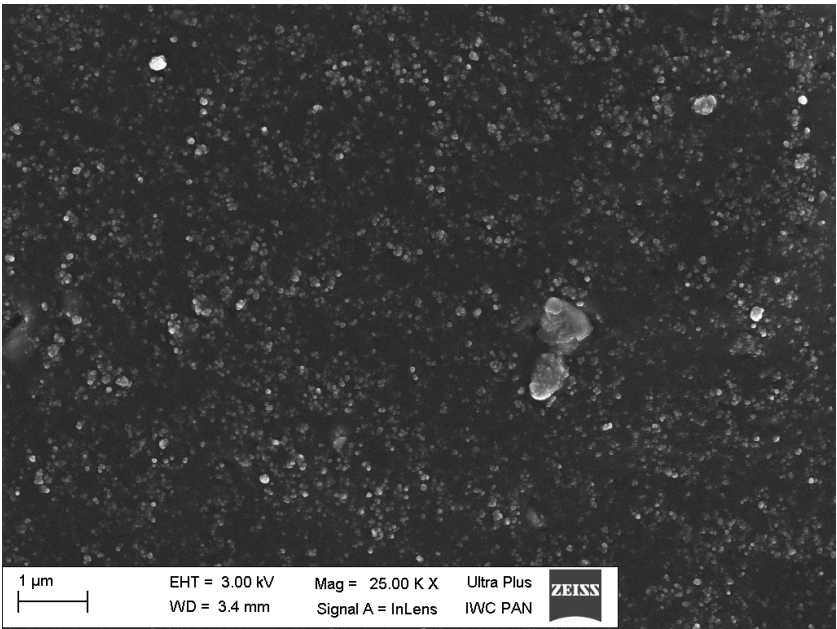


Figure 16. SEM images of NBR vulcanizates containing nZnO with C12mim

3.2.3. Mechanical properties of NBR vulcanizates

Due to the industrial applications of novel ILs as accelerators for the sulfur vulcanization of NBR, their effect on the mechanical properties of vulcanizates should be studied.

NBR	TS (MPa)	EB (%)
ZnO	20.4	531
nZnO	22.6	526
C8DMA	33.4	418
C10DMA	32.1	433
C12TMA	26.5	398
C4mim	29.4	411
C8mim	30.7	415
C12mim	28.3	420

Table 11. Tensile strength (TS) and elongation at break (EB) of NBR vulcanizates

From the data compiled in Table 11, the application of nanosized zinc oxide increases by 2 MPa the tensile strength of vulcanizate compared to the use of conventional ZnO. Therefore, it is possible to reduce the amount of ZnO by 60% without a detrimental effect on the tensile parameters. In addition, ILs used an alternative to standard accelerators considerably increase the tensile strength of NBR vulcanizates, which is very important technologically. The highest

tensile strength is exhibited by vulcanizates with dioctyl- and didecyldimethylammonium salts (approximately 33 MPa). The lowest TS value of the C12TMA-containing vulcanizate is the result of an inhomogeneous distribution of nanoparticles in the elastomer matrix. In the case of alkylimidazolium ILs, the tensile strength of vulcanizates is between 28 MPa (C12mim) and 31 MPa (C8mim). Vulcanizates containing ILs exhibit approximately 100% lower elongation at break compared to reference vulcanizates, which results from their higher crosslink densities.

The effect of nanosized zinc oxide and ILs on the dynamic mechanical properties was examined using DMA and is presented in Table 12 and Figure 17.

NBR	T_g (°C)	$\tan \delta$ at T_g (-)	$\tan \delta$ at 25 °C (-)	$\tan \delta$ at 100 °C (-)
ZnO	-7.3	0.58	0.11	0.06
nZnO	-6.1	0.79	0.15	0.08
C8DMA	-5.9	0.86	0.19	0.10
C10DMA	-5.3	0.84	0.14	0.08
C12TMA	-6.5	0.85	0.14	0.07
C4mim	-4.4	0.88	0.20	0.09
C8mim	-5.5	0.82	0.21	0.10
C12mim	-6.6	0.86	0.17	0.09

Table 12. Glass transition temperatures (T_g) and loss factors ($\tan \delta$) of NBR vulcanizates

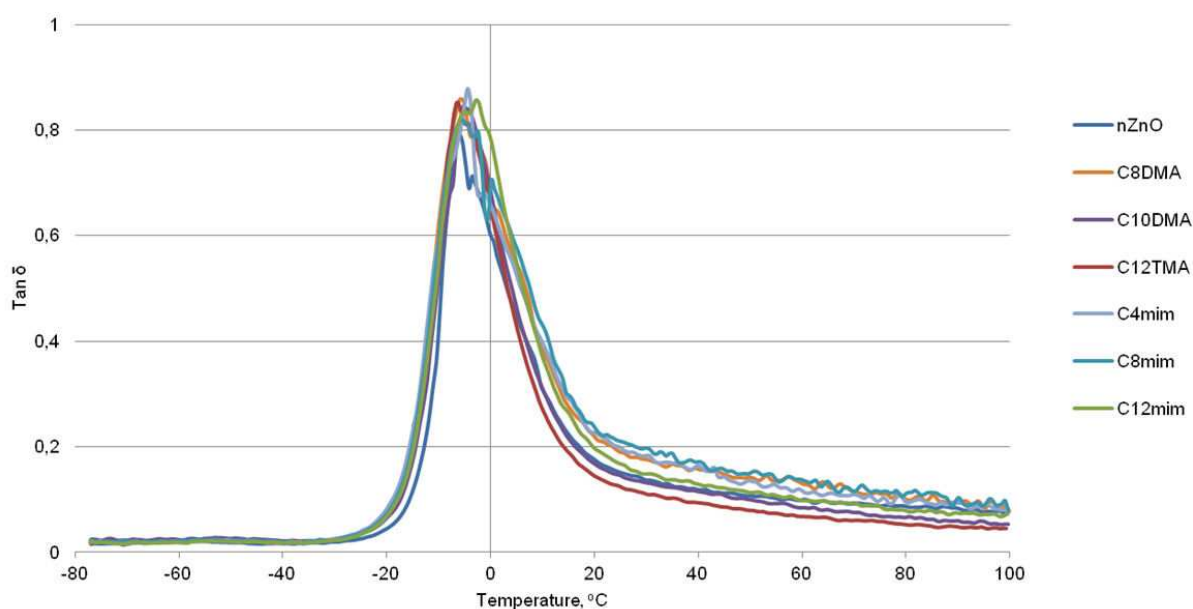


Figure 17. Loss factor ($\tan \delta$) versus temperature for NBR vulcanizates

The glass transition temperature for conventionally crosslinked NBR vulcanizates is $-7.3\text{ }^{\circ}\text{C}$. Nanosized zinc oxide slightly increases the T_g of NBR. An increase is observed for loss factor values at T_g and temperatures of $25\text{ }^{\circ}\text{C}$ and $100\text{ }^{\circ}\text{C}$. ILs cause a further increase in glass transition temperature due to the higher crosslink density of vulcanizates, which reduces the mobility of elastomer chains. An increase in the loss factor is also achieved, so vulcanizates containing ILs should exhibit a higher ability for vibration damping compared with the reference sample. These properties are important for the industrial application of rubber products based on NBR elastomers.

3.2.4. Thermal stability and aging resistance of NBR vulcanizates

In Table 13, the effect of nanosized zinc oxide and ILs on decomposition temperature and weight loss for NBR vulcanizates is given.

NBR	$T_{02}\text{ (}^{\circ}\text{C)}$	$T_{05}\text{ (}^{\circ}\text{C)}$	$T_{50}\text{ (}^{\circ}\text{C)}$	Total weight loss (%)
ZnO	300	368	446	68.5
nZnO	320	367	448	72.6
C8DMA	323	364	447	76.1
C10DMA	324	367	447	77.3
C12TMA	324	369	448	77.3
C4mim	323	371	446	77.8
C8mim	324	370	446	76.1
C12mim	329	374	446	76.6

Table 13. Decomposition temperatures at weight losses of 2% (T_{02}), 5% (T_{05}), 50% (T_{50}) and total weight loss during the decomposition of NBR vulcanizates

Replacing micro-sized zinc oxide with a nanosized activator increases the onset decomposition temperature of NBR by $20\text{ }^{\circ}\text{C}$. Applying ILs as vulcanization accelerators does not considerably influence the thermal stability compared with a vulcanizate containing nanosized ZnO. The thermal decomposition of vulcanizates begins at a temperature range of $323\text{--}329\text{ }^{\circ}\text{C}$. A weight loss of 5% is achieved in the temperature range of $364\text{--}374\text{ }^{\circ}\text{C}$, whereas 50% weight loss occurs at $446\text{--}448\text{ }^{\circ}\text{C}$. ILs increase the total weight loss during NBR decomposition, which is approximately 77%. The positive effect of nanosized ZnO and ILs on the thermal stability of NBR is, as in the case of SBR, caused by the network formed by nanoparticles in the elastomer, which restrains the diffusion of gases and volatile decomposition products in the elastomer matrix.

NBR rubber products often work at elevated temperatures and are exposed to factors that cause aging (e.g., temperature and UV radiation). If ILs are industrially used as accelerators instead of MBT, they should not deteriorate the aging resistance of vulcanizates.

Prolonged exposure to UV radiation and especially elevated temperatures results in further crosslinking of NBR. The increase in crosslink density is comparable for all NBR vulcanizates (Figure 18). Thermo-oxidative aging, despite the increase in crosslink density, has no considerable influence on the tensile strength of vulcanizates (Figure 19). UV degradation deteriorates the tensile strength of vulcanizates with ILs, as it does to vulcanizates with standard accelerator and nanosized zinc oxide. There is no influence of IL structure on the change in crosslink density or tensile strength of vulcanizates. In the case of vulcanizates without ILs, the aging process causes a reduction in elongation at break of approximately 100% for UV radiation and approximately 300% for elevated temperatures (Figure 20). These results arise from the increase in crosslink density of vulcanizates as well as their stiffness and fragility. ILs decrease the changes in elongation at break, especially under thermo-oxidative aging. This result is most evident for vulcanizates containing alkylimidazolium salts. It is possible that these ILs limit the loss of vulcanizate elasticity during aging. Vulcanizates containing these ILs are less rigid, which could confirm this assumption.

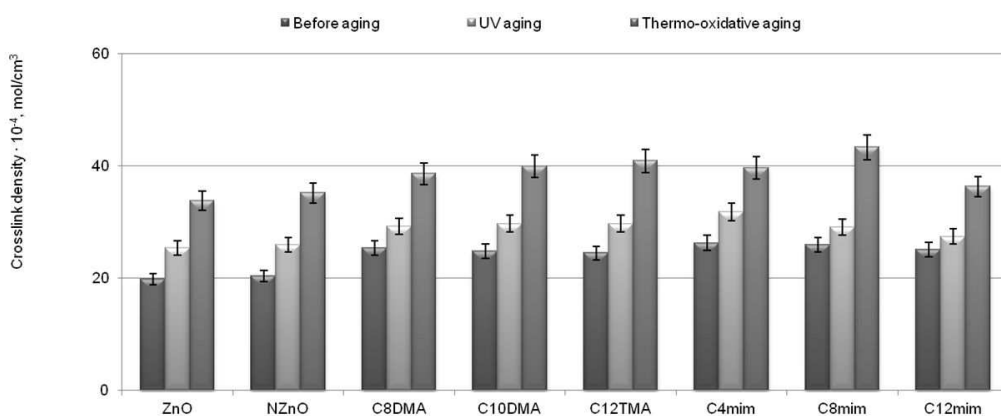


Figure 18. Crosslink density of NBR vulcanizates after aging

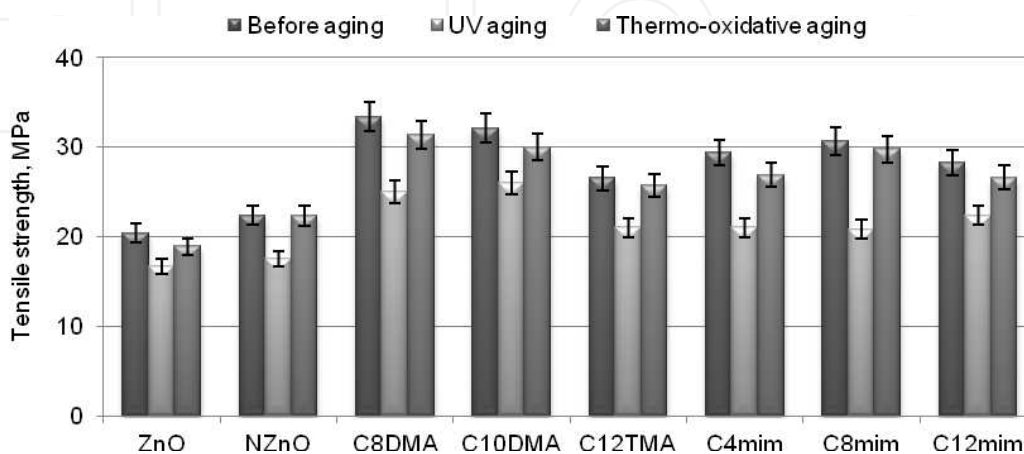


Figure 19. Tensile strength of NBR vulcanizates after aging

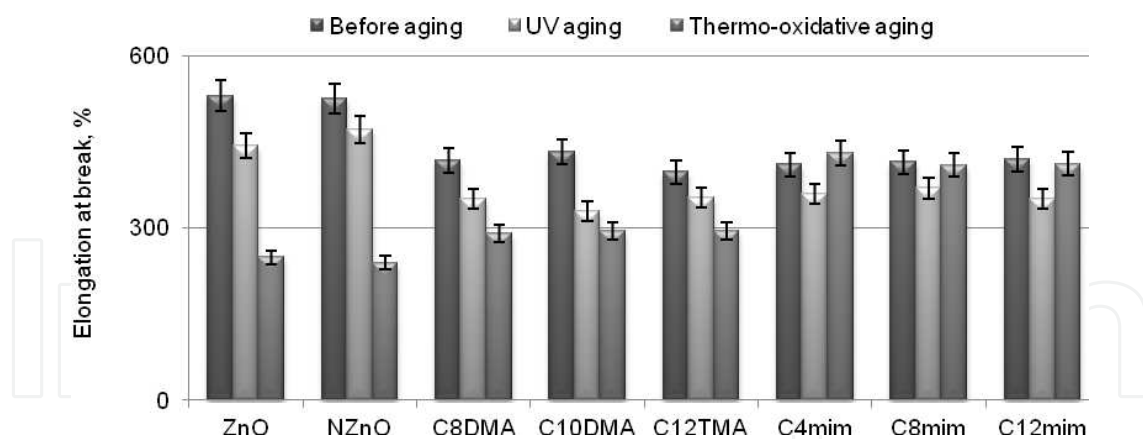


Figure 20. Elongation at break of NBR vulcanizates after aging

Based on the above results, it is difficult to estimate the resistance of NBR vulcanizates to the aging process considering the changes in tensile strength and elongation at break separately. Therefore, UV and thermo-oxidative aging factors were calculated to quantitatively estimate changes in mechanical properties of NBR vulcanizates (Table 14).

NBR	$S_{UV} (-)$	$S_T (-)$
ZnO	0.68	0.43
nZnO	0.70	0.45
C8DMA	0.63	0.65
C10DMA	0.62	0.64
C12TMA	0.70	0.72
C4mim	0.63	0.96
C8mim	0.60	0.96
C12mim	0.66	0.92

Table 14. UV and thermo-oxidative aging factors for NBR vulcanizates

In terms of S_{UV} factor, nanosized zinc oxide and ILs do not affect the resistance of NBR to UV degradation. However, ILs increase the resistance of vulcanizates to thermo-oxidative aging. In the case of vulcanizates containing alkylammonium ILs, an increase in S_T values from approximately 0.45 to 0.72 is achieved. A considerable improvement of resistance to thermo-oxidative degradation is observed for NBR containing alkyimidazolium salts. The values of S_T are close to 1, so the mechanical properties of vulcanizates with alkyimidazolium ILs do not change under the influence of thermo-oxidative aging.

4. Conclusions

Applying ILs allowed for the replacement of standard accelerators in sulfur vulcanization of SBR and NBR elastomers, resulted in the shortening of the optimal vulcanization time and

decreased the temperature of vulcanization by approximately 20 °C. These results are very important for technological and economical reasons. NBR and SBR composites containing ILs exhibited tensile strengths and crosslink densities higher than those of standard vulcanizates crosslinked with MBT and CBS. These results were due to the considerable improvement of crosslinking system nanoparticle distribution in the elastomer. ILs restrained the tendency of nanoparticles to agglomerate in the elastomer; as a result, the surface of contact between nanosized zinc oxide and other components of crosslinking system was maximized and the efficiency of vulcanization increased. Moreover, ILs could catalyze the interface crosslinking reaction that improves the efficiency of vulcanization.

Nanosized zinc oxide and ILs increased the thermal stability of elastomers. The onset decomposition temperature increased by approximately 20 °C. Most likely, the network created by zinc oxide and filler nanoparticles homogeneously distributed in the elastomer may be a barrier for the transport of gases and volatile pyrolysis products during the decomposition process, thus increasing the thermal stability of the elastomer.

NBR and SBR composites containing ILs exhibited stable dynamic properties at the temperature of use. Moreover, NBR vulcanizates could be expected to demonstrate better damping properties than conventionally crosslinked samples. ILs, especially alkylimidazolium salts, increased the resistance of NBR vulcanizates to thermo-oxidative aging. In the case of SBR, improved resistance to UV and thermo-oxidative degradation was achieved, mainly for alkylammonium ILs. Further crosslinking of elastomers during aging was greatly reduced in comparison with vulcanizates containing standard accelerators.

Most important, applying nanosized zinc oxide and ILs allowed for the reduction of zinc oxide amount by 60% as well as the elimination of CBS from SBR composites and, in the case of NBR, reduction in the amount of MBT, an allergic agent, by 30-50% in comparison with conventional rubber compounds (Table 15). This result is very important ecologically.

Accelerator	Accelerator content in NBR compound (g)	MBT content in accelerator (mmol/g)	MBT content in NBR compound (mmol/100 g of NBR)
		NBR	
MBT	2.0	5.98	11.96
C8DM	2.5	1.39	3.48
C10DM	2.5	2.69	6.27
C12TMA	2.5	2.52	6.30
C4mim	2.5	3.25	8.12
C8mim	2.5	2.75	6.88
C12mim	2.5	2.38	5.95

Table 15. MBT content in accelerators applied in NBR compounds

Acknowledgements

The authors wish to acknowledge the National Centre for Research and Development (Poland) for supporting this research.

Author details

Magdalena Maciejewska^{1*} and Filip Walkiewicz²

*Address all correspondence to: magdalena.maciejewska@p.lodz.pl

1 Technical University of Lodz; Institute of Polymer and Dye Technology, Lodz, Poland

2 Poznan Technical University; Institute of Technology and Chemical Engineering, Poznan, Poland

References

- [1] Oenslager G. Organic Accelerators. *Industrial & Engineering Chemistry* 1933;25(2): 232-7.
- [2] Harman M.W., U.S. Patent 2,100,692 (1937).
- [3] Nieuwenhuizen PJ. Zinc Accelerator Complexes. Versatile Homogeneous Catalysts in Sulfur Vulcanization. *Applied Catalysis A: General* 2001;207(1): 55-68. <http://www.sciencedirect.com/science/article/pii/S0926860X0000613X> (accessed 8 May 2000).
- [4] Heideman G, Noordermeer JWM, Datta RN. Effect of Zinc Complexes as Activator for Sulfur Vulcanization in Various Rubbers. *Rubber Chemistry and Technology* 2005;78(2): 245-57. <http://rubberchemtechnol.org/doi/abs/10.5254/1.3547881> (accessed May 2005).
- [5] Lu J, Yan F, Texter J. Advanced Applications of Ionic Liquids in Polymer Science. *Progress in Polymer Science* 2009; 34(5): 431-48. <http://www.sciencedirect.com/science/article/pii/S0079670008001226> (accessed 13 January 2009).
- [6] Rogers RD, Seddon KR. Ionic Liquids-Solvents of the Future? *Science* 2003;302(5646): 792-3. <http://www.sciencemag.org/content/302/5646/792.full.pdf> (accessed 31 October 2003).
- [7] Wasserscheid P, Welton T., editor. *Ionic Liquids in Synthesis*. New York: Wiley-VCH; 2008.

- [8] Kubisa P. Application of Ionic Liquids as Solvents for Polymerization Processes. *Progress in Polymer Science* 2004;29(1): 3-12. <http://www.sciencedirect.com/science/article/pii/S0079670003001199> (accessed January 2004).
- [9] Freemantle M. New Horizons for Ionic Liquids. *Chemical & Engineering News* 2001;79(1): 21-5. <http://pubs.acs.org/doi/pdf/10.1021/cen-v079n001.p021> (accessed 01 January 2001).
- [10] Lu W, Fadeev AG, Qi B, Mattes BR. Fabricating Conducting Polymer Electrochromic Devices Using Ionic Liquids. *Journal of The Electrochemical Society* 2004;151(2): 33-9. <http://jes.ecsdl.org/content/151/2/H33> (accessed 8 January 2004).
- [11] Zhang H, Hong K, Mays JW. Synthesis of Block Copolymers of Styrene and Methyl Methacrylate by Conventional Free Radical Polymerization in Room Temperature Ionic Liquids. *Macromolecules* 2002; 35(15): 5738 – 41. <http://pubs.acs.org/doi/full/10.1021/ma025518x> (accessed 17 June 2002).
- [12] Shen Y, Ding S. Catalyst Separation in Atom Transfer Radical Polymerization. *Progress in Polymer Science* 2004;29(10): 1053-78. <http://www.sciencedirect.com/science/article/pii/S0079670004000814> (accessed October 2004).
- [13] Vijayaraghavan R, MacFarlane DR. Living Cationic Polymerization of Styrene in an Ionic Liquid. *Chemical Communications* 2004; 6: 700-1. <http://pubs.rsc.org/en/content/articlehtml/2004/cc/b315100j?page=search> (accessed 13 February 2003).
- [14] Wang YY, Jiang D, Wang R, Dai LY. Application of Et₃NHCl-AlCl₃ Ionic Liquid as Initiator in Cationic Copolymerization of 1,3-Pentadiene with Styrene, Reaction Kinetics and Catalysis Letters 2007;90(1): 69-76. <http://link.springer.com/article/10.1007%2Fs11144-007-4999-2> (accessed 01 February 2007).
- [15] Wang YY, Li W, Dai LY. Cationic Ring-Opening Polymerization of 3,3-Bis(Chloromethyl)oxacyclobutane in Ionic Liquids. *Chinese Chemical Letters* 2007;18(10): 1187–90. <http://vls2.icm.edu.pl/cgi-bin/sciserv.pl?collection=elsevier&journal=10018417&issue=v18i0010> (accessed October 2007).
- [16] Liu Y, Wu G. On the Mechanism of Radiation-Induced Polymerization of Vinyl Monomers in Ionic Liquid. *Radiation Physics and Chemistry* 2005;73(3): 159-62. <http://www.sciencedirect.com/science/article/pii/S0969806X04004633> (accessed 14 October 2004).
- [17] Harrison S, MacKenzie SR, Haddleton DM. Unprecedented Solvent-Induced Acceleration of Free-Radical Propagation of Methyl Methacrylate in Ionic Liquid. *Chemical Communications* 2002;2850-1. <http://pubs.rsc.org/en/content/articlehtml/2002/cc/b209479g?page=search> (accessed 28 October 2002).
- [18] Zhang H, Hong K, Mays JW. Synthesis of Block Copolymers of Styrene and Methyl Methacrylate by Conventional Free Radical Polymerization in Room Temperature

- Ionic Liquids. *Macromolecules* 2002;35(15): 5738-41. <http://pubs.acs.org/doi/full/10.1021/ma025518x> (accessed 17 June 2002).
- [19] Noda A, Watanabe M. Highly Conductive Polymer Electrolytes Prepared by In Situ Polymerization of Vinyl Monomers in Room Temperature Molten Salts. *Electrochimica Acta* 2000;45(8-9): 1265-70. <http://www.sciencedirect.com/science/journal/00134686/45/8-9> (accessed 3 January 2000).
- [20] Feng S, Xu W, Nakanishi K, Yamago S. Highly Controlled Organotellurium-Mediated Living Radical Polymerization (TERP) in Ionic Liquids (ILs). The New Role of ILs in Radical Reactions. *ACS Macro Letters* 2012;1(1): 146-9. <http://pubs.acs.org/doi/full/10.1021/mz200133d> (accessed 8 December 2011).
- [21] Lu J, Yan F, Texter J. Advanced Applications of Ionic Liquids in Polymer Science. *Progress in Polymer Science* 2009; 34(5): 431-48. <http://www.sciencedirect.com/science/article/pii/S0079670008001226> (accessed 13 January 2009).
- [22] Yoshizawa M, Ogihara W, Ohno H. Novel Polymer Electrolytes Prepared by Copolymerization of Ionic Liquid Monomers. *Polymers for Advanced Technology* 2002;13(8): 589-94. <http://onlinelibrary.wiley.com/doi/10.1002/pat.261/pdf> (accessed 15 August 2002).
- [23] Ohno H. Design of Ion Conductive Polymers Based on Ionic liquids. *Macromolecular Symposia* 2007;249(1): 551-6. <http://onlinelibrary.wiley.com/doi/10.1002/masy.200750435/pdf> (accessed 28 March 2007).
- [24] Batra D, Hay DNT, Firestone MA. Formation of Biomimetic Liquid-Crystalline Hydrogel by Self-Assembly and Polymerization of an Ionic Liquid. *Chemistry of Materials* 2007;19(18): 4423-31. <http://pubs.acs.org/doi/full/10.1021/cm062992z> (accessed 7 August 2007).
- [25] Sun N, Rahman M, Qin Y, Maxim ML, Rodriguez H, Rogers RD. Complete Dissolution and Partial Delignification of Wood in the Ionic Liquid 1-Ethyl-3-Methylimidazolium Acetate. *Green Chemistry* 2009;11(5): 646-55. <http://pubs.rsc.org/en/content/articlehtml/2009/gc/b822702k?page=search> (accessed 13 March 2009).
- [26] Biswas A, Shogren RL, Stevenson DG, Willett JL, Bhowmik PK. Ionic Liquids as Solvents for Biopolymers: Acylation of Starch and Zein Protein. *Carbohydrate Polymers* 2006;66(4): 546-50. <http://www.sciencedirect.com/science/article/pii/S0144861706001834> (accessed November 2006).
- [27] Phillips DM, Drummy LF, Conrady DG, Fox DM, Naik RR, Stone MO, Trulove PC, De Long HC, Mantz RA. Dissolution and Regeneration of Bombyx mori Silk Fibroin Using Ionic Liquids. *Journal of American Chemical Society* 2004; 126(44): 14350-1. <http://pubs.acs.org/doi/full/10.1021/ja046079f> (accessed 19 October 2004).
- [28] Pernak J, Smiglak M, Griffin ST, Hough WL, Wilson TB, Pernak A, Zabielska-Matejuk J, Fojutowski J, Kita K, Rogers RD. Long Alkyl Chain Quaternary Ammonium-Based Ionic Liquids and Potential Applications. *Green Chemistry* 2006;8(9): 798-806. <http://pubs.rsc.org/en/content/articlehtml/2006/gc/b612702k> (accessed 13 March 2009).

- pubs.rsc.org/en/content/articlehtml/2006/gc/b604353d?page=search (accessed 13 July 2006).
- [29] Swatlowksi R, Spear SK, Holbrey JD, Rogers RD. Dissolution of Cellose with Ionic Liquids. *Journal of American Chemical Society* 2002;124(18): 4974-75. <http://pubs.acs.org/doi/full/10.1021/ja025790m> (accessed 17 April 2002).
- [30] Pernak J, Borucka N, Walkiewicz F, Markiewicz B, Fochtman P, Stolte S, Steudte S, Stepnowski P. Synthesis, Toxicity, Biodegradability and Physicochemical Properties of 4-Benzyl-4-Methylmorpholinium-Based Ionic Liquids. *Green Chemistry* 2011;13(10): 2901-10. <http://pubs.rsc.org/en/content/articlehtml/2011/gc/c1gc15468k?page=search> (accessed 2 August 2011).
- [31] Pernak J, Kordala R, Markiewicz B, Walkiewicz F, Poplawski A, Fabianska S, Janowski S, Lozynski M, Synthesis and Properties of Ammonium Ionic Liquids with Cyclohexyl Substituent and Dissolution of Cellulose. *RSC Advances* 2012; 2(22): 8429-38. <http://pubs.rsc.org/en/content/articlehtml/2012/ra/c2ra21502k?page=search> (accessed 24 July 2012).
- [32] Kozirog A, Wysocka-Robak A, Przybysz K, Michalczyk A, Walkiewicz F. Imidazolium Azolates. Antifungal Activity and the Stability to Use in Papermaking. *Chemical Review* 2013;92(9): 1618-1620.
- [33] Kreyenschulte H, Richter S, Götze T, Fischer D, Steinhäuser D, Klüppel M, Heinrich G. Interaction of 1-Allyl-3-Methylimidazolium Chloride and Carbon Black and its Influence on Carbon Black Filled Rubbers. *Carbon* 2012;50(10): 3649-58 <http://www.sciencedirect.com/science/article/pii/S0008622312002850> (accessed 24 March 2012).
- [34] Lei YD, Tang ZH, Guo BC, Zhu LX, Jia DM. Synthesis of Novel Functional Liquid and its Application as a Modifier in SBR/Silica Composites. *eXPRESS Polymer Letters* 2010;4(11): 692-703. http://www.expresspolymlett.com/articles/EPL-0001670_article.pdf (accessed November 2010).
- [35] Guo BC, Chen F, Lei YD, Liu XL, Wan JJ, Jia DM. Styrene-Butadiene Rubber/Halloysite Nanotubes Nanocomposites Modified by Sorbic Acid. *Applied Surface Science* 2009;255(16): 7329-36. <http://www.sciencedirect.com/science/article/pii/S0169433209003663> (accessed 8 August 2008).
- [36] Maslowski M, Zaborski M. Magnetorheological Elastomers Containing Ionic Liquids. In: Handy S. (ed.) *Applications of Ionic Liquids in Science and Technology*. Rijeka: InTech; 2011. p213-32. Available from <http://cdn.intechopen.com/pdfs-wm/20212.pdf> (accessed 22 September 2011).
- [37] Marwanta E, Mizumo T, Nakamura N, Ohno H. Improved Ionic Conductivity of Nitrile Rubber/Ionic Liquid Composites. *Polymer* 2005;46(11): 3795-800. <http://www.sciencedirect.com/science/article/pii/S0032386105003393> (accessed 7 April 2005).

- [38] Subramaniam K, Das A, Heinrich G. Development of Conducting Polychloroprene Rubber Using Imidazolium Based Ionic Liquid Modified Multi-Walled Carbon Nanotubes. *Composites Science and Technology* 2011; 71(11): 1441-9. <http://www.sciencedirect.com/science/article/pii/S0266353811001928> (accessed 2 June 2011).
- [39] Yoshizawa M, Ogihara W, Ohno H. Novel Polymer Electrolytes Prepared by Copolymerization of Ionic Liquid Monomers. *Polymers Advanced Technologies* 2002;13(8): 589-94. <http://onlinelibrary.wiley.com/doi/10.1002/pat.261/pdf> (accessed 15 August 2012).
- [40] Pernak J, Walkiewicz F, Maciejewska M, Zaborski M. Ionic Liquids as Vulcanization Accelerators. *Industrial Engineering & Chemical Research* 2010; 49(10): 5012-17. <http://pubs.acs.org/doi/full/10.1021/ie100151n> (accessed 23 April 2012).
- [41] Maciejewska M, Walkiewicz F, Zaborski M. Novel Ionic Liquids as Accelerators for the Sulfur Vulcanization of Butadiene–Styrene Elastomer Composites. *Industrial Engineering & Chemical Research*, 2013, 52(25): 8410–15. <http://pubs.acs.org/doi/full/10.1021/ie303167z> (accessed 17 May 2013).
- [42] Flory PJ, Rehner J. Statistical Mechanics of Cross-Linked Polymer Networks. II. Swelling. *Journal of Chemical Physics* 1943;11(11): 521-6. <http://scitation.aip.org/content/aip/journal/jcp/11/11/10.1063/1.1723792> (accessed 22 December 2004).
- [43] Masek A, Zaborski M, Kosmalska A. Derivatives of Flavonoides as Anti-Ageing Substances in Elastomers. *Comptes Rendus Chimie* 2011;14(5): 483-8. <http://www.sciencedirect.com/science/article/pii/S1631074811000026> (accessed 15 February 2011).

IntechOpen