Effect of ionic liquids on the dispersion of zinc oxide and silica nanoparticles, vulcanisation behaviour and properties of NBR composites

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Abstract. The aim of this work was to study the activity of several alkylpyrrolidinium, alkylpyridinium, alkylpiperidinium and benzylimidazolium ionic liquids (ILs) for the purpose of improving the dispersion degree of vulcanisation activator and filler nanoparticles in the acrylonitrile-butadiene elastomer (NBR). The effect of the ionic liquids on the vulcanisation kinetics of the rubber compounds, crosslink density and mechanical properties of the vulcanisates and their resistance to thermo-oxidative and UV ageing was studied.
The use of ionic liquids allowed for a homogeneous dispersion of nanoparticles in the elastomer without detrimental effects on the vulcanisation process. The physical properties and the thermal stability of the obtained vulcanisates were significantly improved. Ionic liquids increased the crosslink density of the vulcanisates and their damping properties.
Pirydinium and piperidinium hexafluorophosphates were most effective at increasing the crosslink density and improving the properties of NBR composites.

Keywords: rubber, ionic liquids, nanosized zinc oxide, silica nanoparticles, vulcanisation behaviour

1. Introduction

Zinc oxide is the optimal activator of sulphur vulcanisation. During vulcanisation, zinc ions react with the accelerator to form highly active zinc complexes. The crosslinking reaction is preceded by a reaction of zinc oxide with stearic acid to form hydrocarbon-soluble zinc stearate. The crosslink density increases with the concentration of zinc stearate [1]. Zinc oxide is dispersed in the elastomer in the form of crystalline particles. Particles of the accelerator, sulphur and fatty acids diffuse inside the elastomer and are adsorbed on the surface of zinc oxide to form complexes. Nieuwenhuizen [2] proposed a mechanism wherein the surface of zinc oxide participates in the reaction and is the medium of the reaction. Therefore, the dispersion of inorganic zinc oxide in an organic elastomer is the fundamental parameter affecting the curing process. Because zinc oxide and vulcanisation accelerators are insoluble in rubber, it is assumed that crosslinking reactions occur in a two-phase system and are catalysed by conventional phase transfer catalysts, such as crown ethers or cryptands. ILs are assumed to catalyse the interfacial reactions and could function identically in the crosslinking process [3].

Despite the important role of zinc oxide in the sulphur vulcanisation of elastomers, the amount of zinc oxide in rubber compounds must be reduced to below 2.5% because of its toxicity to aquatic species [4]. Using nanosized zinc oxide as the activator is one method to reduce the amount of ZnO in the elastomer. Because of the reduction in particle size, this powder has a higher and more developed specific surface area. Better contact between the zinc oxide

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nanoparticles and the other components of the cross-linking system is achieved, which increases the activity of ZnO in vulcanisation and reduces the amount used in rubber compounds [5]. The key factor is to ensure the homogeneous dispersion of the nanoparticles in the elastomer matrix. Unfortunately, zinc oxide nanoparticles reveal a high tendency to agglomerate in rubber [6] because of the high surface energy of this powder [7]. Our previous studies showed that surfactants and ionic liquids, such as alkylimidazolium salts, effectively improved the dispersion of zinc oxide nanoparticles in the elastomer [6].

Fukushima and Aida [8] reported that imidazolium ionic liquids can be used to disperse single-walled carbon nanotubes in soft composite materials. The ability of ionic liquids to functionalise and improve the dispersion of carbon nanotubes has been intensively studied [9, 10] also in diene elastomers [11]. Ionic liquids resulted in the development of a conductive polychloroprene rubber containing a low concentration of multi-walled carbon nanotubes (MWCNTs) [12, 13]. The fine homogeneous dispersion of the MWCNTs and their strong secondary network in the elastomer resulted in the high conductivity of the composite. Kreyenschulte *et al.* [14] demonstrated attractive interactions between carbon black and ionic liquids such as 1-allyl-3-methylimidazolium chloride. It is hypothesised that these interactions are because of cation-π-interactions between IL cations and the π-electrons on the carbon black surface. ILs can act as local plasticisers at the carbon black surface and can accelerate the formation of a carbon black secondary network in unsaturated elastomers.

N-ethylmethylimidazolium bis(trifluoromethanesulfonyl)imide (EMITFSI) was used for the preparation of flexible solid polymer electrolytes based on acrylonitrile-butadiene elastomers and poly(ethylene oxide) interpenetrating polymer networks [15]. When swollen in EMITFSI, the NBR/PEO composites exhibited good mechanical properties and elongation at break and ionic conductivity higher than 10^{-4} S·cm^{-1} at room temperature. Similar results were obtained for interpenetrating polymer networks containing alkylpirrolidinium bis(trifluoromethanesulfonyl)imides [16]. Conductive NBR composites with an ionic conductivity of $2.54 \cdot 10^{-4}$ S·cm^{-1} have also been prepared using 1-butyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide [17].

Ionic liquids were also used to improve the dispersion of silica in styrene-butadiene (SBR) composites. 1-Methylimidazolidine methacrylate salt (MimMa) was found to polymerise via a radical-initiated mechanism and was easily grafted onto SBR chains during vulcanisation [18]. Substantial hydrogen bonding between polymerised MimMa and silica facilitated the dispersion of silica in the elastomer and improved the interfacial interactions between SBR and silica particles. Silica agglomerates were significantly decreased, and the filler particles were uniformly distributed in the elastomer matrix. The mechanical properties of the SBR composites were improved. Similar results were reported for 1-methylimidazolium sorbate (MimS) [19]. These findings suggest that ionic liquids have the potential to improve the dispersion of solid nanoparticles in elastomers.

Our previous studies demonstrated that applying alkylimidazolium salts (bromides, chlorides, tetrafluoroborates and hexafluorophosphates) improved the dispersion of zinc oxide nanoparticles in the NBR and allowed for the production of vulcanisates with the amount of zinc oxide, sulphur and MBT reduced to 1.3 phr. These vulcanisates exhibited tensile strengths comparable to those without a dispersing agent [6]. In this work, we applied several alkylpyrrolidinium, alkylpyridinium, alkylpiperidinium and benzylimidazolium ionic liquids to improve the dispersion degree of zinc oxide and silica nanoparticles in NBR. The influence of nanosized zinc oxide and ILs on the curing kinetics of rubber compounds, vulcanisate crosslink density, tensile strength, damping properties, thermal stability and resistance to thermo-oxidative and UV ageing is discussed.

2. Materials and methods
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). The elastomer was vulcanised with sulphur (Siarkopol, Poland), with microsized zinc oxide as the activator (ZnO, Aldrich, USA). To reduce the amount of zinc ions in the rubber compounds, nanosized zinc oxide (nZnO, Nanostructured & Amorphous Materials, Inc., USA) was used as an alternative to microsized ZnO. 2-Mercaptobenzothiazole (MBT, Aldrich, USA) was used as an accelerator. Silica, with a specific surface area

Table 1. Ionic liquids (ILs)

ILs	Symbol
1-Ethyl-1-methylpyrrolidinium bromide	EMPYRRBr
1-Ethyl-1-methylpyrrolidinium hexafluorophosphate	EMPYRRPF$_6$
1-Butyl-1-methylpyrrolidinium chloride	BMPYRRCl
1-Butyl-1-methylpyrrolidinium bromide	BMPYRRBr
1-Butyl-1-methylpyrrolidinium hexafluorophosphate	BMPYRRPF$_6$
1-Butyl-1-methylpyrrolidinium tetrafluoroborate	BMPYRRBF$_4$
1-Benzyl-3-methylimidazolium chloride	BenMICl
1-Benzyl-3-methylimidazolium hexafluorophosphate	BenMIPF$_6$
1-Benzyl-3-methylimidazolium tetrafluoroborate	BenMIBF$_4$
1-Butyl-4-methylpyridinium chloride	BMPYRCl
1-Butyl-4-methylpyridinium hexafluorophosphate	BMPYRPF$_6$
1-Butyl-4-methylpyridinium tetrafluoroborate	BMPYRBF$_4$
1-Butyl-1-methylpiperidinium hexafluorophosphate	BMPIPPF$_6$
1-Butyl-1-methylpiperidinium tetrafluoroborate	BMPIPBF$_4$

of 380 m^2/g (Aerosil 380, Evonic Industries, Germany), was used as the filler. Ionic liquids (Table 1) were obtained from Aldrich.

2.3. Preparation and characterisation 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, which was measured by an oscillating disc rheometer (Monsanto). The kinetics of vulcanisation of the rubber compounds were studied using a DSC1 (Mettler Toledo) analyser by decreasing the temperature from 25 to –60°C at a rate of 10°C/min and then heating to 250°C at the identical heating rate. The crosslink density (v_T) of the vulcanisates was determined by their equilibrium swelling in toluene based on the Flory-Rehner equation [20]. The Huggins parameter of the elastomer-solvent interaction (χ) was calculated from the Equation (1):

$$\chi = 0.3809 + 0.6707 V_r \tag{1}$$

where V_r is the volume fraction of the elastomer in the swollen gel.

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

Ingredient	With micro-ZnO	With nano-ZnO
NBR	100	100
MBT	2	2
Sulphur	2	2
ZnO	5	2
Silica	30	30
Ionic liquid	–	2

The tensile properties of the vulcanisates were measured according to the standard procedures in ISO-37 using a ZWICK 1435 universal testing machine. Dynamic mechanical measurements were performed in tension mode using a DMA/SDTA861e analyser (Mettler Toledo). Measurements of the dynamic moduli were performed over the temperature range of –80 to 100°C with a heating rate of 2°C/min, a frequency of 1 Hz and a strain amplitude of 4 μm. The elastomer glass transition temperature was determined from the maximum of $\tan\delta = f(T)$, in which $\tan\delta$ is the loss factor, and T is the measurement temperature.

The thermal stability of the vulcanisates was studied using a TGA/DSC1 (Mettler Toledo) analyser. Samples were heated from 25 to 700°C in an argon atmosphere (60 mL/min) with a heating rate of 10°C/min.

The thermo-oxidative degradation of the vulcanisates was performed at a temperature of 100°C for 240 h. The UV degradation of the vulcanisates was performed for 120 h using a UV 2000 (Atlas) machine in two alternating segments: a day segment (irradiation 0.7 W/m^2, 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 ageing, their mechanical properties and crosslinking densities after ageing were determined and compared with the values obtained for the vulcanisates before the ageing process. The ageing factor (S) was calculated as the numerical change in the mechanical properties of the samples upon ageing (Equation (2)) [21]:

$$S = \frac{(TS \cdot EB)_{\text{after ageing}}}{(TS \cdot EB)_{\text{before ageing}}} \qquad (2)$$

3. Results and discussion

3.1. Dispersion of activator and filler nanoparticles in the elastomer

The ILs were used to improve the dispersion of the vulcanisation activator (zinc oxide) and filler nanoparticles in the elastomer matrix. The homogeneous dispersion of activator particles is required to maximise the activity of the curing system in the crosslinking process. Agglomeration decreases the specific surface area of the activator and the interphase between its particles and the other components of the curing system (sulphur and accelerator). During the first step of the vulcanisation process, particles of the accelerator, sulphur and fatty acids diffuse through the elastomer matrix and are adsorbed onto the ZnO surface, forming intermediate reactive complexes [1]. Therefore, the contact between the ZnO particles and the accelerator in the elastomer matrix should be maximised to enhance the efficiency of the zinc oxide during vulcanisation. The dispersion of the filler particles controls the reinforcement effect of the filler and determines the mechanical properties of the vulcanisate. Agglomerates concentrate stresses in the material when subjected to external strain that can lead to early destruction. SEM images of the vulcanisate surfaces were obtained to examine the dispersion of the activator and filler nanoparticles in the elastomer. These results are presented in Figure 1a–1j.

Zinc oxide and silica nanoparticles showed a strong tendency to agglomerate in the elastomer. They formed agglomerates several micrometres in size consisting of nanosized primary particles (Figure 1a). The dispersion of the zinc oxide and filler particles in the presence of ILs is presented in Figures 1b–1j. Hexafluorophosphates and tetrafluoroborates significantly improved the dispersion of the nanoparticles in the elastomer. The particles were homogeneously dispersed and tightly bound to the elastomer matrix. Therefore, these salts seem to be active dispersing agents that can improve the dispersion degree of zinc oxide and silica in the NBR elastomer. Chlorides were less effective in preventing the particles from agglomeration. Nanoparticles created small agglomerates approximately 1-2 μm in size. However, these agglomerates were uni-

formly dispersed in the elastomer and were surrounded with elastomer film. They did not affect the tensile properties of the vulcanisates. The lower efficiency of the chlorides can be related to their poor miscibility with the elastomer during the preparation of the rubber compounds. The addition of these ILs resulted in the crumbling of the elastomer during processing with the use of the two-roll mill.

3.2. Curing characteristics and the crosslink density of the vulcanisates

The influence of ILs on the vulcanisation process was estimated based on rheometer measurements. The curing characteristics of the NBR compounds and the crosslink densities of the vulcanisates are given in Table 3.

For curing, the conventional NBR compound system consisting of an accelerator (MBT), sulphur and microsized zinc oxide was used and compared with the system containing nanosized zinc oxide and IL. The use of nanosized zinc oxide increased the torque increment compared with that of the reference rubber compound containing microsized ZnO. No considerable influence on the vulcanisation time or scorch time was observed. The use of the ILs significantly reduced the vulcanisation time and increased the torque increment of the rubber compounds compared to the reference compounds with micro- or nanosized zinc oxide. The crosslink density of the

Table 3. Curing characteristics and crosslink densities of NBR vulcanisates containing ILs

ILs	ΔG [dNm]	t_{90} [min]	t_p [min]	$v_T \cdot 10^4$ [mol/cm^3]
ZnO	44.5	50	2.2	19.8
nZnO	67.8	50	2.9	20.4
EMPYRRBr	123.2	40	2.1	22.5
EMPYRRPF$_6$	106.5	45	3.1	21.9
BMPYRRCl	120.5	25	2.8	23.1
BMPYRRBr	109.2	25	2.9	21.3
BMPYRRPF$_6$	101.5	40	3.6	21.2
BMPYRRBF$_4$	97.4	30	3.6	20.1
BenMICl	109.0	30	3.1	21.4
BenMIPF$_6$	102.3	37	3.0	20.8
BenMIBF$_4$	104.0	35	2.7	20.3
BMPYRCl	104.3	22	2.5	23.6
BMPYRPF$_6$	104.7	40	3.5	21.7
BMPYRBF$_4$	109.9	40	3.5	20.4
BMPIPPF6	111.0	45	3.5	21.5
BMPIPBF4	114.4	45	2.5	21.1

ΔG – increment of torque in the rubber compound during vulcanisation; t_{90} – optimal vulcanisation time; t_p – scorch time, v_T – crosslink density of vulcanisates
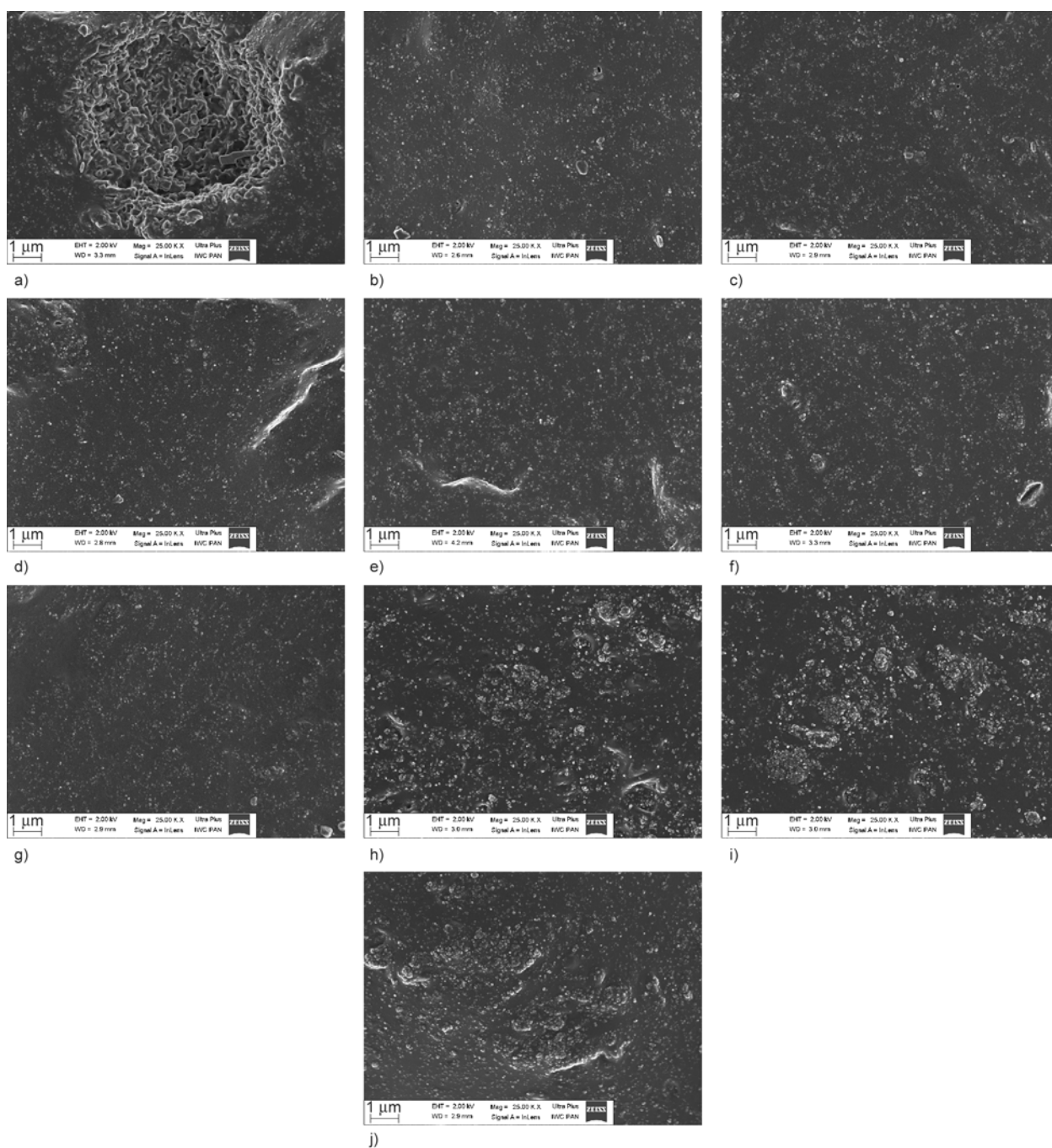
Figure 1. SEM images of vulcanisates: a) without IL, b) with EMPYRRPF$_6$, c) with BMPYRRPF$_6$, d) with BenMIBF$_4$, e) with BMPYRPF$_6$, f) with BMPYRBF$_4$, g) BMPIPPF$_6$, h) with BMPYRRCl, i) with BenMICl, j) with BMPYRCl

vulcanisates also increased. This increase could be because of the more homogeneous dispersion of the zinc oxide nanoparticles in the elastomer that led to better contact between particles of the vulcanisation activator and the other components of the curing system (sulphur, accelerator). ILs may have acted as a catalyst for the interfacial crosslinking reactions. Zinc oxide and vulcanisation accelerators are insoluble in the rubber. Therefore, the crosslinking reac-

tions occur in a two-phase system. ILs are presumed to catalyse the interfacial reactions [3]. This assumption is confirmed by the fact that the composites containing chlorides were characterised by the shortest vulcanisation time and higher crosslink density compared to other ILs, despite poor dispersion of zinc oxide nanoparticles (Figures 1b–1j). There was no simple correlation between the structure of the IL and its influence on the curing charac-

Table 4. Temperature and energetic effects of NBR vulcanisation measured by DSC

ILs	Vulcanisation temperature range [°C]	Energetic effect of vulcanisation [J/g]
ZnO	163–240	10.1
nZnO	165–240	10.3
EMPYRRPF$_6$	168–244	17.6
BMPYRRCl	143–230	9.5
BMPYRRBr	140–230	8.3
BMPYRRPF$_6$	168–240	12.6
BMPYRRBF$_4$	145–230	9.5
BenMIPF$_6$	168–237	13.2
BMPYRPF$_6$	168–230	10.6
BMPIPPF$_6$	168–236	10.9

Table 5. Mechanical properties of NBR vulcanisates containing ILs

ILs	TS [MPa]	EB [%]
ZnO	20.4	531
nZnO	22.4	526
EMPYRRBr	26.6	435
EMPYRRPF$_6$	26.3	490
BMPYRRCl	23.8	429
BMPYRRBr	23.7	411
BMPYRRPF$_6$	27.0	502
BMPYRRBF$_4$	25.0	520
BenMICl	23.4	425
BenMIPF$_6$	25.8	501
BenMIBF$_4$	27.3	530
BMPYRCl	24.7	402
BMPYRPF$_6$	26.8	465
BMPYRBF$_4$	27.0	520
BMPIPPF$_6$	26.4	430
BMPIPBF$_4$	23.7	474

TS – tensile strength; *EB* – elongation at break.

teristics. However, vulcanisates containing pyrrolidinium salts exhibited one of the highest crosslink densities.

We then examined the influence of nanosized zinc oxide and ILs on the temperature and energetic effects of vulcanisation using DSC analysis. The results for exemplary rubber compounds are given in Table 4.

Nanosized zinc oxide had no significant influence on the temperature and heat of vulcanisation compared with those of the NBR compounds containing the microsized activator. The vulcanisation is an exothermic process that took place in a temperature range of 163–240°C, with an energetic effect of 10 J/g. The hexafluorophosphates did not affect the vulcanisation temperature, but the increase in the energetic effect of the process was observed in most of the rubber compounds. Chlorides, bromides and tetrafluoroborates, regardless of the cation type, decreased the vulcanisation onset temperature by 20°C compared with rubber compounds with micro- or nanosized zinc oxide. The application of these ILs allows the NBR elastomer to be cured at lower temperatures than the commonly used 160°C.

3.3. Mechanical properties of the vulcanisates

The aim of applying the ILs was to achieve the homogeneous dispersion of the zinc oxide and silica nanoparticles in the elastomer and to improve the tensile strength of the vulcanisates. The mechanical properties of the NBR vulcanisates were studied under static and dynamic conditions. The results of the tensile tests are presented in Table 5.

NBR conventionally crosslinked with sulphur exhibited a tensile strength of 20.4 MPa and an elongation at break of approximately 531%. Nanosized zinc

oxide increased the tensile strength by 2 MPa, whereas the elongation at break did not change. The ILs increased the tensile strength of the vulcanisates by 2–5 MPa compared with the vulcanisate containing only nanosized zinc oxide. The elongation at break was reduced for vulcanisates with a higher crosslink density than that of the reference nZnO-containing vulcanisate. The highest tensile strength was achieved for vulcanisates with pyridinium hexafluorophosphate and tetrafluoroborate and pyrrolidinium hexafluorophosphate and bromide.

The dynamic mechanical properties are important for the application of rubber products. The rigidity and strength of vulcanisates should be stable and the material must be able to dampen vibration. The influence of ILs on the loss factor (tan δ) was determined with DMA. The loss factor tan δ as a function of temperature for the vulcanisates containing ILs is presented in Figure 2. The presence of one transition can be observed. This is the glass transition of the NBR elastomer, with a maximum that represents the glass transition temperature T_g.

The values of the glass transition temperature and the loss factor at T_g, room temperature and an elevated temperature (100°C) are compiled in Table 6. The glass transition temperature of NBR containing the standard activator – microsized zinc oxide – was –7.3°C. Applying nanosized zinc oxide increased the glass transition temperature of the elastomer because of the higher crosslink density of the vulcanisate. The ILs caused a further small increase in the T_g of
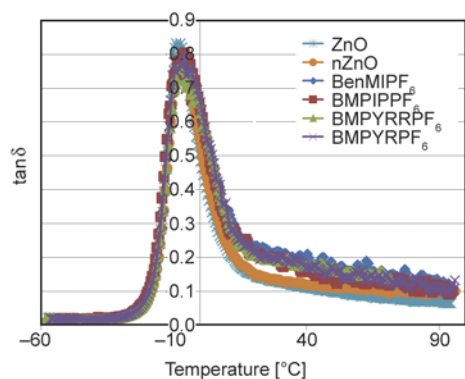
Figure 2. Loss factor (tan δ) versus temperature for NBR vulcanisates containing ILs

Table 6. Glass transition temperature and loss factor of NBR vulcanisates containing ILs

ILs	T_g [°C]	tan δ at T_g [–]	tan δ at 25°C [–]	tan δ at 100°C [–]
ZnO	–7.3	0.58	0.11	0.06
nZnO	–6.5	0.69	0.13	0.10
BMPYRRPF$_6$	–5.7	0.78	0.14	0.10
BenMIPF$_6$	–5.2	0.77	0.22	0.11
BMPYRPF$_6$	–6.2	0.80	0.20	0.11
BMPIPPF$_6$	–6.0	0.80	0.20	0.10

T_g – glass transition temperature; tan δ – loss factor.

the vulcanisates, which was the result of the cross-linked elastomer network that formed during vulcanisation and restricted the mobility of the elastomer chains. The nanosized zinc oxide and the ILs increased the loss factor at T_g, room and elevated temperatures. It is hypothesised that these vulcanisates would demonstrate better damping properties at the examined temperatures.

3.4. Thermal stability and ageing resistance of vulcanisates

Thermal stability and ageing resistance are important properties of rubber products for technological applications. ILs are used to improve the dispersion degree of zinc oxide and silica in the elastomer should not deteriorate these properties. The thermal stability of the vulcanisates was based on the decomposition temperature and total weight loss of the sample determined by TGA analysis. The results are presented in Table 7.

The thermal decomposition of the vulcanisate containing microsized zinc oxide began at 300°C. Replacing the standard activator with nanosized zinc oxide significantly improved the thermal stability of NBR. The decomposition of the vulcanisate started at a temperature that was 50°C higher than that of

Table 7. Decomposition temperatures at a weight loss of 2% (T_{02}), 5% (T_{05}), and 50% (T_{50}) and the total weight loss during decomposition of NBR vulcanisates containing ILs

ILs	T_{02} [°C]	T_{05} [°C]	T_{50} [°C]	Total weight loss [%]
ZnO	300	368	446	68.5
nZnO	350	377	458	70.6
EMPYRRPF$_6$	372	394	465	68.8
BMPYRRPF$_6$	370	392	465	68.9
BenMIPF$_6$	370	390	465	68.9
BMPYRPF$_6$	372	393	465	69.0
BMPIPPF$_6$	369	391	464	69.0

the reference vulcanisate. The use of ILs caused a further increase in the thermal stability of NBR, possibly because of the homogeneous dispersion of the nanoparticles in the elastomer matrix. The network created by the filler particles may be a barrier for the transport of gases and volatile pyrolysis products, thus increasing the thermal stability of the material. ILs also increased the temperatures at 5 and 50% weight loss. The 5% weight loss was achieved at the temperature range of 390–394°C, and 50% weight loss occurred at 464–465°C. The total weight loss during decomposition was similar for all vulcanisates (68.5–70.6%).

After establishing the effects of nanosized zinc oxide and ILs on the thermal stability, we then examined the vulcanisates' resistance to thermo-oxidative and UV ageing. The effect of ILs on ageing resistance was studied through the changes in the mechanical properties and the crosslink density of the vulcanisates.

In Figure 3, the change in crosslink density upon thermo-oxidative and UV ageing is reported for the vulcanisates containing hexafluorophosphates. The ageing process increased the crosslink density of the vulcanisates. This effect was particularly evident in the case of thermo-oxidative ageing. The increase
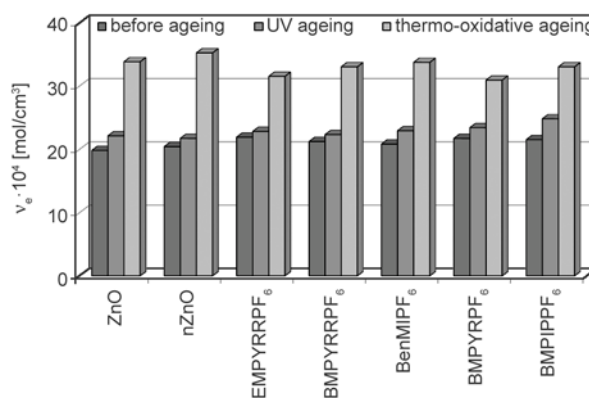
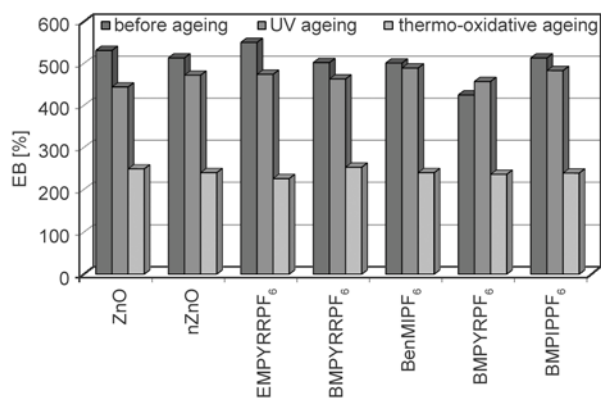

Figure 3. Vulcanisate crosslink density after ageing

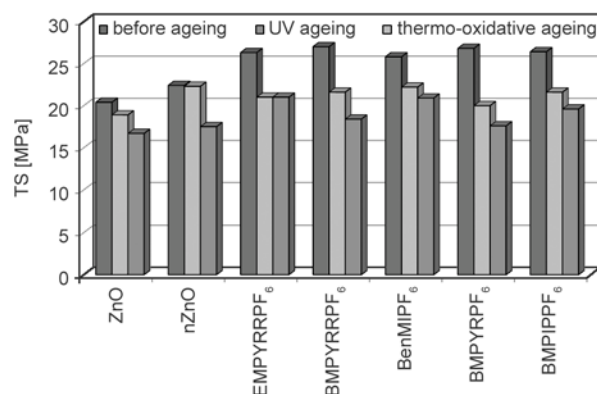**Figure 4.** Vulcanisate elongation at break after ageing

Figure 5. Vulcanisate tensile strength after ageing

Table 8. Thermo-oxidative and UV ageing factors for NBR vulcanisates containing ILs

ILs	S_T [–]	S_{UV} [–]
ZnO	0.43	0.68
nZnO	0.47	0.72
EMPYRRBr	0.39	0.65
EMPYRRPF$_6$	0.38	0.66
BMPYRRCl	0.43	0.59
BMPYRRBr	0.41	0.78
BMPYRRPF$_6$	0.40	0.73
BMPYRRBF$_4$	0.38	0.65
BenMICl	0.49	0.72
BenMIPF$_6$	0.41	0.79
BenMIBF$_4$	0.41	0.59
BMPYRCl	0.46	0.81
BMPYRPF$_6$	0.41	0.71
BMPYRBF$_4$	0.42	0.69
BMPIPPF$_6$	0.38	0.70
BMPIPBF$_4$	0.41	0.82

S_T – thermo-oxidative ageing factor; S_{UV} – UV ageing factor.

in crosslink density resulted in the reduction of the vulcanisates' elongation at break (approximately 300% for thermo-oxidative ageing) (Figure 4.) The vulcanisates became more rigid and brittle, corresponding to a reduction of their tensile strength (Figure 5).

It was difficult to estimate the resistance of the vulcanisates to the ageing process using changes in tensile strength and the elongation at break separately. Therefore, the ageing factor *S* was calculated to quantitatively estimate the change in the mechanical properties of the vulcanisates (Table 8). The ageing factor could be defined as the change in the deformation energy of the material as a result of the ageing process.

The nanosized zinc oxide and the ILs had no considerable influence on the vulcanisates' resistance to thermo-oxidative and UV ageing. A small improvement in the UV ageing resistance was observed for BMPYRCl and BMPIPBF$_4$. The S_{UV} values are significantly higher than the S_T values, indicating that prolonged exposure to elevated temperature is more destructive to material properties than UV radiation.

4. Conclusions

Ionic liquids (alkylpyrrolidinium, alkylpyridinium, alkylpiperidinium and benzylimidazolium salts) were used to improve the dispersion degree of a nanosized vulcanisation activator (zinc oxide) and filler (silica). The use of ILs allowed for the homogeneous dispersion of nanoparticles in the elastomer matrix and resulted in the shortening of the optimal vulcanisation time. Chlorides, bromides and tetrafluoroborates decreased the vulcanisation onset temperature by 20°C. ILs increased the vulcanisates' tensile strength compared with the vulcanisate that contained only nanosized zinc oxide. IL-containing vulcanisates also demonstrated better thermal stability and damping properties at the usage temperature. ILs did not affect the resistance of the vulcanisates to thermo-oxidative and UV ageing.

Using nanosized zinc oxide with ILs reduced the amount of zinc ions by 60% compared with conventional rubber compounds containing 5 phr of microsized ZnO as is required by the European Union legislation.

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