American Journal of Materials Science 2013, 3(4): 63-69
DOI: 10.5923/j.materials.20130304.01

Ionic Liquids Applied to Improve the Dispersion of Calcium Oxide Nanoparticles in the Hydrogenated Acrylonitrile-Butadiene Elastomer

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Abstract Hydrogenated acrylonitrile-butadiene elastomer was cured with dicumyl peroxide in the presence of calcium oxide nanoparticles modified with 2,4-pentadienoic acid as a crosslinking co-agent and ionic liquids (alkylimidazolium salts) as a dispersing agent. In this article, we discuss the effect of the ionic liquids (alkylimidazolium salts) with respect to their anion (bromide, chloride, tetrafluoroborate, hexafluorophosphate) and the length of alkyl chain in the cation (allyl-, ethyl-, butyl-, hexyl-, octyl-) on the vulcanization kinetics of rubber compounds. The influence of ionic liquids on the cross-link density, the mechanical properties of the vulcanizates and their resistance to weather ageing were also studied. Alkylimidazolium salts improve the dispersion of the coagent particles and are active in the crosslinking of HNBR with peroxide. The application of ionic liquids increases the crosslink density of the vulcanizates and improves their resistance to weather aging.

Keywords Calcium Oxide, Coagent, Ionic Liquid, Crosslinking, 2,4-Pentadienoic Acid

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1. Introduction

In recent years, significant attention has been focused on ionic liquids (ILs) due to their intrinsic properties, such as biocides[1]. The surface and interfacial properties are particularly important for the potential applications of ILs[2,3]. In addition, the synthesis of ionic liquids is not complex[4]. Ionic liquids can dissolve both organic and inorganic compounds as well as some polymers[4-7]. They can also be successfully used as accelerators for sulfur vulcanization of elastomers[8]. The preparation of new polymer composites and the improvement of their properties can also be achieved by using ionic liquids, because they may improve the dispersion, wettability and compatibility of the inorganic particles in an organic matrix[9]. Because ILs have very good ionic conductivity up to the decomposition temperature, they can play an important role in electrolyte matrixes[10-12].

Hydrogenated acrylonitrile-butadiene rubber (HNBR) is a saturated elastomer without double bonds in the macromolecule and therefore must be crosslinked using organic peroxide[13].

However, the vulcanizates crosslinked with peroxides have unsatisfactory mechanical properties for their industrial application[13,14].

To eliminate the disadvantages of peroxide vulcanization, coagents are used[14-18]. The application of coagents allows for noncovalent ionic or complex crosslinks due to the presence of functional groups in the coagent molecules that can form additional crosslinks[14,19,20]. In the literature, coagents that form hard domains during vulcanization surrounded by an elastomer with a lower stiffness have been investigated. Hard domains are created by coagents containing rigid aromatic structures. The domains with high rigidity partially contribute to the transfer of stresses in the elastomer network. The stress concentration near the hard coagent domains may deteriorate the physical properties of the vulcanizates[21]. Improvement in the mechanical properties can be achieved using coagents with more flexible structures to form soft domains of lower stiffness during vulcanization. These domains can deform under the influence of an external stress similar to the network formed by reinforcing filler particles[21,22]. The coagent's activity in the crosslinking process is determined by the homogeneous dispersion of its particles in the elastomer matrix. When the dispersion of the coagent particles is more homogeneous, the area of their contact with the elastomer chains and the activity in crosslinking process are greater. Unfortunately, nanosized metal oxides agglomerate in the elastomer due to the nanoparticles' high surface energy[23,24]. In addition, coagents based on mineral metal oxides may also act as fillers for the elastomers. Because the properties of the

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filler's particles affect the structural properties of the composites, a suitable degree of filler dispersion in the elastomer matrix is required to afford effective reinforcement[25]. The difficulties in obtaining a uniform dispersion of coagent or filler in the elastomer contribute to the search for new substances to improve the dispersion of the nanoparticles. The application of ILs appears to be a good solution for this technological problem.

The aim of this work was to improve the dispersion of a novel coagent, a nanosized calcium oxide modified with 2,4-pentadienoic acid in the HNBR elastomer crosslinked with dicumyl peroxide. The choice of ILs as dispersing agents was dictated by our earlier studies, which showed that alkylimidazolium salts improved the dispersion of zinc oxide nanoparticles in acrylonitrile-butadiene rubber[26]. Our studies focused on the effect of the ILs structure (cation and anion type) on the vulcanization kinetics of rubber compounds and the mechanical properties and the crosslink density of vulcanizates as well as their thermal stability and resistance to weather aging. The dispersion of coagent particles in the elastomer matrix was also examined.

2. Experimental Section

2.1. Materials

Hydrogenated acrylonitrile-butadiene elastomer (HNBR, Therban A3407) containing 34 wt.% of acrylonitrile was obtained from Lanxess, Germany. Its Mooney viscosity was 70 at 100℃. The elastomer was cured with dicumyl peroxide (DCP, Aldrich). Nanosized calcium oxide (CaO, Aldrich) with a specific surface area of 50 m^2/g (BET) was combined with an unsaturated carboxylic acid, such as 2,4-pentadienoic acid (PDA, Aldrich), and used as the crosslinking coagent. To improve the dispersion of the coagent's particles in the HNBR elastomer, ionic liquids (Aldrich) were applied, and their characteristics are presented in Table 1.

Table 1. Characteristics of Ionic Liquids (ILs)

Ionic liquid (IL)	Symbol
1-ethyl-3-methylimidazolium chloride	EMICl
1-butyl-3-methylimidazolium chloride	BMICl
1-hexyl-3-methylimidazolium chloride	HMICl
1-allyl-3-methylimidazolium chloride	AMICl
1-ethyl-3-methylimidazolium bromide	EMIBr
1-butyl-3-methylimidazolium bromide	BMIBr
1-allyl-3-methylimidazolium bromide	AMIBr
1-ethyl-3-methylimidazolium	EMIBF$_6$
1-butyl-3-methylimidazolium	BMIBF$_6$
1-hexyl-3-methylimidazolium	HMIBF$_6$
1-ethyl-3-methylimidazolium tetrafluoroborate	EMIBF$_4$
1-butyl-3-methylimidazolium tetrafluoroborate	BMIBF$_4$
1-hexyl-3-methylimidazolium tetrafluoroborate	HMIBF$_4$
1-methyl-3-octylimidazolium tetrafluoroborate	MOIBF$_4$

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℃ until they developed a 90% increase in torque, which was measured using an oscillating disc rheometer (WG-02, Monsanto) according to ASTMD 2084-81.

Table 2. Composition of the HNBR-Based Rubber Compounds (phr)

HNBR	100	100	100
Dicumyl peroxide (DCP)	2	2	2
Coagent (CaO/PDA)	-	5	5
Ionic liquid (IL)	-	-	1

The temperature range and thermal effect of the rubber compounds' vulcanization was measured using a DSC1 (Mettler Toledo) analyzer. The samples were heated from -60℃ to 250℃ in a nitrogen atmosphere at a heating rate of 10℃/min.

2.3. Characterization of Vulcanizates

The crosslink density (ν_T) of the vulcanizates was determined by their equilibrium swelling in toluene based on the Flory-Rehner equation[27]. The Huggins parameter of the elastomer-solvent interaction (χ) was calculated from the equation $\chi = 0.501 + 0.228V_r$ (Equation (1))[28], where V_r is the volume fraction of the elastomer in the swollen gel. To determine the content of ionic crosslinks in the elastomer network, samples were swollen in toluene in a desiccator with saturated ammonia vapor (25% aqueous solution). The content of ionic crosslinks ($\Delta\nu$) was calculated from Equation (2), where ν_A is the crosslink density determined for samples treated with ammonia vapor.

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

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

The dispersion of the coagent in the elastomer matrix was estimated using scanning electron microscopy with a ZEISS SEM. The vulcanizates were broken down in liquid nitrogen, and the surfaces of their fractures were examined. Prior to the measurements, the samples were coated with carbon.

The aging of the vulcanizates under weather conditions was performed for 100 hours with an Atlas CI 4000 "Xenon Arc Weather-Ometer" instrument. The aging process followed a simulated day-night cycle with the following parameters: day (102 minutes, irradiation of 60 W/m^2, 367 kJ, humidity 50%, spray, temperature: black panel 80°C, panel chamber 38°C); night (18 minutes, irradiation 60 W/m^2, 64 kJ, humidity 5%, no spray, temperature: black panel 80°C, panel chamber 38°C). To estimate the resistance of the samples to weather aging, their mechanical properties and crosslink density after aging were determined and compared with the values obtained for the vulcanizates prior to aging. An aging factor (S) was calculated as the numerical change in the mechanical properties of the samples upon aging (Equation 3)[29], which is a measurement of the changes in the sample deformation energy caused by the weather aging process.

$$S = (TS \cdot EB)_{after\ aging} / (TS \cdot EB)_{before\ aging} \qquad (3)$$

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

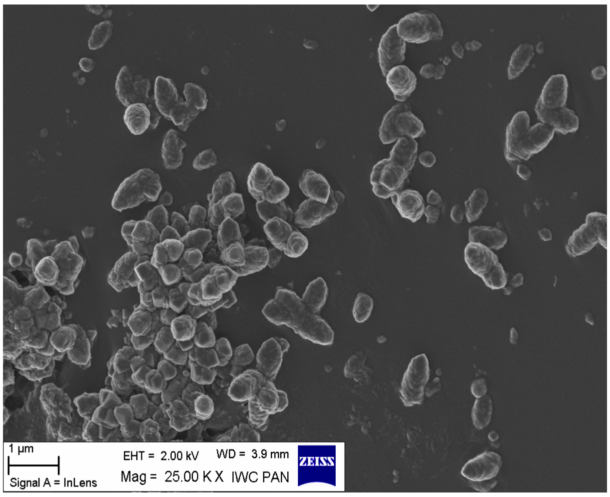
3. Result and Discussion

3.1. Coagent Dispersion in the Elastomer

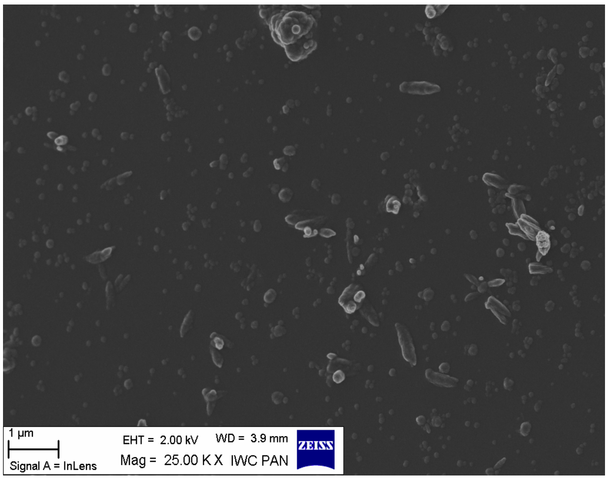
As we previously reported, nanosized calcium oxide modified with unsaturated carboxylic acids had relatively large dispersive components of surface energy[24], which has a significant effect on their dispersion in the elastomer matrix. It may be expected that nanoparticles of CaO/PDA will agglomerate in the elastomer reducing the activity of coagent in the crosslinking process. To directly examine the dispersion of the coagent particles in the HNBR elastomer, SEM images of the vulcanizate surfaces were recorded. These results are presented in Figure 1 (a-d).

CaO/PDA nanoparticles created agglomerates with complex morphologies that were several µm in size, which revealed poor adhesion to the elastomer matrix (Figure 1a). Such agglomerates may concentrate the stress in a sample subjected to external deformations initiating its premature destruction. Agglomerates also decrease the surface area of the coagent and as a result the surface of contact between coagent particles and elastomer chains. Therefore, the homogeneous dispersion of coagent particles is required to ensure the optimum activity of the coagent.

The ILs improved the dispersion of CaO/PDA in the HNBR elastomer. The nanoparticles were homogeneously distributed in the elastomer matrix. For the BMIBr application, some aggregates were observed in the SEM image. However, their size was on the nanometer scale, and they exhibited good wettability by the elastomer.



a)



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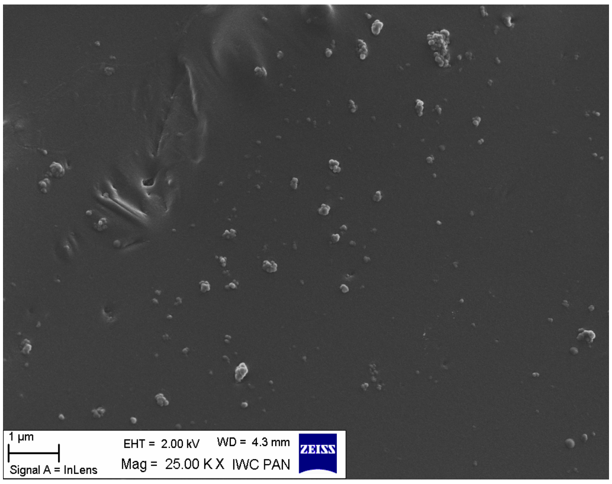

c)

Figure 1. SEM images of vulcanizates containing: a) CaO/PDA, b) BMICl, and c) BMICl

3.2. Cure Characteristics and Crosslink Density of Vulcanizates

Table 3. Cure Characteristics and Crosslink Density of HNBR Vulcanizates containing the Coagent (ΔG - Increment of Torque in the Rubber Compound during Vulcanization; t_{90} - Optimal Vulcanization Time; ν_T – Crosslink Density; Δν – Ionic Crosslink Content)

Vulcanizate	ΔG (dNm)	t_w(min)	ν_T *10^4 (mol/cm^3)	Δν (%)
DCP	40.6	50	28.5	3.3
CaO/PDA	47.9	43	40.2	13.0
EMICl	65.6	31	45.1	15.8
BMICl	66.7	30	44.4	15.1
HMICl	65.1	30	49.4	14.9
EMIBr	61.8	30	45.6	13.0
BMIBr	67.0	35	46.9	16.1
$EMIBF_6$	61.1	35	42.2	13.6
$BMIBF_6$	67.5	35	45.4	18.3
$HMIBF_6$	67.4	35	47.6	16.0
$EMIBF_4$	58.0	34	42.9	14.9
$BMIBF_4$	65.7	32	45.6	13.9
$HMIBF_4$	69.5	35	44.6	15.4
$MOIBF_4$	68.1	36	47.2	14.1

The main goal of coagent application is to increase the crosslink density of vulcanizates and reduce the vulcanization time of rubber compounds, which is important for technological reasons. The ILs that are reported to catalyze interphase reactions[30] should affect the kinetics of the vulcanization of rubber compounds. The influence of the coagent and ILs was estimated based on rheometer measurements. The cure characteristics of the HNBR compounds are provided in Table 3.

The HNBR compound crosslinked only with dicumyl peroxide in the absence of the coagent and characterized by an increase in the torque by approximately 40 dNm during vulcanization. The application of CaO/PDA increased the torque increment during vulcanization compared to the conventional HNBR compound. Because the torque increment is an indirect measurement of the degree of elastomer crosslinking, it can be concluded that CaO/PDA is actively involved in the crosslinking process. The participation of CaO/PDA in crosslinking was confirmed by the values of the vulcanizate crosslink density, which was significantly higher than the pure peroxide-crosslinked vulcanizate. The crosslink density was improved by the formation of additional ionic crosslinks in the presence of the coagent. The application of ILs caused an additional and considerable increase in the torque increment during vulcanization. In addition to the increase in the crosslink density of the vulcanizates, a slight increase in the ionic crosslink content was observed, which may be due to a more homogeneous dispersion of the coagent in the presence of the ILs. Uniform dispersion of the CaO/PDA particles improves the contact between the coagent's functional groups and the elastomer chains, which is crucial for high coagent activity in the crosslinking process. The anion type as well as the length of the alkyl chains in the imidazolium cation in the ILs does not appear to have a significant influence on the vulcanizates crosslink density or ionic crosslink content.

The application of CaO/PDA reduced the vulcanization time by 7 minutes compared to the rubber compound containing only DCP. The catalytic effect of the ILs on the rate of the interfacial crosslinking reactions resulted in a further reduction in the vulcanization time to 30-36 minutes.

To examine the influence of the coagent and the ILs on the temperature range and thermal effect of vulcanization, differential scanning calorimetry (DSC) was employed. These results are presented in Table 4.

Although CaO/PDA and the ILs accelerated the crosslinking process, as shown in Table 3, they had no significant influence on the temperature of vulcanization. HNBR compounds undergo vulcanization in the temperature range of 158-203 ℃. The vulcanization of HNBR compounds is an exothermic process. ILs did not substantially affect the thermal effect of vulcanization. A slight increase in the amount of heat evolved in the crosslinking process was only observed for alkylimidazolium chlorides and bromides. This result is important for technological reasons, because strongly exothermic reactions could be dangerous during the processing of rubber compounds.

Table 4. Temperature Range and Thermal Effect of Vulcanization for HNBR Compounds containing the Coagent (T$_o$ – Vulcanization Onset Temperature; T$_e$ – Vulcanization Endset Temperature)

Rubber compound	Vulcanization temperature (°C)		Peak maximum temperature (°C)	Thermal effect of vulcanization (J/g)
	T$_o$	T$_e$		
DCP	159	202	184	20.5
CaO/PDA	161	200	185	17.7
EMICl	158	201	184	24.2
BMICl	158	201	184	24.9
HMICl	160	201	185	24.2
EMIBr	159	203	184	24.1
BMIBr	158	203	184	26.7
EMIBF$_6$	163	202	184	16.5
BMIBF$_6$	161	201	184	18.7
HMIBF$_6$	161	203	185	18.4
EMIBF$_4$	161	202	185	19.6
BMIBF$_4$	161	198	185	20.6
HMIBF$_4$	161	202	186	18.9
MOIBF$_4$	161	203	186	20.7

3.3. Mechanical Properties of Vulcanizates

The aim of coagent application is not only to improve crosslinking efficiency and the crosslink density of vulcanizates but also to increase their tensile strength. Therefore, the effect of CaO/PDA and ILs on the mechanical properties of vulcanizates was determined, and the results are provided in Table 5.

Table 5. Mechanical Properties of HNBR Vulcanizates containing the Coagent (SE300 – Module at 300% Vulcanizate Relative Elongation; TS – Tensile Strength; EB – Elongation at Break)

Vulcanizates	SE$_{300}$ (MPa)	TS (MPa)	EB (%)
DCP	1.04	10.3	656
CaO/PDA	1.36	16.0	577
EMICl	2.07	13.9	446
BMICl	1.78	13.4	463
HMICl	1.62	12.5	477
EMIBr	1.94	14.4	464
BMIBr	1.90	14.0	465
EMIBF$_6$	2.23	12.8	416
BMIBF$_6$	1.96	12.4	444
HMIBF$_6$	1.86	12.4	445
EMIBF$_4$	1.84	11.6	444
BMIBF$_4$	2.32	12.9	414
HMIBF$_4$	1.89	11.7	445
MOIBF$_4$	2.13	12.1	423

Pure peroxide crosslinked HNBR exhibited a tensile strength of 10.3 MPa and an elongation at break of approximately 656%. In terms of the CaO/PDA influence on the mechanical properties of vulcanizates, it was noted that the tensile strength increased by 6 MPa. The increased tensile strength resulted from the formation of labile ionic crosslinks in the elastomer network, which are able to rearrange upon external deformation of the sample increasing its tensile strength. The elongation at break was reduced by approximately 100% due to the increase in the vulcanizates crosslink density. A further decrease in the elongation at break was observed when the ILs were applied in combination with CaO/PDA. In addition, the increase in the module at a relative 300% elongation of the vulcanizates was achieved due to the crosslink density increment.

Unfortunately, despite improving the dispersion of the coagent in the HNBR elastomer, ILs reduced the tensile strength of the vulcanizates by 2-4 MPa compared to the vulcanizate containing only CaO/PDA. This result could be due to the high crosslink density of the vulcanizates prepared with ILs. Tensile strength increases as the crosslink density increases until the optimal value of the crosslink number in the elastomer network is reached. Further increase in the crosslink density results in a reduction in the vulcanizate tensile strength. The structure of the ILs does not substantially affect the mechanical properties of vulcanizates.

3.4. Thermal Stability of Vulcanizates

Rubber products often work at elevated temperatures. If ILs are used as dispersing agents, they should not deteriorate the thermal stability of vulcanizates.

Thermogravimetric analysis (TGA) was used to determine the thermal decomposition temperature of the HNBR vulcanizates and the total weight loss during decomposition. The results from these studies are presented in Table 6.

Table 6. Decomposition Temperatures at a Weight Loss of 2% (T_{02}), 5% (T_{05}), 50% (T_{50}) and the Total Weight Loss during Decomposition of HNBR Vulcanizates containing the Coagent

Vulcanizates	T_{02} (°C)	T_{05} (°C)	T_{50} (°C)	Total weight loss (%)
DCP	392	420	454	98.2
CaO/PDA	401	425	462	90.7
EMICl	399	424	458	92.2
BMICl	404	426	460	92.8
HMICl	399	425	460	93.1
EMIBr	398	424	460	91.5
BMIBr	403	426	461	91.3
$EMIBF_6$	407	427	462	93.2
$BMIBF_6$	399	423	462	92.8
$HMIBF_6$	397	424	461	92.5
$EMIBF_4$	398	423	461	91.4
$BMIBF_4$	400	423	462	90.4
$HMIBF_4$	397	423	460	92.0
$MOIBF_4$	399	423	461	90.9

The application of the coagent and ILs slightly improved the thermal stability of HNBR. The thermal decomposition of the vulcanizate containing only DCP started at 395℃, the temperature of the 50% weight loss was approximately 454℃, and the total weight loss of the vulcanizate during decomposition was approximately 98%. Vulcanizates with CaO/PDA and ILs began to decompose in the temperature range of 397-407℃. The temperature of 50% weight loss ranged from 423 to 427℃. The total weight loss was also lower compared to pure peroxide-crosslinked vulcanizate (90-93%).

3.5. Vulcanizates Resistance to Weather Aging

Rubber products from HNBR elastomer during Rubber products from the HNBR elastomer are typically exposed to factors, such as elevated temperature, UV radiation, and humidity, that cause aging. Therefore, the effect of the ILs on the vulcanizates resistance to weather aging was examined via changes in the mechanical properties and the crosslink density of the vulcanizates (Figures 2-4).

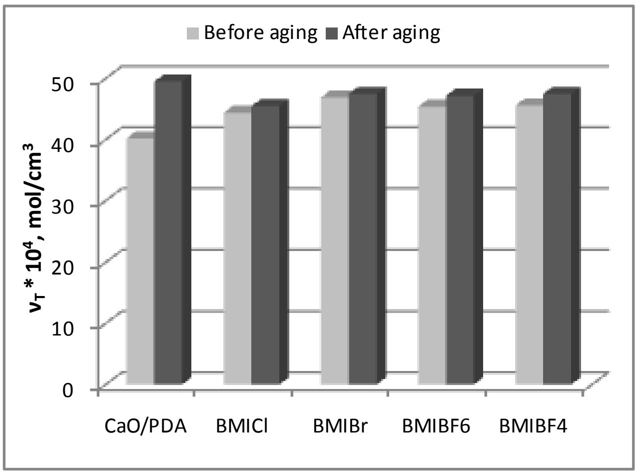

Figure 2. Effect of weather aging on the crosslink density of vulcanizates

Weather aging caused the significant increase in the crosslink density of vulcanizate containing only CaO/PDA. Weather aging caused a significant increase in the crosslink density of the vulcanizate containing only CaO/PDA. The application of ILs substantially limited the increase in the vulcanizates crosslink density during the aging process (Figure 2). Therefore, the reduction of the elongation at break for the vulcanizates containing ILs was significantly smaller compared to the vulcanizate without ILs (Figure 3).

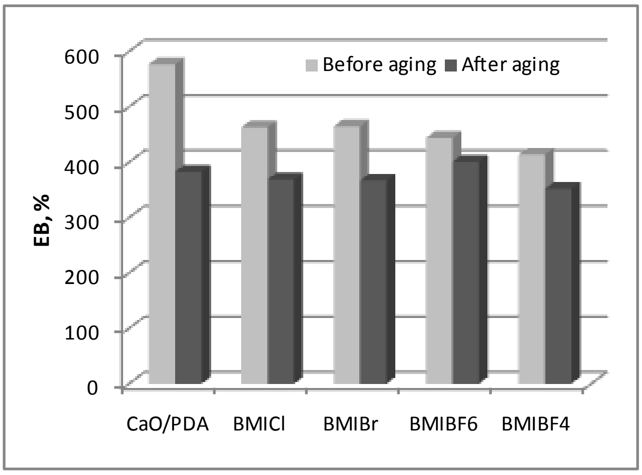

Figure 3. Effect of weather aging on the elongation at break of vulcanizates

Weather aging decreased the tensile strength of the vulcanizate without ILs, which is most likely due to a substantial increase in the crosslink density. For the vulcanizates containing ILs, an adverse effect from weather aging on tensile strength was observed. The tensile strength of the vulcanizates increased slightly (Figure 4).

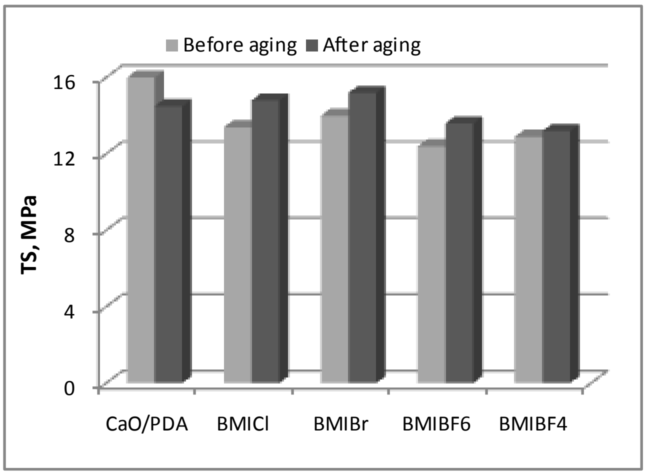

Figure 4. Effect of weather aging on the tensile strength of vulcanizates

It is difficult to determine the resistance of vulcanizates to weather aging by evaluating the changes in the tensile strength and elongation at break separately. Therefore, to quantitatively estimate the change in the mechanical properties of the vulcanizates, the aging factor (S) was calculated (Table 7). The aging factor is a measurement of the changes in the sample deformation energy caused by the weather aging process. The S-factor for the vulcanizate containing only the coagent is 0.60. The application of ILs substantially increased the values of S. The highest value of S was observed for the vulcanizate containing BMIBr and $BMIBF_6$ and was close to 1. Thus, the ILs provided protection for HNBR against weather aging, which was most likely due to the limitation of the increase in the vulcanizate crosslink density as a function of the aging factors.

Table 7. Weather Aging factor of HNBR Vulcanizates containing the Coagent

Vulcanizate	CaO/KPD	BMICl	BMIBr	$BMIPF_6$	$BMIBF_4$
S	0.60	0.88	0.95	1.08	0.87

4. Conclusions

Nanosized calcium oxides modified with 2,4-pentadienoic acid reduced the vulcanization time of rubber compounds and increased the crosslink density and tensile strength of vulcanizates, which were due to the formation of labile, ionic crosslinks in the elastomer network. Therefore, CaO/PDA could be considered a suitable coagent for HNBR crosslinking with peroxides.

CaO/PDA revealed a tendency to agglomerate in the elastomer, which decreased its activity in the crosslinking process. The application of ILs improved the dispersion of the coagent particles in the HNBR elastomer, reduced the vulcanization time, and increased the crosslink density of the vulcanizates. These results are mostly likely due to improved contact between the coagent particles and the elastomer chains resulting from its homogeneous dispersion as well as the catalytic effect of ILs on the interphase crosslinking reactions.

The ILs did not improve the tensile strength of the vulcanizates. However, an increase in the thermal stability and resistance to weather was observed for HNBR.

ACKNOWLEDGEMENTS

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

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