

Research Article

Ionic Liquids Applied to Improve the Dispersion of Coagent Particles in an Elastomer

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The aim of this work was to study the activity of several ionic liquids (alkylimidazolium salts) that are used to improve the dispersion of coagent particles in peroxide-cross-linked hydrogenated acrylonitrile butadiene elastomer (HNBR). Hydrotalcite grafted with monoallyl maleate was applied as a coagent for the HNBR vulcanization. In this paper, we discuss the effect of the ionic liquids (alkylimidazolium salts) with respect to their anion (bromide, chloride, tetrafluoroborate, and hexafluorophosphate) and the length of alkyl chain in the cation (allyl-, ethyl-, butyl-, hexyl-, and 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 seem to improve the dispersion of the coagent particles and to be active in the cross-linking of HNBR with peroxide. The type of ionic liquid considerably influences the activity of the coagent particles toward the HNBR. The application of ionic liquids increases the cross-link density of the vulcanizates and improves their resistance to weather aging.

1. Introduction

Ionic liquids (ILs) are generally defined as salts with melting points below 100°C [1, 2]. The definition of ILs clearly distinguishes them from other molten salts. Research on ILs has been one of the most rapidly growing fields in chemistry and industry in recent years. This rapid growth is mainly due to the many unique properties of ionic liquids. They are able to solvate a large variety of polar and nonpolar organic compounds and show potentially “environmentally friendly” characteristics (negligible vapor pressure, flammability) [3]. Their chemical and physical properties can be tuned for a wide range of potential applications by varying the cations and anions. The antielectrostatic properties of ILs have also been recognized [3]. In the past few years, ILs not only have been employed as solvents for various types of polymerization [4, 5] but also have been used to dissolve polymers [6, 7], to impart functionality and to create new polymer composites [8]. Applications of ILs as solvents for polymerization processes, as components of polymeric matrices (such as polymer gels), as templates for porous polymers, and as novel

electrolytes for electrochemical polymerizations have been reviewed [9, 10]. However, the application of ILs to improve the dispersion of coagents based on hydrotalcite for elastomer cross-linking with peroxides has not yet been reported. Thus, this work represents an innovative solution.

Coagents are applied to improve the physical properties and processing of peroxide-cross-linked elastomers. Coagent application allows for the generation of materials with higher tensile and tear strengths, higher modulus and hardness values, and better abrasion resistance and adhesion to metal [11, 12]. Most coagents are relatively polar compounds, which are difficult to mix with nonpolar polymers. Despite being homogeneously dispersed in a polymer matrix, coagent molecules can agglomerate again, form domains, and then homopolymerize [13]. The polymerized coagent domains are most likely covalently bonded to the surrounding polymer matrix [14]. Commonly used coagents for cross-linking of polymers are diallyl terephthalate, triallyl cyanurate, and zinc acrylates. They are incorporated into the polymer network because of the covulcanization of their domains with the surrounding polymer matrix [15]. However, the use of

these coagents has one major disadvantage that restricts their industrial application: deterioration of the mechanical properties of the vulcanizates. This is most likely due to the presence of rigid aromatic structures of coagent molecules, which form hard domains during vulcanization that are strongly bonded to the surrounding “soft” elastomer. Stress is then concentrated near the hard coagent domains, which leads to the destruction of the sample upon deformation [16]. Recently, we reported the high activity of hydrotalcite grafted with monoallyl maleate as the coagent in the peroxide cross-linking of saturated elastomer [17]. The application of this coagent allowed for the realization of vulcanizates with considerably improved mechanical properties and a higher cross-link density compared with vulcanizates cross-linked only with peroxide. However, the ionic cross-link content and tensile strength of vulcanizates decreased with the increase in the amount of coagent in the elastomer because of the agglomeration of the coagent particles in the elastomer. Therefore, it is necessary to develop a substance to improve the dispersion of coagent particles in the elastomer. We applied long-chain ILs with different numbers of alkyl groups to improve the dispersion of the coagent. It is believed that ILs could polymerize during vulcanization and create a structure in the elastomer composed of soft domains of in situ polymerized IL, similar to the mechanism proposed by Lu et al. [18] for interactions between a polar elastomer and zinc dimethacrylate. A structure consisting of poly-IL domains could be deformed upon the application of external stresses, improving the mechanical strength of the material. It is also possible that ILs could participate in the formation of additional noncovalent cross-links in the elastomer network. Elastomer composites with this type of morphology should reveal the ability to relax stress upon external deformation of the sample. The ability of imidazolium salts containing vinyl groups covalently introduced on IL cation or anion moieties to facilitate polymerization has been confirmed [19, 20]. Moreover, its application was shown to improve silica dispersions in elastomers and the mechanical performance of the vulcanizates. The positive effect of ILs on the dispersion of zinc oxide in the elastomer and the mechanical properties of vulcanizates was also confirmed [21].

In this work, we employed hydrotalcite grafted with monoallyl maleate (HTA/MMA) as a coagent for the cross-linking of HNBR with dicumyl peroxide. This method allowed hydrotalcite to act as the filler and coagent simultaneously. To improve the dispersion of HTA/MMA particles in the elastomer, ILs (alkylimidazolium salts) were applied. The influence of ILs on the cure kinetics of rubber compounds and their cross-linking efficiency, vulcanizate cross-link density, tensile strength, and resistance to weather aging was discussed.

2. Experimental Section

2.1. Materials. Hydrogenated acrylonitrile-butadiene elastomer HNBR (Therban A3407) containing 34 wt% acrylonitrile was obtained from Bayer Co. The Mooney viscosity was (ML1+4 (100°C): 70). It was vulcanized with dicumyl peroxide DCP (Aldrich). Synthetic hydrotalcite (HTA, Aldrich)

TABLE I: Characteristics of ionic liquids (ILs).

ILs	Producer	Symbol
1-allyl-3-methylimidazolium bromide	Aldrich	AMIBr
1-ethyl-3-methylimidazolium bromide	Aldrich	EMIBr
1-butyl-3-methylimidazolium bromide	Aldrich	BMIBr
1-allyl-3-methylimidazolium chloride	Aldrich	AMICl
1-ethyl-3-methylimidazolium chloride	Aldrich	EMICl
1-butyl-3-methylimidazolium chloride	Aldrich	BMICl
1-hexyl-3-methylimidazolium chloride	Aldrich	HMICl
1-ethyl-3-methylimidazolium tetrafluoroborate	Aldrich	EMIBF ₄
1-butyl-3-methylimidazolium tetrafluoroborate	Aldrich	BMIBF ₄
1-hexyl-3-methylimidazolium tetrafluoroborate	Aldrich	HMIBF ₄
1-methyl-3-octylimidazolium tetrafluoroborate	Aldrich	OMIBF ₄
1-ethyl-3-methylimidazolium hexafluorophosphate	Aldrich	EMIPF ₆
1-butyl-3-methylimidazolium hexafluorophosphate	Aldrich	BMIPF ₆
1-hexyl-3-methylimidazolium hexafluorophosphate	Aldrich	HMIPF ₆

with the molecular formula $Mg_6Al_2(CO_3)(OH)_{16} \cdot 4H_2O$ was grafted with monoallyl maleate (MMA, Technical University of Lodz) with the procedure described previously [22]. The characteristics of the ionic liquids applied are presented in Table I.

2.2. Preparation and Characterization of Rubber Compounds. Rubber compounds containing 100 phr of HNBR, 2 phr of dicumyl peroxide, 5 phr of coagent (HTA/MMA), and 1.5 phr of IL 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. The kinetics of rubber compound vulcanization was studied using a DSC1 (Mettler Toledo) analyzer by decreasing the temperature from 25 to -60°C at a rate of 10°C/min and then heating to 250°C with the same heating rate.

The cross-link density (ν_T) of the vulcanizates was determined by their equilibrium swelling in toluene based on the Flory-Rehner equation [23]. The Huggins parameter of the elastomer-solvent interaction (χ) was calculated from the equation

$$\chi = 0.501 + 0.273V_r. \quad (1)$$

See [22], where V_r is the volume fraction of the elastomer in the swollen gel. To determine the content of noncovalent cross-links in the elastomer network, samples were swollen in toluene in a desiccator with saturated ammonia vapor

(25% aqueous solution). The content of noncovalent cross-links ($\Delta\nu$) was calculated from (2), where ν_A is the cross-link density determined for samples treated with ammonia vapor:

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

The tensile properties and stress relaxation tests of the vulcanizates were measured according to ISO-37 using a ZWICK 1435 universal machine. The strain rate of tensile tests was 500 mm/min. To determine the stress relaxation properties, a sample was subjected to prolonged constant tension at a constant temperature. Deformation was recorded at specified time intervals (0–10 s, 10–100 s, and 100–1000 s), and a stress relaxation versus time diagram was plotted. The slope of the curve at any point was the stress relaxation rate.

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 vulcanizates under weather conditions was carried out 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/m², 367 kJ, humidity 50%, spray, temperature: black panel 80°C, panel chamber 38°C); night (18 minutes, irradiation 60 W/m², 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 cross-link density after aging were determined and compared with the values obtained for the composites before aging. An aging factor (K) was calculated as the numerical change in the mechanical properties of the samples upon aging (3):

$$K = \frac{(TS \cdot EB)_{\text{after aging}}}{(TS \cdot EB)_{\text{before aging}}}. \quad (3)$$

3. Results and Discussion

3.1. Cure Characteristics and Cross-Link Density of Vulcanizates. The influence of ILs (alkylimidazolium salts) on the vulcanization process was estimated based on rheometer measurements. The cure characteristics of HNBR compounds and cross-link densities of vulcanizates are given in Table 2.

The rubber compound cross-linked only with dicumyl peroxide and the coagent. Without the addition of ILs, the rubber compound was characterized by an increase of torque during vulcanization of approximately 40 dNm. The application of ILs did not considerably affect the torque increment compared with the reference rubber compound. There was no correlation between the torque increment and the structure of the cation or anion in the IL molecules.

The ILs had a catalytic effect on the vulcanization process. The vulcanization time of HNBR compounds decreased to as little as 25 minutes when EMICI, BMICI, HMIBF₄, and BMIPF₆ were present.

TABLE 2: Cure characteristics and cross-link density of HNBR vulcanizates containing ILs.

ILs	ΔG (dNm)	t_{90} (min)	t_p (min)	$\nu_T \cdot 10^{-4}$ (mol/cm ³)	$\Delta\nu$ (%)
—	40.6	35	183	29.5	10.3
AMIBr	38.9	35	182	24.4	8.3
EMIBr	44.3	30	184	36.4	10.4
BMIBr	39.3	30	194	35.6	10.1
AMICI	38.9	30	170	24.0	8.2
EMICI	39.2	30	170	35.6	16.6
BMICI	36.7	25	192	35.5	14.6
HMICI	37.3	30	188	34.9	16.6
EMIBF ₄	42.8	30	186	40.9	18.3
BMIBF ₄	41.7	25	162	34.8	10.9
HMIBF ₄	43.7	25	162	32.4	13.9
OMIBF ₄	45.6	30	182	26.3	18.6
EMIPF ₆	42.9	32	204	36.0	14.4
BMIPF ₆	38.3	25	168	35.0	12.6
HMIPF ₆	41.7	28	188	34.9	12.9

ΔG : increment of torque in the rubber compound during vulcanization; t_{90} : optimal vulcanization time; t_p : scorch time; ν_T : cross-link density of vulcanizates; $\Delta\nu$: noncovalent cross-link content.

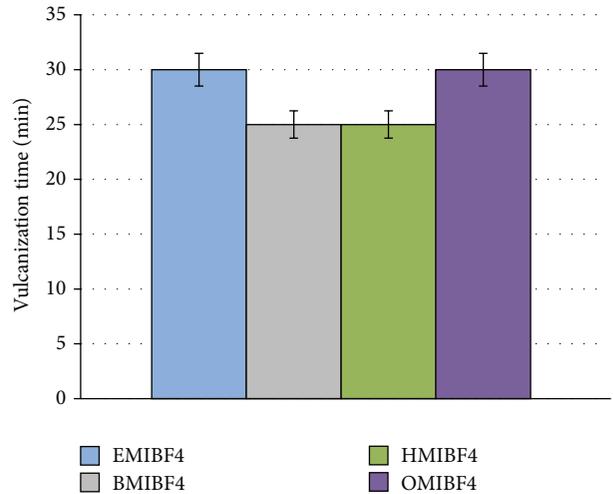


FIGURE 1: Vulcanization time for rubber compounds containing ILs with tetrafluoroborate anions.

In terms of the influence of the IL structure, it was noted that the rubber compounds containing ILs with butyl- and hexyl-chains in the cation and chloride, hexafluorophosphate, or tetrafluoroborate anions showed the shortest vulcanization times (Figures 1 and 2). However, this was not a significant effect from a technological point of view.

ILs caused changes of approximately 20 seconds in the scorch time compared with the time observed for the rubber compound containing only coagent. The shortest scorch time was exhibited by rubber compounds containing BMIBF₄ and HMIBF₄ (approximately 162 s).

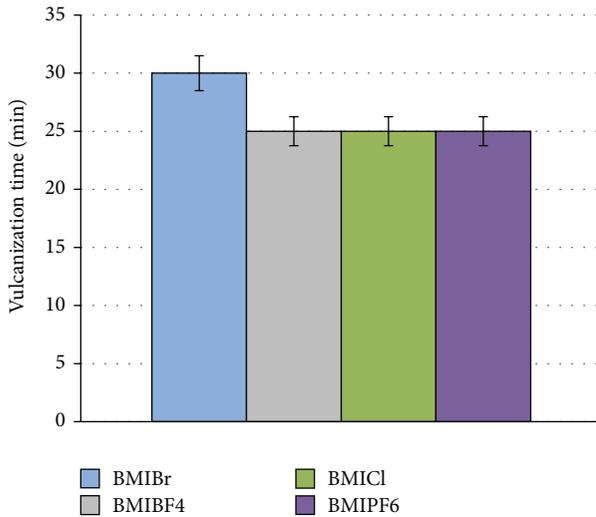


FIGURE 2: Vulcanization time for rubber compounds containing ILs with 1-butyl-3-methylimidazolium cations.

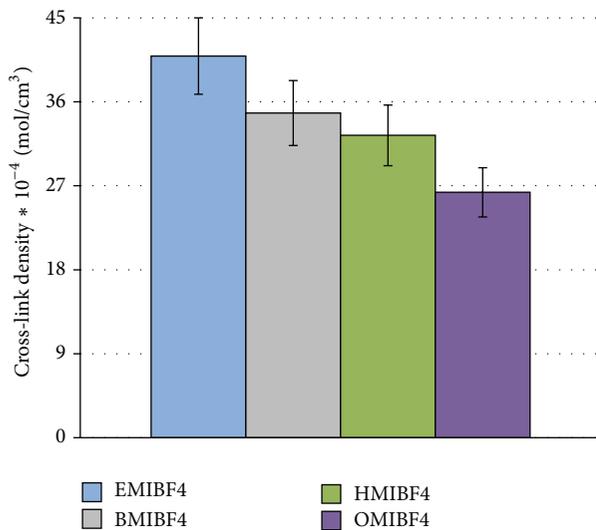


FIGURE 3: Cross-link density of vulcanizates containing ILs with tetrafluoroborate anions.

To estimate the influence of ILs on the vulcanization temperature and the energetic effect of the vulcanization process, a DSC analysis was used. The results are presented in Table 3. ILs had no influence on the vulcanization kinetics. The vulcanization of HNBR is an exothermic process that took place in the temperature range of 155–202°C and had an energetic effect of 15.4–23.4 J/g.

ILs are used as catalysts in interfacial reactions. Cross-linking reactions occur at the interface, so IL application may increase the cross-link density of vulcanizates. The effect of ILs on the cross-link density and on the content of noncovalent cross-links in the elastomer network is presented in Table 2 and Figures 3 and 4.

ILs considerably increased the cross-link density in comparison with the reference HNBR vulcanizate. Only

TABLE 3: Vulcanization temperature and energetic effect of vulcanization determined by DSC.

ILs	Vulcanization temperature range (°C)	Temperature of vulcanization peak (°C)	Energetic effect of vulcanization (J/g)
—	161–201	184	21.8
AMIBr	156–202	183	23.4
BMIBr	161–197	182	15.4
BMICI	155–195	180	16.5
EMIBF ₄	160–201	185	20.9
BMIBF ₄	160–201	185	21.0
HMIBF ₄	161–201	185	21.4
MOIBF ₄	160–202	185	20.1
BMIPF ₆	161–196	186	21.9

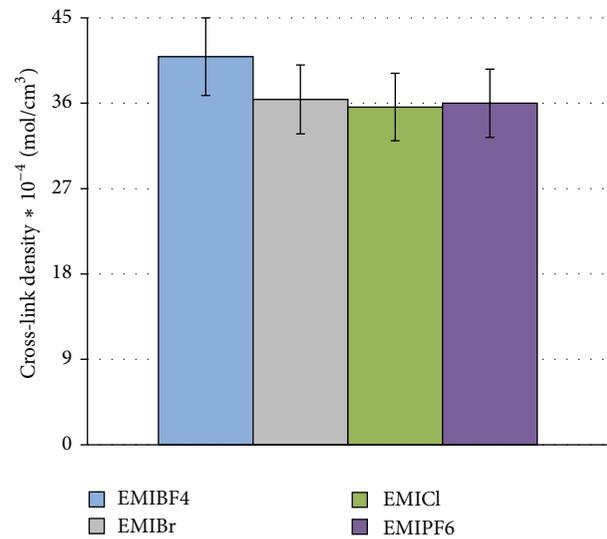


FIGURE 4: Cross-link density of vulcanizates containing ILs with 1-ethyl-3-methylimidazolium cations.

ILs with 1-allyl-3-methylimidazolium cations decreased the vulcanizates cross-link density. These ILs could most likely promote the ionic decomposition of part of the dicumyl peroxide, deteriorating the cross-linking efficiency.

Based on vulcanizates containing tetrafluoroborates, the effect of the IL cation structure was studied (Figure 3). The cross-link density of vulcanizates increased with the length of alkyl chains attached to the imidazolium ring in the IL cation. Similar results were obtained for rubber compounds containing hexafluorophosphates.

In terms of the influence of IL anions, the highest cross-link density was obtained for vulcanizates containing tetrafluoroborates; the influence of the other anions was negligible (Figure 4).

The application of a coagent resulted in the formation of noncovalent cross-links in the elastomer network; the cross-link content was approximately 10%. These were ionic cross-links, which decomposed when the samples were treated with ammonia vapor. Because of their ionic character, most of the

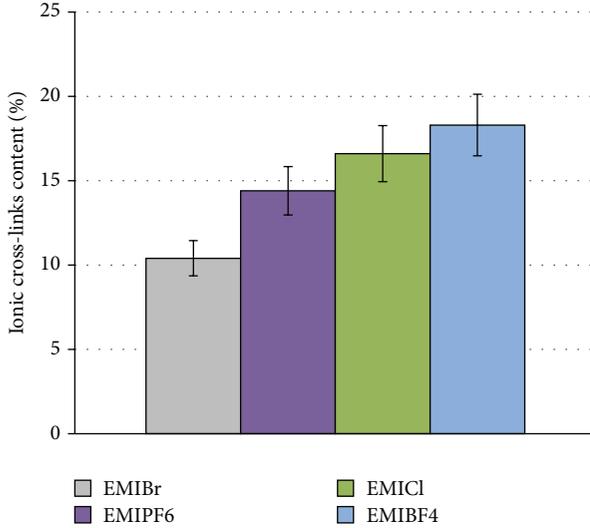


FIGURE 5: Ionic cross-link content in vulcanizates containing ILs with 1-ethyl-3-methylimidazolium cations.

examined ILs increased the content of ionic cross-links in the vulcanizates, up to 18% in the case of tetrafluoroborates. Another reason for the increased number of cross-links could be more the homogeneous dispersion of coagent particles in the elastomer containing IL, which leads to better accessibility of the coagent functional groups for interactions with the elastomer and a higher activity of the coagent in the cross-linking process. The increase in the number of ionic cross-links is important because the cross-links are able to rearrange inside the elastomer network upon external deformation of the vulcanizate, resulting in an improvement in the tensile strength. The lowest activity was observed for bromides (no influence on the ionic cross-link content) or ILs containing 1-allyl-3-methylimidazolium cations (decrease in the ionic cross-link content by 2% compared with the reference vulcanizate) (Figure 5).

3.2. Mechanical Properties of Vulcanizates. Having established the influence of ILs on the vulcanization process and on the cross-link density of vulcanizates, we then examined their mechanical properties. The results are given in Table 4.

HNBR vulcanizate containing only coagent had a tensile strength of approximately 10.1 MPa and an elongation at break of 573%. ILs did not considerably affect the vulcanizate tensile strength or the elongation at break. The highest tensile strength, approximately 12 MPa, was obtained for vulcanizates containing 1-methyl-3-butylimidazolium bromide, tetrafluoroborate, or hexafluorophosphate, whereas the lowest tensile parameters were achieved in the presence of ILs with 1-allyl-3-methylimidazolium cations. Similar effects were observed for the cross-link density and the ionic cross-link content of the vulcanizates.

The application of ILs increased the stress relaxation rates of the vulcanizates at the first stage of the stress relaxation process (Table 5). The first stage of stress relaxation was characterized by a rapid rate (n_1), which slowed with time.

TABLE 4: Mechanical properties of HNBR vulcanizates containing ILs.

ILs	TS (MPa)	EB (%)
—	10.1	573
AMIBr	9.0	594
EMIBr	12.0	527
BMIBr	12.0	532
AMICl	8.8	609
EMICl	11.8	560
BMICl	10.9	562
HMICl	11.4	566
EMIBF ₄	11.9	514
BMIBF ₄	12.5	537
HMIBF ₄	12.0	549
MOIBF ₄	12.3	586
EMIPF ₆	11.1	524
BMIPF ₆	12.3	525
HMIPF ₆	11.8	556

TS: tensile strength; EB: elongation at break, the standard deviation for TS 1.5 MPa, EB 25%.

TABLE 5: Stress relaxation rates of HNBR vulcanizates containing ILs.

ILs	$n_1 * 10^{-3} (s^{-1})$	$n_2 * 10^{-3} (s^{-1})$	$n_3 * 10^{-3} (s^{-1})$
—	164	63	38
EMIBr	188	65	24
EMICl	183	70	26
EMIBF ₄	191	69	45
EMIPF ₆	175	80	37

n_1 , n_2 , and n_3 : rates of stress relaxation for the time intervals 0–10 s, 10–100 s, and 100–1000 s, respectively, the standard deviation $10 s^{-1}$.

The second stage had a relatively uniform rate (n_2). The application of hexafluorophosphate also increased the stress relaxation rate in the second and third stage of the stress relaxation process.

These results confirm that the tensile strength improvement of the vulcanizates is also partially caused by the increase of the vulcanizates stress relaxation ability. The considerable chain slippage and reformation of ionic bonds in the elastomer network under external stress contribute to the increase in the vulcanizate tensile strength.

3.3. Coagent Dispersion in the Elastomer. The aim of the IL application was to improve the dispersion of HTA/MMA particles in the elastomer matrix. The homogeneous dispersion of coagent particles is crucial for maximizing the activity of the coagent in the cross-linking process. Agglomeration decreases the specific surface area of the coagent and, as a result, the interphase between the particles and elastomer chains. SEM images of the vulcanizate surfaces were taken to directly examine the dispersion of coagent particles in the elastomer. These results are presented in Figures 6(a)–6(e).

HTA/MMA particles showed a high ability to agglomerate in the elastomer. They formed agglomerates several

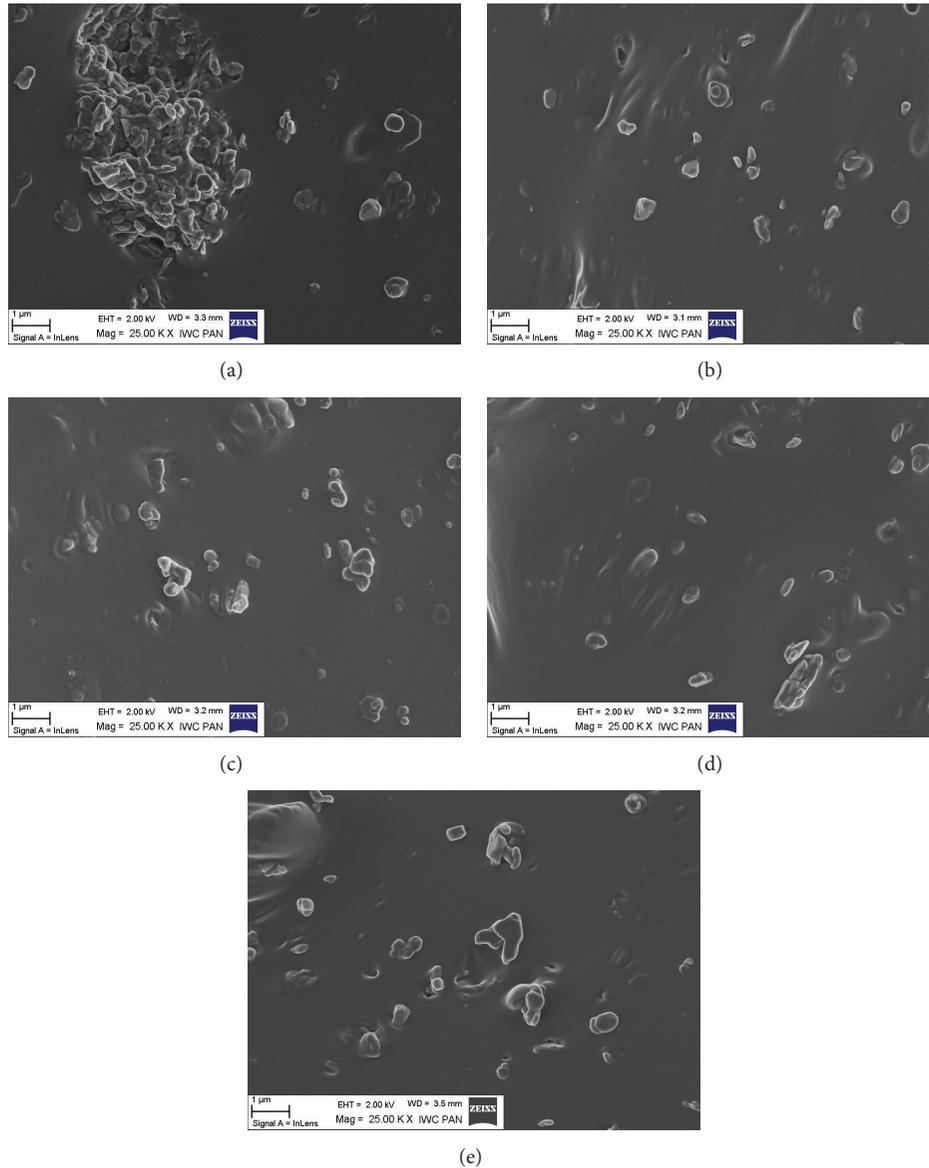


FIGURE 6: SEM images of vulcanizates containing HTA/MMA: (a) without IL, (b) with BMIBr, (c) with BMIBF₄, (d) with BMICl, (e) and with BMIPF₆.

micrometers in size, which were surrounded with elastomer film (Figure 6(a)). Assuming that the coagent particles diffuse through the elastomer matrix and react with elastomer chains, forming ionic cross-links, their agglomeration in the elastomer decreases the activity of the coagent.

The dispersion of coagent particles in the presence of ILs containing 1-butyl-3-methylimidazolium cation is presented in Figures 6(b)–6(e). It follows that ILs significantly improved the dispersion of HTA/MMA particles in the elastomer. The particles created small agglomerates, approximately 0.5–1 μm in size, which were homogeneously dispersed in the elastomer and tightly bound to the elastomer matrix. Therefore, alkylimidazolium salts seem to be active dispersing agents of hydrocalcite and can be applied to improve the dispersion of HTA used both as a coagent and a filler for HNBR elastomers.

3.4. Resistance of Vulcanizates to Weather Aging. Having established the effect of ILs on the dispersion of coagents in the elastomer, we then examined their influence on vulcanizate resistance to weather aging. Saturated elastomers cross-linked with peroxides usually demonstrate a strong aging resistance. Therefore, the substances chosen to increase the activity of the coagent should not deteriorate the vulcanizate's resistance to weather aging. The effect of ILs on vulcanizate resistance to weather aging was examined through the changes in the mechanical properties and cross-link density of the vulcanizates.

In Figure 7, the change in elongation at break upon weather aging is given for vulcanizates containing ILs. Weather aging caused the elongation at break to decrease by approximately 100% in comparison with vulcanizates before

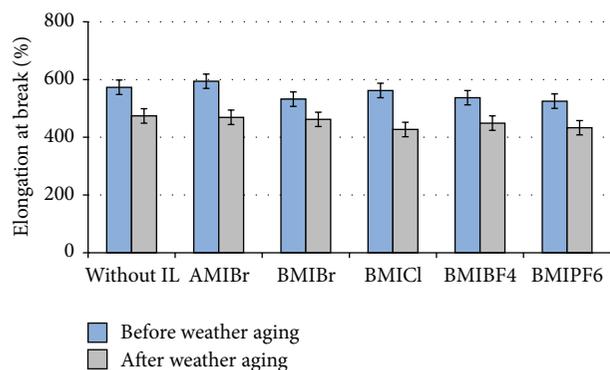


FIGURE 7: Vulcanizate elongation at break after weather aging.

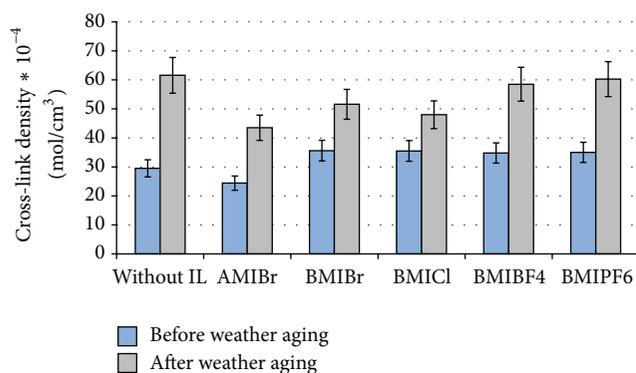


FIGURE 8: Vulcanizate cross-link density after weather aging.

aging process. This change was due to the large increase in the cross-link density of the vulcanizates (Figure 8). It could be concluded that aging factors such as UV radiation and elevated temperature resulted in the further cross-linking of the elastomer. However, the increase in the cross-link density was considerably smaller in the case of vulcanizates containing ILs. Weather aging deteriorated the tensile strength of vulcanizates with ILs, as it did to the vulcanizate with HTA/MMA. The smallest change in tensile strength was achieved for vulcanizates containing BMIBr and BMIBF₄ (Figure 9).

From the results presented in Figures 7–9, it follows that it is difficult to determine the resistance of vulcanizates to weather aging by considering changes in the tensile strength and elongation at break separately. Therefore, to quantitatively estimate the change in the mechanical properties of vulcanizates, the aging factor K was calculated (Table 6).

The aging factor K is a measurement of the changes in the sample deformation energy caused by the weather aging process. The closer to 1 the values of the K -factor are, the smaller the changes in the mechanical properties of the vulcanizates from the aging process will be. The aging factor (K) for vulcanizate containing only coagent is 0.30. The application of ILs increased the values of K considerably. The highest value of K was observed for the vulcanizate containing the BMIBr and BMIBF₄ and was close to 0.7. It can be concluded that ILs provided protection for the HNBR

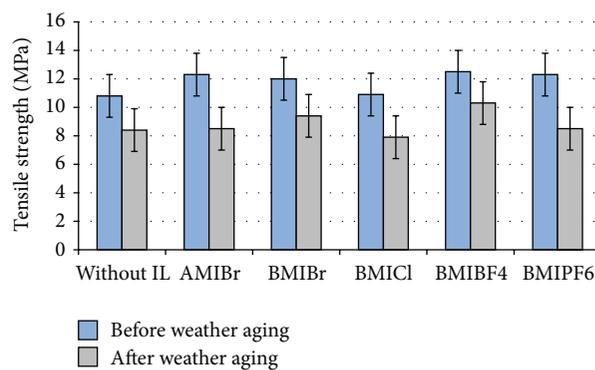


FIGURE 9: Vulcanizate tensile strength after weather aging.

TABLE 6: Weather aging factor K of HNBR vulcanizates containing ILs.

ILs	K (—)
—	0.30
AMIBr	0.54
BMIBr	0.68
BMIBF ₄	0.72
BMICl	0.55
BMIPF ₆	0.57

The standard deviation 0.08.

against weather aging, which was most likely due to the limitation of the increase in the vulcanizate cross-link density as a function of the aging factors (UV radiation, increased temperature, and humidity).

4. Conclusions

Hydrotalcite combined with monoallyl maleate was used as a coagent for peroxide cross-linking of hydrogenated acrylonitrile butadiene elastomers. ILs (alkylimidazolium salts) consisting of different anions (bromides, chlorides, tetrafluoroborates, and hexafluorophosphates) and cations (imidazolium rings with allyl-, ethyl-, butyl-, hexyl-, and octyl- chains) were used to improve the dispersion of the coagent in the elastomer.

HTA/MMA particles agglomerated in the elastomer matrix, forming clusters of particles several micrometers in size. ILs significantly improved the dispersion of the coagent particles in the elastomer, resulting in a higher activity of the coagent in the cross-linking process. The use of ILs yielded vulcanizates with a higher cross-link density and content of noncovalent cross-links compared with vulcanizates containing only coagent. The ILs did not considerably influence the vulcanizate tensile strength. ILs increased the resistance of vulcanizates to weather aging. Further cross-linking of the elastomer containing ILs upon aging was greatly reduced in comparison with the vulcanizate containing only the coagent.

The structure of ILs had an impact on their activity in the cross-linking process and the properties of the vulcanizates. The length of the alkyl chains attached to the imidazolium

ring in the IL cations was particularly important; the effect of the anion was smaller. Analyzing the results obtained for tetrafluoroborates, it can be concluded that cross-linking density and tensile strength of vulcanizates decreased with increasing alkyl chain lengths.

Acknowledgments

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