Thermal characterization of the effect of fillers and ionic liquids on the vulcanization and properties of acrylonitrile–butadiene elastomer

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Abstract

Different thermal analysis techniques were used to study the effect of fillers and ionic liquids (ILs) on the vulcanization process, thermal and dynamic mechanical properties of acrylonitrile–butadiene elastomer (NBR). The products of the studies were composites of NBR filled with hydrotalcite, nanosized silica or carbon black. ILs such as 1-butyl-1-methylpyrrolidinium (BMpyrrolBF₄), 1-butyl-4-methylpyridinium (BMpyrBF₄) or 1-butyl-1-methylpiperidinium (BMpipBF₄) tetrafluoroborates were applied to improve the dispersion degree of the curatives and filler particles in the elastomer and to increase the efficiency of vulcanization. The differential scanning calorimetry results indicated that ILs reduced the vulcanization temperature of NBR compounds and increased the homogeneity of cross-link distribution in the elastomer network. NBRs filled with carbon black or silica exhibited similar thermal stabilities, whereas hydrotalcite reduced the temperature of thermal decomposition. The lowest mechanical loss factors were determined for vulcanizates filled with nanosized silica.

Keywords Ionic liquids · NBR · Vulcanization temperature · Thermal stability · Damping behavior

Introduction

A wide variety of fillers have been used for years in the rubber industry to improve or modify the physical properties of elastomeric composites. The addition of a filler usually increases the modulus due to the inclusion of rigid particles in the soft elastomeric matrix and significantly improves the abrasion and tear resistance as a result of the filler's reinforcing effect. Moreover, filler–elastomer interactions can affect the structure of the elastomeric network, leading to additional cross-links [1]. No less important are the interactions between the particles of the filler, resulting in the formation of a filler network inside the elastomeric matrix. This network not only influences the mechanical properties of vulcanizates in static

conditions but also significantly changes the dynamic properties of the rubber. The mechanical performance of the final elastomeric composite depends on both the filler–filler and filler–elastomer interactions. Two of the main factors affecting the filler–elastomer interaction are the dispersion of filler particles in the elastomer matrix and the adhesion between these two phases. Usually, coupling agents are used to improve the compatibility and, consequently, the interaction between the elastomer chains and the filler surface. One of the most popular and effective coupling agents used in rubber technology is silanes [2, 3]. However, an analysis of the recent literature reports indicates that ILs are increasingly being used in elastomeric composites as a new class of dispersing agents for fillers. Due to their negligible vapor pressure, non-flammability and thermal stability in the temperature range for processing of elastomeric composites, ILs can be successfully applied in the field of elastomer technology [4]. Alkylimidazolium ILs are commonly used to improve the dispersion of carbon fillers, such as multi-walled carbon nanotubes [5], carbon black [6] or graphene [7]. The attractive interactions between the imidazolium cation of these ILs and the π -electrons on the filler surface were reported to improve the compatibility between the

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elastomer matrix and the filler and, consequently, the extent of dispersion in the elastomer. ILs with specific structures were employed as interfacial modifiers for silica-filled polymer composites [8]. Lei and Tang reported using 1-methylimidazolium methacrylate as a modifier for styrene-butadiene rubber (SBR) to improve the dispersion of silica and increase the interfacial interactions between SBR and the filler [9]. On the other hand, hydrophobic ILs with bis(trifluoromethanesulfonyl)imide anions were applied to improve the dispersion of layered fillers, such as montmorillonite (MMT) [10] or hydrotalcite [11]. A homogeneous dispersion in the polymer matrix accompanied by exfoliation of the filler layers was achieved, which are required to enhance the functional properties of the composites.

Despite being used to improve the mechanical performance of elastomeric composites, fillers can also influence other properties, such as the thermal and dimensional stability or fire retardancy [12]. Additionally, fillers were reported to affect the vulcanization process and the efficiency of the cross-linking system. This effect was particularly evident for silica, the surface of which adsorbs the curatives, especially vulcanization accelerators. This phenomenon deteriorates the efficiency of vulcanization, leads to changes in the filler–elastomer interaction and has an influence on the cross-link distribution in the elastomer network formed during vulcanization [13]. An influence on the thermal stability of elastomer composites or their vulcanization was also described for ILs [11, 14, 15]. For example, applying MMT intercalated with ILs improved the thermal stability of the NBR composites, which was explained by the extra interactions between the cations present in the clay layers and the elastomer chains and by the homogeneous dispersion of the intercalated filler in the elastomer matrix. Moreover, MMT modified with ILs added to NBR improved the efficiency of the vulcanization process [10]. The accelerating effect of ILs on the curing process was also reported by Marzec et al. for carboxylated NBR/HTA composites that contain 1-butyl-3-methylimidazolium tetrachloroaluminate [11]. This ionic liquid considerably shortened the scorch time and optimal vulcanization time of rubber compounds. A similar effect was also observed for 1-ethyl-3-methylimidazolium thiocyanate and 1-methyl-3-octylimidazolium chloride in silica-filled NBRs [15]. Therefore, in this work, we applied different thermal analysis methods to determine the effects of fillers and ILs on the vulcanization and performance of elastomer composites. Differential scanning calorimetry (DSC) was used to estimate the influence of fillers and ILs on the temperature range and enthalpy of the vulcanization process, which is very important from a technological point of view. The thermal stabilities of the vulcanizates were examined based on their decomposition temperatures and

the total mass losses of the samples determined by thermogravimetric analysis (TG). The mechanical properties of ILs containing vulcanizates under dynamic conditions were determined using dynamic mechanical analysis (DMA). ILs were applied to improve the activity of nanosized zinc oxide in the sulfur cross-linking of NBR and the dispersion degree of fillers in the elastomer matrix. ILs are thought to catalyze interfacial reactions; therefore, they can be assumed to play the same role in the cross-linking process [16, 17]. Moreover, zinc oxide nanoparticles can be dispersed more homogeneously in the elastomer matrix when ILs are present [18], which increases their accessibility in reactions with accelerators and sulfur.

Experimental section

Materials

NBR (EUOPRENE N3960) containing 39 mass% of acrylonitrile was obtained from Versalis S.p.A, San Donato Milanese, Italy. Its Mooney viscosity was ML1 + 4 (100 °C):60. It was cured with sulfur (Siarkopol, Tarnobrzeg, Poland) in the presence of 2-mercaptobenzothiazole (MBT) (Sigma-Aldrich, Schnelldorf, Germany) or benzalkonium 2-mercaptobenzothiazolate (BA-MBT) (Poznan University of Technology, Poznan, Poland) as an accelerator. Nanosized zinc oxide (NZnO) with a specific surface area of 42.5 m² g⁻¹ and a distribution of particle sizes as a function of particle number 185–295 nm, with a number-average particle size of 234 nm (Qinetiq Nanomaterials Limited, Hampshire, United Kingdom), was applied along with ionic liquids as a vulcanization activating system. ILs with the structure of cations depicted in Schema 1 and the thermal characteristics given in Table 2 were provided by Iolitec Ionic Liquids Technologies GmbH (Heilbronn, Germany). Silica with a specific surface area of 380 m² g⁻¹ (Aerosil 380, Evonic Industries, Essen, Germany), carbon black N330 purchased from Konimpex (Konin, Poland) and synthetic hydrotalcite (magnesium aluminum hydroxycarbonate) with the molecular formula

Schema 1 Structure of the ILs cations

Mg₆Al₂(CO₃)(OH)₁₆·4H₂O (Merck, Darmstadt, Germany) were used as fillers.

Preparation and characterization of rubber compounds

Rubber compounds with the general formulations given in Table 1 were prepared using a laboratory two-roll mill. Each of the examined samples contained one of the fillers and one of the ILs (with the exception of the reference samples without ILs).

The samples were cured at 160 °C for the optimal vulcanization time t_{90} determined using a rotorless D-RPA 3000 rheometer (MonTech, Buchen, Germany) and defined as the time at which the rheometric torque is given by Eq. (1), where ΔG is the torque increment and $G_{\min}$ is the minimum rheometric torque during the vulcanization of rubber compounds. Vulcanized plates of approximately 1 mm thickness were obtained and used for testing.

$$G_{90} = 0.90\Delta G + G_{\min} \quad (1)$$

The temperature and enthalpy of rubber compound vulcanization were studied using a DSC1 (Mettler Toledo, Greifensee, Switzerland) analyzer by decreasing the temperature from 25 to −100 °C at a rate of 10 °C min^{−1} and then heating to 250 °C with the same heating rate. Liquid nitrogen was used as the cooling agent. DSC measurements for ILs were performed in the temperature range of −100 to 180 °C with a heating rate 10 °C min^{−1}.

The distribution of cross-links in the elastomer network was estimated based on the solvent freezing point depression of the solvent confined in the polymer gel [19]. Curves of solidification were recorded on a DSC1 instrument (Mettler Toledo, Greifensee, Switzerland) by decreasing the temperature from 40 to −90 °C at a rate of 10 °C min^{−1}. Prior to this measurement, samples were swollen in benzene for 24 h. Liquid nitrogen was used as a cooling agent.

The thermal stability of the vulcanizates was studied using a TGA/DSC1 (Mettler Toledo, Greifensee, Switzerland) analyzer. Samples filled with CB or HTA were heated from 25 to 800 °C in an argon atmosphere (50 mL min^{−1}) at a heating rate of 10 °C min^{−1} and then from 800 to 900 °C in air (60 mL min^{−1}) with the same heating rate. Vulcanizates containing silica A380 were heated from 25 to 600 °C in an argon atmosphere and next to 900 °C in air, with the same heating rate and gas flow as for the samples with CB or HTA. The decomposition temperatures at 5% ($T_{5\%}$) or 50% ($T_{50\%}$) and the total mass loss during decomposition of the vulcanizates were determined. TG measurements for ILs were performed in the temperature range of 25–600 °C in argon atmosphere (50 mL min^{−1}) with a heating rate of 10 °C min^{−1}.

Dynamic mechanical measurements were taken in tension mode using a DMA/SDTA861e analyzer (Mettler Toledo, Greifensee, Switzerland). Measurements of the dynamic moduli were performed over the temperature range of −80 to 50 °C with a heating rate of 3 °C min^{−1}, a frequency of 1 Hz, and a strain amplitude of 4 μm. 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.

To unambiguously confirm the influence of fillers and ILs on the course and efficiency of vulcanization, additional studies were performed to complement the DSC results. The cross-link density of the vulcanizates (ν_e) was determined by equilibrium swelling in toluene, based on the Flory–Rehner equation [20] using the Huggins parameter of the elastomer–solvent (toluene) interaction [21]

$$\mu = 0.381 + 0.671V_r \quad (2)$$

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

The presented data were submitted to statistical analysis (one-way ANOVA) to compare the group means. Analysis of variance (ANOVA) was performed with the objective of

Table 1 General composition of the NBR-based rubber compounds, phr (R1–R3—reference NBR compounds without ILs, NBR4–12—NBR compounds containing ILs in the following order: BMpyrrolBF₄, BMpyrBF₄, and BMpipBF₄)

Ingredient	R1	R2	R3	NBR4-6	NBR7-9	NBR 10-12
NBR	100	100	100	100	100	100
Sulfur	2	2	2	2	2	2
NZnO	3	3	3	3	3	3
MBT	2	2	2	—	—	—
BA-MBT	—	—	—	2	2	2
Silica A380	30	—	—	30	—	—
Hydrotalcite	—	30	—	—	30	—
Carbon black N330	—	—	30	—	—	30
Ionic liquid*	—	—	—	6	6	6

*BMpyrrolBF₄, BMpyrBF₄ or BMpipBF₄

analyzing the influence of the fillers and ILs on thermal behavior, vulcanization time, cross-links density, and mechanical properties of vulcanizates in dynamic conditions. The significance level was taken as $P \leq 0.05$, i.e., for a level of confidence of 95%. Results of ANOVA analysis are given in the supplementary material.

Results and discussion

Thermal properties of ILs and fillers

TG was used to study the thermal stability of ILs with tetrafluoroborate anions. This method is commonly used to study the thermal behavior of ILs [22, 23]. The results are presented in Fig. 1 and Table 2.

The type of cation significantly affected the temperature of IL thermal decomposition. The lowest thermal decomposition onset temperature was exhibited by BMpyrBF₄ with the alkylpyridinium cation (354 °C), whereas the highest $T_{5\%}$ temperature was determined for BMpipBF₄ with the alkylpiperidinium cation (383 °C). BMpyrrolBF₄ showed a slightly lower $T_{5\%}$ than did alkylpiperidinium salt. The same relationships were observed for the temperature of the DTG peak. It is commonly known that the properties of ILs depend strictly on their structure. It should be noticed that the cations of BMpyrrolBF₄ and BMpipBF₄ exhibit similar structures consisting of a five- or six-membered saturated heterocyclic ring and alkyl chains directly bonded to the same nitrogen atom, so their thermal stability is also similar. On the other hand, the cation of the lowest thermal stability, BMpyrBF₄, consists of a 6-membered unsaturated heterocyclic ring, a butyl chain directly bonded to the nitrogen atom and a methyl group tied to the carbon of the pyridinium ring in position 4 (Schema 1).

Fig. 1 TG and DTG curves of BA-MBT and tetrafluoroborate ILs

TG was also performed for BA-MBT ionic liquid used as a vulcanization accelerator, as an alternative to pure MBT (Fig. 1). The thermal decomposition of BA-MBT is a two-stage process, which began at 154 °C ($T_{5\%}$). The first stage with a DTG peak temperature of 206 °C was mainly related to the decomposition of the benzalkonium cation, since other ILs with this cation exhibit similar thermal stability [17]. During the second stage, thermal decomposition of the MBT anion proceeded in the temperature range of 240–300 °C. Taking into account that the vulcanization temperature of NBR in this study was 160 °C, the most important factor is that the main thermal decomposition of BA-MBT, which was used as the vulcanization accelerator, occurred at a temperature above 160 °C.

Having established the thermal stability of the used ILs, we studied their phase transitions, such as melting and glass transitions, using DSC. The results are presented in Fig. 2 and Table 2.

The physical state and phase transitions of ILs are strictly dependent on their structure. BMpyrrolBF₄ and BMpipBF₄, which exhibit similar structures (five- or six-membered saturated heterocyclic ring), were characterized by similar T_g values (− 66 °C and − 62 °C, respectively). Moreover, these ILs were solids at room temperature and melted at about 150 °C [24]. In the case of BMpipBF₄, a small endothermic peak was also observed at 80 °C revealing a thermotropic mesomorphism of this ionic liquid. Heating of BMpipBF₄ from crystalline solid leads first to mesophase and finally at a temperature approximately 150 °C to isotropic liquid. A mesophase behavior of alkylpiperidinium tetrafluoroborates was confirmed by Lava et al. [24]. Thermotropic smectic liquid crystalline mesomorphism was also observed for tetrafluoroborates with different alkylimidazolium cations [25]. On the other hand, BMpyrBF₄, which contains a 6-membered unsaturated heterocyclic ring in the cation, was liquid at room temperature, and only a glass transition with T_g at approximately − 73 °C was identified for this ionic liquid on the DSC curve.

Regarding BA-MBT, a glass transition with a significant relaxation peak could be seen on the DSC curve, with T_g at about − 22 °C, and an endothermic peak of melting was present at 83 °C. The last endothermic peak at 138 °C could have resulted from the beginning of BA-MBT thermal decomposition because the onset temperature of the first DTG peak was about 110 °C and the $T_{5\%}$ decomposition temperature determined by TG was 154 °C.

The thermal stability of a filler can significantly affect the resistance of elastomer composites to elevated temperatures. Therefore, TG was performed to study the thermal behavior of fillers, such as nanosized silica A380, CB and synthetic HTA. The results are presented in Fig. 3.

Table 2 Thermal characteristics of ILs ($T_{5\%}$ —decomposition temperature at 5% mass loss, $T_{\text{peak (DTG)}}$ —peak temperature on the DTG curve, Δm_{total} —total mass loss during thermal decomposition, T_g —glass transition temperature, T_{mes} —temperature of mesophase, T_m —melting temperature) (standard deviations: $T_{5\%}$, $T_{\text{peak(DTG)}} \pm 2^\circ\text{C}$; $\Delta m_{\text{total}} \pm 0.6\%$; T_g , T_{mes} , $T_m \pm 2^\circ\text{C}$)

Ionic liquid	$T_{5\%}/^\circ\text{C}$	$T_{\text{peak(DTG)}}/^\circ\text{C}$	$\Delta m_{\text{total}}/\%$	$T_g/^\circ\text{C}$	$T_{\text{mes}}/^\circ\text{C}$	$T_m/^\circ\text{C}$
BMpyrrolBF ₄	378	466	100.0	− 66	—	152
BMpipBF ₄	383	452	100.1	− 62	81	148
BMpyrBF ₄	354	444	99.7	—	—	—
BA-MBT	154	206; 294	98.6	− 22	—	83

Fig. 2 DSC curves of the studied ILs **Fig. 3** TG and DTG curves of fillers

The examined fillers exhibit completely different thermal characteristics. The most stable filler is CB, which practically did not undergo any thermal changes during the measurement. The total mass loss of CB was about 0.5%. It should be mentioned that the TG measurements were performed in argon atmosphere, so no burning of CB was observed. Regarding nanosized silica A380, a total mass

loss of approximately 3.2% was determined in the temperature range of 25–130 °C, with a DTG peak temperature of 49 °C. This corresponds to the desorption of water, which was physically absorbed by the highly hygroscopic surface of this filler. The most complex thermal decomposition was achieved for synthetic hydrotalcite, which is magnesium aluminum hydroxycarbonate ($\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$). The mass loss curve can be divided into two major steps. The first was the loss of physically absorbed water and waters of hydration in the temperature range of 100–250 °C with a DTG peak temperature of 237 °C and a mass loss of 12.9%. The second was dehydroxylation above 250 °C (DTG peak temperature 326 °C), accompanied by the release of CO_2 (decarbonation) due to the decomposition of carbonate at higher temperatures, in the range of 400–650 °C (DTG peak at 434 °C) [26]. The total mass loss after HTA thermal decomposition was about 41.5%.

Upon comparing the thermal properties of the examined fillers, it was observed that HTA exhibited the lowest thermal stability. Therefore, it can be assumed that HTA will have the greatest impact on the thermal behavior of NBR composites.

Thermal stability of vulcanizates

TG was employed to study the effects of fillers and ILs on the thermal stability of NBRs. In the case of vulcanizates, measurements were performed in the first stage in argon atmosphere to study the elastomer pyrolysis and thermal decomposition of organic additives, such as vulcanization accelerators or ILs. Next, the atmosphere of measurement was changed to air to burn carbon black and carbon residue after pyrolysis of the elastomer. The results are presented in Table 3 and Figs. 4–6.

Upon analyzing the $T_{5\%}$ decomposition temperatures for the reference vulcanizates without ILs, the highest thermal stability was exhibited by NBR filled with carbon black. Thermal decomposition of this vulcanizate began at 402 °C. A similar thermal stability was shown for NBR containing A380 as the filler ($T_{5\%}$ at 400 °C). As expected,

Table 3 Decomposition temperatures at 5% ($T_{5\%}$), 50% ($T_{50\%}$), DTG peak temperature and total mass loss during the decomposition of NBR vulcanizates (standard deviations: $T_{5\%}$, $T_{\text{peak(DTG)}} \pm 3$ °C; $\Delta m_{\text{total}} \pm 1.5\%$)

NBR vulcanizate	$T_{5\%}/^{\circ}\text{C}$	$T_{\text{peak(DTG)}}/^{\circ}\text{C}$	$\Delta m_{\text{total}}/\%$
NBR filled with A380			
Ref. without IL	400	464	76
BMpyrrolBF ₄	385	472	77
BMpyrBF ₄	391	470	78
BMpipBF ₄	378	469	77
NBR filled with HTA			
Ref. without IL	379	464	84
BMpyrrolBF ₄	338	465	82
BMpyrBF ₄	342	459	81
BMpipBF ₄	335	458	79
NBR filled with CB			
Ref. without IL	402	464	94
BMpyrrolBF ₄	386	467	86
BMpyrBF ₄	390	468	85
BMpipBF ₄	380	465	84

Fig. 4 TG and DTG curves for NBR vulcanizates filled with A380 and containing ILs

the lowest thermal stability was exhibited by NBR filled with HTA. The $T_{5\%}$ temperature determined for this vulcanizate was about 20 °C lower than those for NBR with CB or silica A380. This effect was due to the low thermal stability of HTA, which started decomposing above 100 °C. The type of the filler had no significant influence on the temperature of the DTG peak or, correspondingly, the temperature of elastomer pyrolysis. The addition of ILs reduced the thermal stability of NBR vulcanizates regardless of the filler used. The highest detrimental effect of ILs on thermal stability was achieved for NBRs filled with HTA. The $T_{5\%}$ temperatures for these vulcanizates were

Fig. 5 TG and DTG curves for NBR vulcanizates filled with HTA and containing ILs

Fig. 6 TG and DTG curves for NBR vulcanizates filled with CB and containing ILs

reduced by about 40 °C compared to the reference vulcanizate without ionic liquid. The type of IL used did not considerably affect the thermal stability of the NBR. However, the lowest $T_{5\%}$ temperatures were determined for NBR containing BMpipBF₄, whereas the highest were for NBR containing BMpyrBF₄. This trend does not follow the thermal stability of ILs themselves, so it could be supposed that the reduction in the thermal decomposition temperature of NBR is not only due to the slightly lower thermal stability of tetrafluoroborate ILs but results mainly from the addition of the vulcanization accelerator BA-MBT. It should be noted that BA-MBT exhibited a $T_{5\%}$ temperature at 154 °C, which was about 200 °C lower than that of ILs with the tetrafluoroborate anion. ILs did not significantly affect the temperature of the DTG peak.

Table 4 Temperature and enthalpy of NBR vulcanization and post-curing measured by DSC (standard deviations: temperature ± 3 °C; enthalpy ± 1.4 Jg⁻¹)

NBR compound	Vulcanization temperature/°C	Vulcanization peak temp./°C	Vulcanization enthalpy/Jg ⁻¹	Post-curing temperature/°C	Post-curing enthalpy/Jg ⁻¹
NBR filled with A380					
Ref. without IL	164–195	179	3.2	201–236	2.5
BMpyrrolBF ₄	152–172	162	2.2	–	–
BMpyrBF ₄	146–173	159	2.6	–	–
BMpipBF ₄	150–172	162	2.4	–	–
NBR filled with HTA					
Ref. without IL	117–185	161	13.2	195–231	8.5
BMpyrrolBF ₄	116–170	137	6.0	177–232	6.8
BMpyrBF ₄	137–168	148	1.7	167–209	8.6
BMpipBF ₄	114–169	138	6.7	175–224	8.2
NBR filled with CB					
Ref. without IL	147–184	167	4.2	194–240	2.2
BMpyrrolBF ₄	117–171	150	6.8	–	–
BMpyrBF ₄	134–174	159	5.8	–	–
BMpipBF ₄	117–175	151	7.9	–	–

Fig. 7 DSC curves for the vulcanization of NBR filled with silica A380 and containing ILs **Fig. 8** DSC curves for the vulcanization of NBR filled with HTA and containing ILs

Temperature and enthalpy of vulcanization

Having established that fillers and ILs influence the thermal stability of NBR, we studied the effects of these additives on the vulcanization process. DSC was employed to study the temperature and enthalpy of NBR vulcanization. This method is commonly applied to examine the curing of elastomers [27, 28]. The results for NBR compounds are given in Table 4 and Figs. 7–9.

The vulcanization of NBR composites that did not contain ILs (reference samples) was a two-step exothermic process. The cross-linking in the lower temperature range (the first step) proceeded due to the formation of sulfur

bridges (cross-links) between elastomer chains. During the second step in the temperature range of about 200–240 °C, some post-curing processes took place, probably due to the cross-polymerization of butadiene units in the NBR macromolecules, accompanied by the cyclization or fragmentation of chains and the formation of low quantities of volatile products of their thermal decomposition. Such behavior was observed for butadiene–styrene [29] or cis-1,4-poly(butadiene) [30]. After analyzing the results obtained for the reference NBR compounds, the significant influence of the filler type on the vulcanization temperature and enthalpy could be seen. Rubber compounds filled with

Fig. 9 DSC curves for the vulcanization of NBR filled with CB and containing ILs

A380 vulcanized at the highest temperatures and with the lowest enthalpy of vulcanization in comparison with other fillers. It is known that during vulcanization, the surface of silica can adsorb accelerators, decreasing the efficiency of vulcanization [13]. The adsorption of accelerator by silanol groups on the silica surface was confirmed by Rattanasom et al. for natural rubber cross-linked in the presence of sulfenamide accelerators [31]. Moreover, sulfur vulcanization prefers alkaline conditions, whereas silica can absorb some water and form acidic silanol groups on its surface in acidic conditions. These processes reduce the efficiency of the cross-linking system. The vulcanization of NBR filled with CB started at temperatures approximately 17 °C lower than those for A380-filled rubber compounds and proceeded with a slightly higher enthalpy of vulcanization. The lowest onset vulcanization temperature was determined for NBR filled with HTA. The exothermic vulcanization peak of HTA-containing elastomer occurred in the temperature range of 117–185 °C, and its enthalpy was about 10 Jg⁻¹ higher than those of other fillers. The beneficial effect of HTA on vulcanization may be due to its alkaline properties. As has already been mentioned, vulcanization proceeds more effectively in an alkaline environment. The presence of basic HTA increases the alkalinity of the environment in which cross-linking reactions take place, thus having an impact on the temperature and enthalpy of this process. However, it should be noted that in the case of NBR containing this filler, intensive post-curing reactions proceeded, with an enthalpy approximately fourfold higher than those for other reference rubber compounds. This could affect the cross-link density of the obtained vulcanizates.

The effects of ILs on the vulcanization temperature and enthalpy depend on the type of filler and the structure of the IL cation. In the case of A380-filled elastomer, ILs reduced

the onset vulcanization temperature by about 15 °C, as well as the temperature of vulcanization peak and the enthalpy of this process. This could be due to the catalytic activity of ILs in the interfacial cross-linking reactions. Furthermore, ILs can adsorb onto the silica surface, as postulated in the literature [9], reducing the ability of the silica to adsorb curatives and water. As a result, the efficiency of the cross-linking system increases. Moreover, the presence of ILs eliminated the post-curing processes and made vulcanization a one-step process occurring in the temperature range of 150–172 °C. The structure of the IL cation had no significant influence on the vulcanization temperature and enthalpy of A380-filled NBR composites. A positive effect of ILs on vulcanization was also achieved for rubber compounds containing CB, especially for pyrrolidinium and piperidinium salts with a saturated heterocyclic ring in the cation. These ILs reduced the onset vulcanization temperature by 30 °C and increased the enthalpy of vulcanization. Additionally, ILs eliminated the second step of the vulcanization process, similar to the case A380-filled NBR. Different influences of ILs were obtained for NBRs containing HTA. ILs with similar structures (BMpyrrolBF₄ and BMpipBF₄) did not affect the onset vulcanization temperature, but reduced the enthalpy of vulcanization by two-fold. On the other hand, pyridinium salt with an unsaturated heterocyclic ring in the cation (BMpyrBF₄) increased the onset vulcanization temperature by 20 °C. It should be noted that ILs did not eliminate the post-curing step or reduce its enthalpy but shifted it to a temperature about 20–30 °C lower in comparison with HTA-filled rubber without ILs. The vulcanization and post-curing took place continuously, one after the other. Another important observation was that for each filler, rubber compounds containing ILs with a saturated heterocyclic ring exhibited similar vulcanization temperature and enthalpy as opposed to NBRs containing a pyridinium salt with an unsaturated ring in the cation. Therefore, it could be concluded that the structure of the IL cation has a very important influence on its activity in vulcanization. Furthermore, it should be noted that the reduction of the vulcanization temperature could not only result from the presence of tetrafluoroborate ILs but also from the application of BA-MBT, which is a very active accelerator of sulfur vulcanization, as has been reported previously [16, 32].

To confirm the specific effects of the filler type and ILs, which were shown by the results of DSC analysis, additional measurements were performed to study the optimal vulcanization times of NBR compounds and the cross-link densities of vulcanizates. These parameters correspond directly with the activity of the cross-linking system and the efficiency of vulcanization and are presented in Table 5.

Table 5 Optimal vulcanization times (t_{90}) of NBR and cross-link densities of vulcanizates (v_e) (standard deviations: $t_{90} \pm 2$ min; $v_e \pm 1.5 \times 10^{-5}/\text{mole cm}^{-3}$)

NBR vulcanizate	t_{90}/min	$v_e \times 10^{-5}/\text{mole cm}^{-3}$
NBR filled with A380		
Ref. without IL	43	18.7
BMpyrrolBF ₄	23	22.2
BMpyrBF ₄	21	22.9
BMpipBF ₄	20	22.3
NBR filled with HTA		
Ref. without IL	25	20.2
BMpyrrolBF ₄	8	20.1
BMpyrBF ₄	5	20.9
BMpipBF ₄	7	19.8
NBR filled with CB		
Ref. without IL	36	22.5
BMpyrrolBF ₄	28	25.1
BMpyrBF ₄	33	24.3
BMpipBF ₄	27	26.5

The rheological property results and cross-link density measurements fully correlate with DSC analysis. The highest optimal vulcanization time of reference rubber compounds without ILs was determined for A380-filled NBR (43 min) due to the adsorption of curatives onto the silica surface that decreased the activity of the cross-linking system. Moreover, the reference vulcanizate containing silica exhibited the lowest cross-link density. Applying ILs reduced the optimal vulcanization time of A380-filled NBR by 20 min and significantly increased the cross-link density. This result confirmed that ILs can adsorb onto the silica surface, reducing the ability of this filler to adsorb curatives and water and, consequently, increasing the efficiency of the cross-linking system. The optimal vulcanization time of the reference rubber compound filled with CB was 7 min shorter than that for A380-containing NBR. ILs with similar structures (BMpyrrolBF₄ and BMpipBF₄) reduced this time by approximately 10 min, whereas BMpyrBF₄ reduced the time by only 3 min. CB-filled NBR showed the highest cross-link density of the reference composites. ILs additionally increased the cross-link density of vulcanizates with CB. The HTA-filled reference rubber compound exhibited the shortest t_{90} . This confirmed the positive effect of this filler on the vulcanization temperature and time. On the other hand, vulcanizates containing HTA showed the lowest cross-link densities. This result was probably due to the intensive post-curing reactions, which followed the vulcanization. The cross-polymerization of butadiene units in the NBR macromolecules, along with cyclization or fragmentation

of elastomer chains, could decrease the efficiency of vulcanization and affect the cross-link density and the structure of the elastomer network. ILs reduced the optimal vulcanization time of NBR/HTA compounds by approximately 20 min but had no influence on the cross-link density of vulcanizates. It should be emphasized that in the case of NBR compounds with HTA, ILs did not eliminate the post-curing stage or even decrease the enthalpy of this process or, therefore, its effectiveness. This may support the assumption that the lowest cross-link density of HTA-filled vulcanizates was due to a decrease in the vulcanization efficiency through post-curing reactions. The results of rheological properties and cross-link density measurements confirmed the catalytic effect of ILs on vulcanization.

Distribution of cross-links in the elastomer network

Having established that the types of filler and ILs used affected the vulcanization process and the cross-link density of vulcanizates, we wanted to study their effect on the structure of the elastomer network formed during vulcanization. DSC was employed to examine the distribution of cross-links in the elastomer network. The method focused on measuring the freezing point depression of the solvent confined inside the swollen polymeric gel and allowed estimation of the mesh size distribution of the elastomeric network. According to Baba et al. [19, 33], a polymeric gel is equivalent to a three-dimensional network composed of adjacent cells, called a “mesh.” Swelling the cross-linked elastomer sample in a suitable solvent yields a swollen gel, and part of the solvent is trapped inside this gel (confined solvent), whereas the excess solvent remains outside (free solvent). Regarding the phase transitions, the free solvent behaves like a pure solvent. Phase transitions of the confined solvent occur at different temperatures depending on the characteristics of the surrounding elastomer network, especially depending on the size of the network mesh. The size of the mesh of elastomers can be related to the difference in the transition temperature (ΔT) between the free and confined solvent, and ΔT can be measured precisely using DSC. Moreover, according to Baba and co-workers, the width of the confined solvent solidification peak corresponds to the distribution of the mesh sizes. The wider the peak of the confined solvent, the wider (more heterogeneous) is the distribution of the mesh sizes [19]. Therefore, the half-widths of the peaks of solvents trapped in the swollen polymeric gel were determined and are presented in Table 6.

Figures 10–12 show the DSC cooling curves of NBR vulcanizates swollen in benzene for 24 h prior to the measurement. Although measurements were carried out for

Table 6 Freezing points (T_f) of free and confined benzene and half-widths of the peaks ($W_{1/2}$) for benzene confined in the swollen polymeric gel (standard deviations: $T_{f(\text{free benzene})} \pm 1.6$ °C, $T_{f(\text{confined benzene})} \pm 1.9$ °C, $W_{1/2} \pm 1.9$ °C)

NBR vulcanizate	$T_{f(\text{free benzene})}/^{\circ}\text{C}$	$T_{f(\text{confined benzene})}/^{\circ}\text{C}$	$W_{1/2}/^{\circ}\text{C}$
NBR filled with A380			
Ref. without IL	− 5.0	− 11.9	8.6
BMpyrBF ₄	− 7.0	− 15.9	8.2
NBR filled with HTA			
Ref. without IL	− 7.0	− 13.2	8.6
BMpyrBF ₄	− 8.2	− 13.0	7.1
NBR filled with CB			
Ref. without IL	− 7.6	− 16.8	10.7
BMpyrBF ₄	− 6.3	− 22.7	5.0

Fig. 10 DSC cooling curves of A380-filled NBR vulcanizates swollen in benzene

all tested vulcanizates, the best separation of the solidification peaks for free and confined benzene was obtained only for the reference vulcanizates without ILs or containing BMpyrBF₄. In the case of vulcanizates with other ILs, these peaks were too close and overlapped, so it was impossible to determine and compare the half-width of the peak for benzene trapped in the swollen polymeric gel.

Two peaks were observed on the DSC cooling curves of NBR vulcanizates swollen in benzene. The first peak, which is sharp, corresponds to the solidification of free benzene, whereas the other, which is relatively broad, results from the solidification of benzene entrapped in the swollen gel. The peak of the confined solvent is shifted toward a lower temperature compared to the peak of free benzene. Its position is directly related to the radius of the mesh (R_p) by the following relationship (Eq. 3) and

Fig. 11 DSC cooling curves of HTA-filled NBR vulcanizates swollen in benzene

Fig. 12 DSC cooling curves of CB-filled NBR vulcanizates swollen in benzene

consequently depends on the cross-link density of the elastomer network [33]:

$$R_p = \frac{-A}{\Delta T} + B \quad (3)$$

where $\Delta T = T_0 - T$; T_0 is the triple point temperature of the solvent (5.5 °C for benzene) and A and B are constants depending on the solvent.

Upon analyzing the data presented in Table 6, it was observed that the peaks of benzene entrapped in the swollen network of vulcanizates containing BMpyrBF₄ are shifted toward lower temperatures in comparison with the reference vulcanizates without ionic liquid. This behavior results from the higher cross-link density of vulcanizates containing BMpyrBF₄ and corresponds to a decrease in the mesh size in the elastomer network. It should be noted that

Table 7 Storage modulus (E') of NBR vulcanizates in the glassy state and rubbery elastic region (standard deviations: E' at $-40\text{ }^{\circ}\text{C} \pm 85\text{ MPa}$, E' at $25\text{ }^{\circ}\text{C} \pm 2.2\text{ MPa}$, E' at $40\text{ }^{\circ}\text{C} \pm 2.2\text{ MPa}$)

NBR vulcanizate	E' at $-40\text{ }^{\circ}\text{C}/\text{MPa}$	E' at $25\text{ }^{\circ}\text{C}/\text{MPa}$	E' at $40\text{ }^{\circ}\text{C}/\text{MPa}$
NBR filled with A380			
Ref. without IL	4884	12	10
BMpyrrolBF ₄	4592	22	20
BMpyrBF ₄	4609	20	19
BMpipBF ₄	4650	19	18
NBR filled with HTA			
Ref. without IL	4489	8	7
BMpyrrolBF ₄	4418	9	8
BMpyrBF ₄	4422	8	7
BMpipBF ₄	4415	7	8
NBR filled with CB			
Ref. without IL	4681	9	8
BMpyrrolBF ₄	4744	9	8
BMpyrBF ₄	4698	8	7
BMpipBF ₄	4709	9	8

the lowest freezing point of confined benzene was determined for vulcanizates filled with CB, which exhibited the highest cross-link densities. On the other hand, BMpyrBF₄ did not affect the cross-link density of vulcanizates filled with HTA, and consequently, no effect of this ionic liquid on the freezing point of benzene entrapped in the swollen polymeric gel was achieved. Taking into account the half-widths of confined benzene solidification peaks, using BMpyrBF₄ had no influence on this parameter in the case of A380-filled vulcanizates but reduced its value for vulcanizates containing other fillers. This effect was particularly evident for CB-filled vulcanizates (Fig. 12). Narrowing of the confined solvent solidification peaks suggests a narrowing of the distribution of mesh sizes of the elastomer network. Therefore, it could be concluded that the distribution of cross-links in the elastomer network of BMpyrBF₄-containing vulcanizates filled with HTA or CB is more homogeneous than that in the reference samples. This behavior may be related to the influence of BMpyrBF₄ on the dispersion of the filler and curatives in the elastomer matrix. ILs were reported to improve the dispersion of CB [6, 14], or HTA [11] and, most importantly, the dispersion of curatives in the elastomers [6, 17]. This effect is not so evident in the case of A380-filled NBR. It could be supposed that the adsorption of ILs onto the silica surface, which was confirmed by DSC and rheometrical measurements, improves the dispersion of the filler but decreases the ability of ILs to prevent the curative particles from agglomeration. Taking into account that cross-linking takes place at the interface between the curatives and the elastomer chains, the better (more uniform) is the dispersion of curatives in the elastomer matrix, the more homogeneous is the distribution of cross-links in the elastomer network formed during vulcanization.

Dynamic mechanical properties

DMA is a very useful method of thermal analysis that provides information about the mechanical properties of viscoelastic materials as a function of time, temperature or frequency [34, 35]. In this work, DMA was employed to study the effects of fillers and ILs on the viscoelastic properties of NBR, such as storage and loss moduli and the loss factor ($\tan \delta$). DMA measurements were performed as a function of temperature to examine the glass transition of elastomer composites and their properties in the rubbery elastic region. The results are presented in Tables 7–8 and Figs. 13–14.

The storage modulus values of the examined NBR composites decreased with increasing temperature (Fig. 14). In the temperature range from -25 to $15\text{ }^{\circ}\text{C}$, the main loss of storage modulus, by more than 2 decades, was observed due to the glass transition of the elastomer. After the transition to the rubbery elastic region, the storage modulus values of the examined vulcanizates did not change significantly in the measured temperature range. The type of filler influenced the storage modulus of NBRs in a glassy state and in the rubbery elastic region. The effect of filler type on the storage modulus was much more dominant than the influence of cross-link density of vulcanizates. The results obtained correlate with the stiffness of vulcanizates, which in the case of the tested composites depended mainly on the type of filler. Regarding the reference composites, the highest storage modulus in the glassy state was shown by vulcanizate filled with nanosized silica A380. It should be noted that vulcanizates containing this filler were much stiffer than those containing CB or HTA. However, the rubbery elastic region E' of the A380-filled reference vulcanizate was only approximately

Table 8 Glass transition temperatures (T_g) and loss factors ($\tan \delta$) of NBR vulcanizates (standard deviations: $T_g \pm 0.7$ °C, $\tan \delta$ at $T_g \pm 0.09$, $\tan \delta$ at 25 °C ± 0.02 , $\tan \delta$ at 40 °C ± 0.02)

NBR vulcanizate	T_g /°C	$\tan \delta$ at T_g /–	$\tan \delta$ at 25 °C/–	$\tan \delta$ at 40 °C/–
NBR filled with A380				
Ref. without IL	– 11.2	0.77	0.22	0.19
BMpyrrolBF ₄	– 10.1	1.05	0.12	0.10
BMpyrBF ₄	– 10.2	1.10	0.12	0.09
BMpipBF ₄	– 10.5	1.02	0.13	0.10
NBR filled with HTA				
Ref. without IL	– 6.4	1.74	0.15	0.11
BMpyrrolBF ₄	– 4.9	1.56	0.17	0.13
BMpyrBF ₄	– 4.5	1.59	0.18	0.14
BMpipBF ₄	– 5.3	1.48	0.15	0.11
NBR filled with CB				
Ref. without IL	– 7.0	1.57	0.16	0.14
BMpyrrolBF ₄	– 6.9	1.47	0.15	0.13
BMpyrBF ₄	– 6.0	1.50	0.17	0.14
BMpipBF ₄	– 6.8	1.45	0.15	0.11

Fig. 13 Storage modulus versus temperature for NBR vulcanizates

3–4 MPa higher than those of other vulcanizates, so the ability to store energy during deformation was quite similar taking into account the potential technological applications of such materials. ILs did not considerably affect the storage modulus of CB or HTA-filled vulcanizates in the measured temperature range. On the other hand, vulcanizates containing A380 and ILs exhibited approximately 7–10 MPa higher storage modulus values in the rubbery elastic region than did the reference vulcanizate and even three times higher modulus values than did vulcanizates with ILs and other fillers. So, it could be concluded that ILs increased the ability of NBR filled with A380 to store energy during deformation.

Regarding the curves of $\tan \delta$ as a function of temperature (Fig. 14), the existence of one transition can be observed the glass transition of the NBR elastomer, with a

Fig. 14 Loss factor ($\tan \delta$) versus temperature for NBR vulcanizates

maximum that represents T_g . The type of filler seemed to influence the T_g value only in the case of A380-filled vulcanizates, which exhibited a T_g of approximately 4 °C lower than those containing other fillers (Table 8). ILs and their structure did not considerably affect the T_g of the elastomer, although their application increased the cross-link density of the vulcanizates. However, elastomer composites are materials with low cross-link densities in comparison with, for example, resins or polyurethanes. In the case of such materials, a relatively small increase in the cross-link density does not considerably restrict the mobility of the elastomer chains and, as a consequence, does not affect the T_g value significantly.

The loss factor is a measurement of a material's ability to dampen vibration. Regarding the reference vulcanizates without ILs, the lowest loss factor at T_g was determined for

A380-filled vulcanizate, which was much stiffer than the other samples. The highest $\tan \delta$ at T_g was exhibited by the vulcanizate with the highest elasticity, which contained HTA. The loss factor at T_g for the CB-filled reference vulcanizate was approximately 0.2 lower than that for HTA-filled NBR. The type of filler had a smaller influence on the damping properties of the reference vulcanizates in the temperature range of 25–40 °C, which was in the rubbery elastic region. NBR filled with CB or HTA exhibited similar values of $\tan \delta$, whereas a slightly higher loss factor was determined for the vulcanizate containing A380. Applying ILs had no significant influence on the loss factor of NBRs filled with CB. Regarding HTA, ILs slightly reduced the value of $\tan \delta$ at T_g but did not affect the loss factor in the rubbery elastic region. A different effect of ILs was observed for NBR containing A380. ILs increased the loss factor at T_g but slightly reduced this parameter in the rubbery elastic region. This effect must have been due to the reduction of the loss modulus, taking into account that ILs increased the storage modulus of silica-filled NBR as presented in Table 7. Generally, ILs had the greatest impact on the loss factor for vulcanizates filled with silica A380. This may have resulted from the possible adsorption of ILs onto the silica surface, which was also indicated by the results of DSC analysis and cross-link density measurements. The adsorption of ILs could affect the dispersion degree of silica particles in the elastomeric matrix, their interaction with elastomer chains, and, consequently, the viscoelastic properties of NBR composites. The examined vulcanizates exhibited stable dynamic properties at the temperatures of use. The storage modulus values and mechanical loss factors did not change considerably with increasing temperature in the rubbery elastic region.

Conclusions

The structures of the IL cations considerably affected their thermal stability and phase transitions. BMpyrrolBF₄ and BMpipBF₄, which exhibit similar cation structures with a five- or six-membered saturated heterocyclic ring, showed similar thermal stabilities and glass transition temperatures. On the other hand, BMpyrBF₄, with a cation consisting of a 6-membered unsaturated heterocyclic pyridinium ring, exhibited the lowest thermal stability and the highest glass transition temperature. The most stable filler was CB, which practically did not undergo thermal changes during heating. Regarding A380, the desorption of water physically absorbed by the surface of the filler occurred at a temperature below 130 °C. The thermal decomposition of HTA proceeded with the loss of physically absorbed water and waters of hydration (100–250 °C), followed by a

dehydroxylation process at higher temperatures, accompanied by decarbonation due to decomposition of the carbonate.

The types of filler and ILs affected the thermal stability of the NBR. Vulcanizates filled with CB or A380 showed similar thermal stabilities, with a $T_{5\%}$ temperature above 400 °C. The lowest thermal stability was exhibited by NBR filled with HTA due to the low thermal stability of the filler, the decomposition of which preceded the pyrolysis of the elastomer. The addition of ILs reduced the thermal stability of NBR vulcanizates without regard to the filler used or the structure of the ionic liquid cation.

The vulcanization of NBR composites without ILs was a two-step exothermic process. Apart from cross-linking, some post-curing reactions proceed at temperatures above 200 °C. The types of filler and ILs affected the vulcanization process. The adsorption of curatives onto the A380 surface reduced the efficiency of vulcanization, resulting in the highest temperature and lowest enthalpy of this process. The lowest temperature and highest enthalpy of vulcanization were determined for NBR filled with HTA. This could be due to the basic characteristics of HTA, since vulcanization proceeds more effectively in an alkaline environment. The influence of ILs on the vulcanization parameters depends on the type of filler. ILs reduced the vulcanization temperature, increased the enthalpy and eliminated the second step of vulcanization (post-curing) for NBR filled with A380 or CB. Regardless of the filler used, rubber compounds containing ILs with a saturated heterocyclic ring exhibited similar vulcanization temperatures and enthalpies as opposed to NBR containing a pyridinium salt with an unsaturated ring in the cation.

BMpyrBF₄ seemed to increase the homogeneity of the cross-link distribution in the elastomer network of vulcanizates filled with HTA or CB. This may be due to the influence of BMpyrBF₄ on the dispersion of the filler and curatives in the elastomer matrix.

The type of filler influenced the viscoelastic properties of NBR. Regarding the reference composites, the highest storage modulus in the glassy state was shown by vulcanizate filled with A380, which was much stiffer than the others. In the rubbery elastic region, the storage modulus values of vulcanizates containing different fillers were quite comparable. ILs did not considerably affect the storage modulus of vulcanizates filled with CB or HTA, whereas they increased the ability of NBRs containing A380 to store energy during deformation. Vulcanizates containing CB or HTA exhibited similar values of $\tan \delta$ in the rubbery elastic region, whereas a slightly higher loss factor was determined for the A380 filler. ILs had the most impact on the loss factor of vulcanizates containing A380. This may result from the possible adsorption of ILs onto the silica surface. The adsorption of ILs could affect the

dispersion degree of silica particles in the elastomeric matrix, their interaction with elastomer chains, and, consequently, the viscoelastic properties of the NBR composites.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflicts of interest.

Informed consent Informed consent was obtained from all individual participants included in the study.

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