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Investigations of Nitrile Rubber Composites Containing Imidazolium Ionic Liquids

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Summary: This work aimed to investigate the impact of hydrophobic imidazolium ionic liquids with alkyl chains of varying length attached to the cation imidazolium ring on the rheometric data, the mechanical, morphological, thermal and conductive properties of acrylonitrile-butadiene rubber (NBR) composites. The presence of ionic liquids not only increased the conductivity (AC) of the composites but also influenced their curing behaviour and mechanical properties. A maximum conductivity of $8.9 \cdot 10^{-8}$ $S \cdot cm^{-1}$ was achieved at room temperature in the NBR sample containing 15 phr (parts per hundred rubber) of 1-hexyl-3-methylimidazolium bis(trifluoromethane- sulfone)imide (HMIM TFSI). Moreover, the presence of HMIM TFSI at 15 phr loading in the NBR composite contributed most significantly to the downward shift in the glass transition temperature (T_g) from -30 to -33 °C, indicating a plasticizing effect

Keywords: acrylonitrile-butadiene rubber; elastomer composites; ionic conductivity; ionic liquids; reinforcing filler

Introduction

Ionic liquids (ILs) have recently attracted considerable attention due to their useful physicochemical properties like non-flammability, low vapour pressure, good chemical and electrochemical stability, and high ionic conductivity.[1–4] ILs have been investigated as potential electrolytes for applications in electrochemical devices including lithium ion batteries,[5] fuel cells,[6,7] and solar batteries.[8,9] Given their unique properties, ILs can potentially find use in polymers as plasticizers[10,11] and antistatic additives.[12] In elastomers, ionic liquids are used to enhance the ionic conductivity, mechanical and thermal properties of the polymer composites and to improve the filler dispersion (e.g., carbon nanotubes,[13–15] carbon black,[16,17] halloysite nanotubes,[18,19] or silica[20–22]) in the hydrophobic matrices. Cho[23] and Marwanta[24] employed NBR and an ionic liquid to prepare elastic polymer electrolytes. NBR was expected to be suitable as polymer electrolytes because of its polar chemical structure and excellent mechanical properties such as high tensile strength and good elasticity. The rubber composites characterised by the before mentioned properties must be cured, which is typically performed with a sulfur-based system. During this process, the long chains of the rubber molecules react with the vulcanisation agents to become crosslinked, forming three-dimensional structures. This reaction transforms the soft plastic-like material into a strong elastic product.[25] Previous studies[26] have indicated that the addition even of 1 phr (parts per hundred rubber) ionic liquids can affect the sulfur curing system and thus the crosslink density of the final composites. The authors concluded that alkylimidazolium and alkylammonium salts catalyse the

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interface crosslinking reactions by improving the dispersion of the curatives, particularly zinc oxide, within the polymer matrix. Therefore, the vulcanization time of the rubber compounds decreases significantly, and the crosslink density of the vulcanizates increases. However, no information regarding the influence of higher highly conductive ionic liquid content is available in the literature (for example, the effect of the bis(trifluoromethanesulfone)imide anion on the properties of elastomer composites that crosslink via a sulfur-based system). Heinrich[13] studied the influence on the elastomer properties of varying the IL proportions and discussed the efficacy of ionic liquid-modified MWCNTs on polychloroprene rubber. Likozar[27] described the properties of HNBR polymer films that contain different ionic liquids. Samples were prepared by pressing the compounds reinforced with MWCNT-OH between steel plates (180 °C) to obtain a crosslinked structure. Then, the HNBR composites were immersed in an excessive quantity of the ionic liquids (including ionic liquids containing the bis (trifluoromethanesulfone)imide anion), thus avoiding elastomer curing in the presence of ionic liquids. We investigate the effect of the hydrophobic imidazolium salts 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfone)imide (EMIM TFSI), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfone) imide (BMIM TFSI), and 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfone) imide (HMIM TFSI) on the rheometric data for acrylonitrile-butadiene rubber (NBR) in which silica was used as a reinforcing filler. The effect of the imidazolium salts on the mechanical, morphological, thermal and ionic conductivity properties of the NBR/SiO_2/IL composites was also investigated.

Materials and Methods

Acrylonitrile-butadiene rubber NBR (Perbunan 28-45F) containing 28 wt% acrylonitrile was obtained from Lanxess, GmbH. The Mooney viscosity was (ML1 + 4 (100 °C):45). The NBR rubber was cured using a conventional sulfur (Siarkpol, Poland)-based crosslinking system in the presence of a mercaptobenzothiazole accelerator (MBT Lanxess, GmbH). Zinc oxide (Lanxess, GmbH) and stearic acid (Sigma Aldrich, GmbH) were used to activate the sulfur vulcanization. Hydrophilic fumed silica Aerosil 380, supplied by Evonik Degussa, GmbH, was used as a reinforcing filler. The ionic liquids 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfone) imide (EMIM TFSI), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfone) imide (BMIM TFSI), and 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfone) imide (HMIM TFSI) were provided by Sigma Aldrich. The rubber mixtures consisted of the following: NBR rubber (100 phr), sulphur (2 phr), mercaptobenzothiazole (2 phr), zinc oxide (5 phr), stearic acid (1 phr), Aerosil 380 (30 phr) and ionic liquid at different loadings (5, 10, 15 phr). The rubber mixes were prepared via a two-step procedure. The rubber and SiO_2 filler mixed with an ionic liquid were homogenised in an internal mixer (Brabender Measuring Mixer N50). The rubber compounds were processed at a rotor speed of 50 rpm and at an initial temperature of 50 °C. The compounded rubbers were then milled with sulfur, mercaptobenzothiazole, zinc oxide and stearic acid in a laboratory rolling mill (roll dimensions: D = 200 mm, L = 450 mm).

The rheometric study was conducted in a rheometer (MonTech MDR 3000, Germany) at 160 °C. The difference between the maximum (M_H) and the minimum torque (M_L) of the vulcanization curve is defined as the ultimate rheometric torque (ΔM). The time required to reach 90% (M_H-M_L) which is the optimum cure time (t_{90}). The mixed stocks were cured in a standard hot press at 160 °C and at the optimum cure time for the samples. The stress-strain tests were performed on a universal material testing machine (Zwick model 1435) with a crosshead speed of 500 mm/min according to the standard PN-ISO 37-2005. To measure the mechanical properties, five different dumbbell-shaped specimens were punched from each rubber sample. The crosslinking density in the vulcanized network was determined by the method of equilibrium swelling. The vulcanizates were subjected to equilibrium swelling in toluene for 48 h at room temperature. The swollen samples were then weighed on a torsion balance, dried to a constant weight in a dryer at 60 °C and reweighed after 48 h. The crosslinking density was determined using the Flory–Rehner equation.[28] The tensile strength and elongation at break were measured at room temperature. The morphology of the elastomer matrix containing the ionic liquids was estimated using scanning electron microscopy with a Zeiss SEM microscope. The NBR vulcanizates were broken down in liquid nitrogen, and their fracture surfaces were examined. Prior to the measurements, the samples were coated with carbon. The samples underwent DSC (Q 200 DSC, TA Instruments, USA) at a heating rate of 10 °C/min over the temperature range from -80 to 180 °C under a nitrogen atmosphere. The glass transition temperatures (T_g) were determined at the midpoint of this step. A dynamic mechanical analysis of the composites was performed in a dynamic mechanical analyzer (TA Instrument Q 800 DMA, USA). The storage modulus (E′) and loss tangent (tan δ) were measured in the tension mode at temperatures ranging from -90 to 100 °C at a frequency of 10 Hz and a heating rate of 2 °C/min. The dielectric measurements were conducted using broadband dielectric spectroscopy (Novocontrol alpha analyser, Hundsagen, Germany) over the frequency range from 10^{-1} to 10^{7} Hz at room temperature. The samples were placed between two copper electrodes with diameters of 20 mm.

Result and Discussion

The crosslinks form due to chemical reaction between the rubber matrix and the curing agent during the vulcanization process that is performed at the time of moulding. The vulcanization characteristics, expressed in terms of the scorch time (t_{02}), the optimum cure time (t_{90}) and the difference between the maximum and minimum torque values (ΔM) for the NBR/SiO_2 and NBR/SiO_2/IL systems are reported in Table 1. The rheographic profiles of the NBR/SiO_2 and NBR/SiO_2/IL composites with varying ionic liquid loading are represented in Figure 1. The high value of specific surface area of the silica in NBR/SiO_2 resulted in a higher viscosity and stiffness and contributed to the high torque values (M_L, M_H, ΔM). Also

Table 1.
Curing characteristics of the NBR, NBR/SiO_2 and NBR/SiO_2 ionic liquid-filled composites.

NBR composites	IL [phr]	M_L[a] [dNm]	M_H[b] [dNm]	ΔM[c] [dNm]	t_{02}[d] [min]	t_{90}[e] [min]	CRI[f] [min]
–		0.6	9.6	9.0	0.7	6.5	17.2
SiO_2	–	4.0	31.6	27.6	0.8	29.4	3.5
SiO_2EMIM TFSI	5	3.4	32.5	29.1	0.3	22.8	4.4
SiO_2EMIM TFSI	10	3.3	28.6	25.3	0.7	28.0	3.7
SiO_2EMIM TFSI	15	3.2	26.8	23.6	0.9	29.3	3.5
SiO_2BMIM TFSI	5	4.4	32.7	28.3	0.6	26.1	3.9
SiO_2BMIM TFSI	10	3.8	27.7	23.9	0.6	27.8	3.6
SiO_2BMIM TFSI	15	3.1	25.5	22.4	0.8	28.8	3.6
SiO_2HMIM TFSI	5	4.6	30.5	25.9	0.6	27.7	3.7
SiO_2HMIM TFSI	10	3.3	26.4	23.1	0.6	28.3	3.6
SiO_2HMIM TFSI	15	3.2	25.2	22.0	0.7	28.9	3.6

[a] M_L- min. torque,
[b] M_H- max. torque,
[c] $\Delta M = M_H - M_L$,
[d] t_{02}- scorch time,
[e] t_{90}–optimum curing time,
[f] CRI – curing rate index ($100/\, t_{90}–t_{02}$).

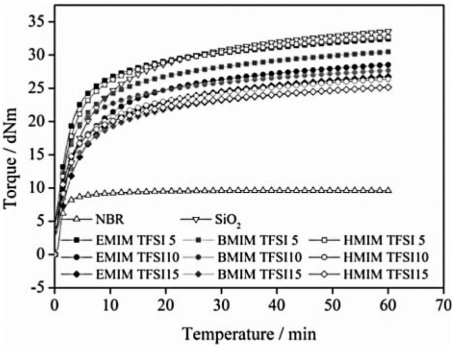

Figure 1.
Cure characteristics of NBR, NBR/SiO$_2$ and NBR/SiO$_2$ ionic liquid - filled composites.

the high value of specific surface area of silica contributes to the extension of curing reaction time (t$_{90}$). The sulfur crosslinking system is adsorbed onto the silica surface, which results in a vulcanization that is slower than the crosslink kinetics of pure NBR.[29] When the silica is accompanied by 5 phr EMIM TFSI, the curing reaction becomes more rapid (higher CRI).

While no appreciable differences were observed in scorch times (t$_{90}$) for the composites containing 10 and 15 phr IL in comparison with neat (NBR/SiO$_2$), the 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfone)imide (EMIM TFSI)-filled compound exhibited a considerable reduction in the scorch and curing time at a reduced imidazolium-salt loading (5 phr). This result can be ascribed to the accelerating effect of ionic liquids on the sulfur curing-based system. The literature indicates that some ionic liquids act as accelerators by the interface crosslinking reactions and improve the dispersion of zinc oxide.[26] The authors also found that the optimal vulcanization time decreased with the length of the alkyl chain attached to the imidazolium ring in an ionic liquid molecule. For the ionic liquids with longer alkyl chains (1-butyl-3-methylimidazolium bis(trifluoromethanesulfone)imide (BMIM TFSI) and 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfone)imide (HMIM TFSI) the accelerating effect on the curing time was less pronounced than for EMIM TFSI, when the ionic liquid concentration in the rubber composites was 5 phr and the rheometric data for the BMIM TFSI and HMIM TFSI composites were similar to those of the neat material. The mobility of the BMIM TFSI and HMIM TFSI in the polymer matrix is most likely reduced by the longer alkyl chains of the cations, what can explain their lower activity during the curing process. By increasing the quantity of EMIM TFSI ionic liquid (for 10 and

Table 2.
The properties of NBR, NBR/SiO$_2$ and the ionic liquid-filled composites.

NBR composites	IL phr	$\nu^{a)}$ $*10^{-5}$ [mol cm^{-3}]	SE$_{300}$$^{b)}$ [MPa]	TS$^{c)}$ [MPa]	EB$^{d)}$ [%]	$Tg^{e)}$ [°C]	$\sigma_{AC}$$^{f)}$ [S · cm^{-1}]
–	–	5.9	2.2 ± 0.2	4.0 ± 0.9	450 ± 14	−28	$7.6 \cdot 10^{-10}$
SiO$_2$	–	5.4	3.9 ± 0.3	18.1 ± 2.0	640 ± 25	−30	$3.6 \cdot 10^{-10}$
SiO$_2$EMIM TFSI	5	6.4	4.7 ± 0.3	23.8 ± 1.7	690 ± 20	−30	$1.3 \cdot 10^{-8}$
SiO$_2$EMIM TFSI	10	5.7	3.9 ± 0.2	21.8 ± 2.1	706 ± 21	−30	$3.1 \cdot 10^{-8}$
SiO$_2$EMIM TFSI	15	5.3	3.3 ± 0.1	20.9 ± 1.9	715 ± 18	−30	$6.0 \cdot 10^{-8}$
SiO$_2$BMIM TFSI	5	5.8	4.3 ± 0.2	22.8 ± 1.6	700 ± 19	−30	$1.3 \cdot 10^{-8}$
SiO$_2$BMIM TFSI	10	5.5	3.7 ± 0.3	21.9 ± 1.6	751 ± 21	−31	$3.9 \cdot 10^{-8}$
SiO$_2$BMIM TFSI	15	5.1	3.3 ± 0.2	19.9 ± 2.0	755 ± 24	−32	$7.3 \cdot 10^{-8}$
SiO$_2$HMIM TFSI	5	5.8	4.2 ± 0.3	22.5 ± 2.1	685 ± 18	−30	$1.6 \cdot 10^{-8}$
SiO$_2$HMIM TFSI	10	5.5	3.3 ± 0.2	18.9 ± 1.7	711 ± 19	−31	$4.0 \cdot 10^{-8}$
SiO$_2$HMIM TFSI	15	5.2	2.7 ± 0.1	18.2 ± 1.9	820 ± 23	−33	$8.9 \cdot 10^{-8}$

[a)] ν - crosslink density,
[b)] SE$_{300}$–modulus at 300% elongation
[b)] TS – tensile strength,
[c)] EB – elongation at break,
[d)] Tg - glass transition temperatures from DSC
[e)] σ_{AC} – AC conductivity, 1 kHz, 25 °C.

15 phr) in the composites, the torque values (M_L, M_H, ΔM) demonstrated a downward trend, while the scorch and curing times increased. A similar tendency was observed for composites containing BMIM TFSI and HMIM TFSI. The crosslink densities of the NBR/SiO_2 and the filled ionic liquid vulcanizates are provided in Table 2. As previously mentioned, some of the ionic liquids may affect the sulfur crosslinking system and therefore the final crosslink density. Our investigation of the swelling method indicated that the addition of 5 phr ionic liquid increases the number of network nodes to 6.4 mol/cm^3 (EMIM TFSI) when the NBR/SiO_2 density was 5.4 mol/cm^3. For the ionic liquids with longer alkyl chains (BMIM TFSI, HMIM TFSI) the crosslink densities of the samples are lower. This trend is in good agreement with the rheometric data and confirmed that EMIM TFSI had the highest activity in the curing process. The crosslink density was also found to decrease with increasing the ionic liquid loading, which suggests that a higher ionic liquid content can hinder the formation of the polymer network.

The tensile strength was improved up to 23.8 MPa for the NBR/SiO_2/EMIM TFSI 5 composite, the NBR/SiO_2/BMIM TFSI 5 samples (up to 22.8 MPa) and the NBR/SiO_2/HMIM TFSI 5 (up to 22.5 MPa) in comparison with neat NBR/SiO_2 (18.1 MPa). The addition of imidazolium salts made the NBR/SiO_2/IL composites less stiff, as was evident from the higher percentage of elongation at break. The highest EB value was observed for a composite containing 15 phr ionic liquid with a hexyl group (HMIM TFSI). Moreover, the modulus at 300% elongation of the NBR/SiO_2/IL composites demonstrated a downward trend with an increasing quantity of ionic liquid in the samples. This

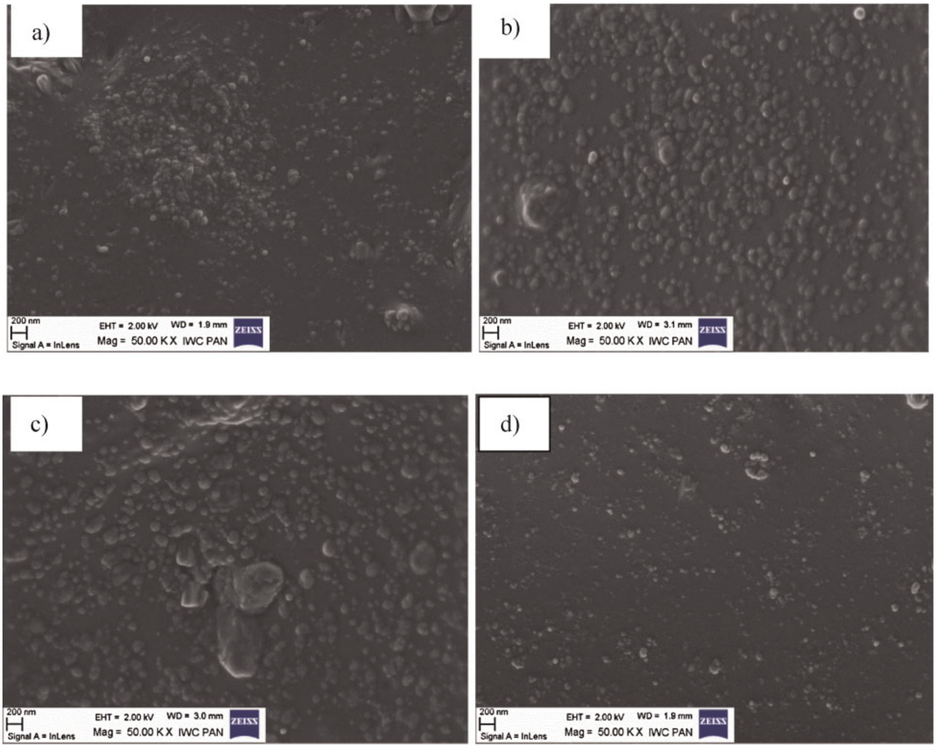

Figure 2.
SEM micrographs of (a) NBR/SiO_2, (b) NBR/SiO_2/EMIM TFSI 5 phr, (c) NBR/SiO_2/EMIM TFSI 10 phr, (d) NBR/SiO_2/EMIM TFSI 15 phr.

result correlates with the fact that an IL can act as a plasticizer and affect the physical properties of the composite. The improved mechanical properties may be attributed to the slight increase in crosslink density and likely improved silica dispersion in the presence of imidazolium salts (Fig. 2); higher IL quantities (10 phr, 15 phr) led to the deterioration of the mechanical properties in the composites. This effect can be explained by the plasticizing of the composites containing a higher IL concentration. It is worth to note that the presence of nitrile polar groups (–CN) in the NBR rubber results in interactions between the silica filler (–OH) and the NBR rubber and provides good mechanical properties in the composites. Marwanta[24] reported a Raman study of NBR/EIMM TFSI composites that detected the existence of an interaction between the TFSI anion and the –CN group, which may be responsible for the improved compatibility of this type of ionic liquid with a polar matrix.

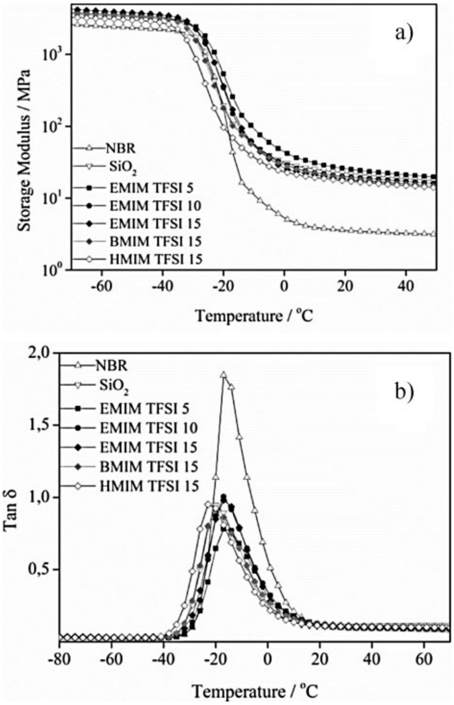

Figure 3.
Temperature dependence of the storage modulus E′ (a) and the loss tangent tan δ (b) values at 10 Hz for the NBR, NBR/SiO_2 and NBR/SiO_2 composites with differing IL mass ratios.

Figure 3 (a, b) presents the temperature dependence of the storage modulus (E′) and the loss tangent (tan δ) values for the NBR/SiO_2/IL composites with different IL ratios. The storage modulus and loss tangent curves display only one transition, and the plots of E′ and tan δ versus the temperature shift toward lower temperatures as the quantity of the BMIM TFSI and HMIM TFSI imidazolium salts increases.

This effect was the most prominent for composites containing 15 phr HMIM TFSI ionic liquid. The T_g shift toward lower temperatures can be attributed to the plasticizing effect of the ionic liquids investigated by Scott,[10,11] who employed 1-ethyl-3-methyl imidazolium tetrafluoroborate as a plasticizer for the polymer and reported that ionic liquids are better than conventional plasticizers. The curves on the storage modulus (E′) graph in both the glassy and rubbery regions shifted toward lower values when the ionic liquid concentration increased, which can be explain by plasticizing effect of the ionic liquid in the polymer matrix. The glass transition temperatures of the NBR/SiO_2/IL composites obtained via DSC demonstrate two tendencies as observed in Table 2: With an increase in the proportion of ionic liquid for NBR composites containing BMIM TFSI and HMIM TFSI, the T_g values of the NBR/SiO_2/IL are decreased to −32 °C and −33 °C at 15 phr.

The plasticizing effect was most prominent for ionic liquid with a long side chain attached to the imidazolium ring (HMIM TFSI). The increase in the ionic liquid content increases the conductivity, but the alkyl chain length was found to have only a small impact on the ionic conductivity (Table 2). The ionic conductivity was the best around $8.9 \cdot 10\text{-}8\ \mathrm{S \cdot cm^{-1}}$ when the content of HMIM TFSI was 15 phr. The higher conductivity can be attributed to the plasticizing effect of longer alkyl chain on the polymer matrix and consequently an

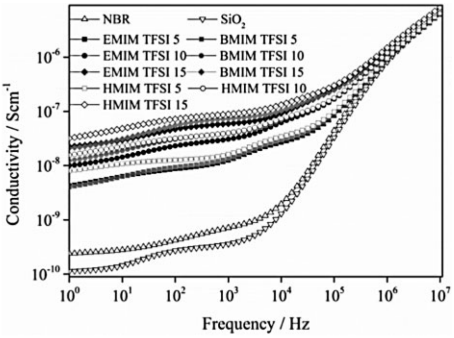

Figure 4.
Variation of the ionic conductivity with frequency and ionic liquids loadings.

improved mobility of the charge carriers. In addition, Figure 4 provides the ionic conductivity of the NBR/SiO_2/IL composites in comparison with the NBR and NBR/SiO_2 as a function of the frequency at room temperature. The presence of silica in the polymer resulted in a decreased conductivity ($3.6 \cdot 10^{-10}\ S \cdot cm^{-1}$) in comparison with that of the unfilled NBR ($7.6 \cdot 10^{-10}\ S \cdot cm^{-1}$).

The conductivity measurements show three characteristic spectral regions: at high frequencies (10 kHz – 10 Hz), an increase in the values of σ' is observed due to local charge fluctuations corresponding to a capacitive response of the material. This is due to the fact the hoping-time of the charge carriers is much longer than the experimental time-scale. In the frequency range between ≈100–10 kHz the development of a quasi-plateau becomes evident and correspond to the long-range diffusion of the charge carriers corresponding, by extrapolation to lower frequencies, to the value of the DC-conductivity. The transition between this plateau and the increase in σ' observed in the high frequency range is marked by a characteristic frequency f_e corresponding to the hoping time of charge carriers $\tau_e = 1/2\pi f_e$. It is observed that the addition of the ionic liquid shifts the characteristic frequency f_e to higher values, which is related to an enhanced mobility of the charge carriers due to plasticizing effects. In the same time, the DC-conductivity value increases with increasing the concentration of the ionic liquid in the material. In the low frequency region (1 Hz – 100 Hz), a week decrease in the values of σ' is noticed, due to the phenomenon of the electrode polarization caused by a blocking effect of the charge carriers in the vicinity of the electrodes.

Conclusion

This study examined the influences of the alkyl chain length of an imidazolium cation and the IL concentration on the properties of NBR/SiO_2 composites. Increasing the quantity of IL in the NBR/silica composites increased the AC conductivity from $3.6 \cdot 10^{-10}\ S \cdot cm^{-1}$ to $8.9 \cdot 10^{-8}\ S \cdot cm^{-1}$ at the highest IL content of 15 phr. The T_g of NBR/SiO_2 composites decreased as the length of the pendant alkyl chain in the IL cation increased, changing from 1-ethyl-3-methylidazolium to 1-hexyl-3-methylimidazolium. The most significant plasticizing effect was noted for the NBR/SiO_2 composite filled with 15 phr HMIM TFSI as the T_g decreased with the increasing ionic liquid content from –30 °C to –33 °C. Moreover, the alkyl chain length was found to slightly affect the ionic conductivity of the polymers. The higher ionic conductivity in the NBR/SiO_2 composites can be correlated to the plasticizing nature of the IL-containing 1-hexyl-3-methylimidazolium cation HMIM. Although the NBR/SiO_2 composites exhibited improved conductivity in the presence of ILs, a higher IL concentration decreased the mechanical properties of the composites due to plasticization of the IL in the NBR matrix. The presence of an ionic liquid with a TFSI anion provides quite good dispersion of the silica filler at each concentration; however, the mechanical properties of the composites were found to deteriorate. The highest increase in the strain-stress behaviour was observed for composites containing 5 phr EMIM TFSI. Moreover, EMIM TFSI in this quantity contributed most significantly to the formation of crosslinks and to the accelerated curing process.

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