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# Applications of Ionic Liquids in Elastomeric Composites: A Review

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## Abstract

Ionic liquids (ILs) are organic salts that are liquid at ambient temperatures. ILs are considered a versatile class of chemicals because their properties can be easily tailored for specific applications. Due to their negligible vapor pressure, non-flammability, and thermal stability in the temperature range for preparation and processing of elastomeric composites, ILs are being used increasingly in the field of elastomer science and technology. In this review, the advantages of ILs as functional additives for elastomeric composites are discussed, with special emphasis on their use as dispersing agents for fillers, components of conducting rubber composites, crosslinkers or components of crosslinking systems.

**Keywords:** ionic liquids, elastomer, composites, dispersion degree, conductive composites

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## 1. Introduction

ILs are generally defined as salts with melting temperatures lower than 100°C [1]. Recently, IL research has been one of the most rapidly growing fields in chemistry and in industry, mainly due to many unique properties of ionic liquids. ILs can solvate a large variety of organic polar and nonpolar compounds, and they show potentially “environmentally friendly” characteristics due to their negligible vapor pressure and non-flammability [2, 3]. Therefore, ILs are used as “green” solvents for numerous applications [4]. Moreover, their chemical and physical properties can be tuned for a wide range of potential applications by varying their cation and anion components. The anti-electrostatic properties of ILs have also been described [5]. Recently, ILs have not only been employed as solvents for various types of polymerizations [6–8] but they

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have also been used to dissolve polymers (cellulose [9], silk fibroin [10] and starch [11]) to create new polymer composites [12], as plasticizers for many kinds of polymers [13] or for the preparation of polymer gels [14] and finally as effective wood preservatives [15]. The applications of ILs as novel electrolytes for electrochemical polymerization have also been reviewed [16]. ILs, due to their high-boiling points (300–450°C, which are also their decomposition temperatures), their low vapor pressure, their low volatility, their ability to create nonexplosive mixtures of their vapors with air, and their high flash-point, can be used successfully in elastomer technologies.

This chapter presents an overview of different applications of ILs in elastomeric composites. The main applications of ILs in elastomer technology include the improvement of fillers and the dispersion of other solids in the elastomer matrix, the preparation of conducting rubber composites, or using ILs as crosslinkers or other components of crosslinking systems (e.g., activators or vulcanization accelerators).

## 2. Use of ILs to improve the dispersion of solids in elastomers

The basic requirement for the reinforcement effect is to produce a homogeneous dispersion of the filler particles in the elastomeric matrix that results in good interphase adhesion [17]. However, most fillers exhibit a high degree of agglomeration, which makes it technologically difficult to obtain a homogenous dispersion in the elastomer. The unique chemical structure of ILs promotes the dispersion of nanoparticles in polymers owing to the surface modification of the nanoparticles with the ILs, which increases the interactions between filler particles and the elastomer matrices, especially in the case of silica, clays, carbon black and carbon nanotubes (CNTs). Because ILs are nonvolatile and nonflammable, the process of carbon nanotube modification and incorporation into an elastomeric matrix could be environmentally friendly. Moreover, ILs act as a lubricant; so, the process of modification is not accompanied by structural disruption of CNTs [18].

In 2007, Fukushima and co-workers reported a novel use for ILs as modifiers for carbon nanotubes, which enabled the production of soft composite materials that contained CNTs [19]. The use of ILs allowed for the noncovalent and covalent modifications of CNTs and for the formation of polymer composites with improved physical properties. In the presence of ILs, CNT bundles were reduced and unrolled. The result was fine bundles of CNTs that formed a network structure in the elastomeric matrix. This was related to the possible specific interactions between the imidazolium cation of ILs and the  $\pi$ -electronic carbon nanotube surface. The use of ILs during the processing of CNTs did not require solvents and did not alter the structure of the  $\pi$ -conjugated nanotube.

Subramaniam et al. reported an effect of the 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BmiTFSI) on the properties of polychloroprene rubber (CR) composites that contained multi-walled carbon nanotubes (MWCNTs) and suggested an optimum weight ratio (MWCNTs:BmiTFSI) to achieve an appropriate balance between mechanical and electrical properties of the composites [20]. After the modification process, the structure of the carbon nanotubes was well maintained, indicating a physical interaction between  $\pi$ -electrons on the MWCNT surface and the imidazolium cation of the BmiTFSI. This improved the dispersion of

the MWCNT in the CR elastomer, and as a consequence, increased the filler network, which was supported by strain sweep measurements. The optimum MWCNT/BmiTFSI ratio was reported to be 1:5. Higher loading of BmiTFSI caused deterioration of the composites mechanical properties. It was concluded that the use of an imidazolium ionic liquid resulted in increased electrical conductivity, as well as a reinforcing effect of the nanotubes in the CR elastomer. Addition of BmiTFSI-modified MWCNTs increased the tensile modulus and hardness of the CR composites, which clearly promoted dispersion of the nanotubes in the elastomeric matrix.

Das et al. [21] confirmed that the addition of ILs ensures better interactions between rubber and the MWCNTs, and therefore, improves the compatibility between the nanotubes and the elastomer and, consequently, their dispersibility in the elastomeric matrix. ILs, such as 1-allyl-3-methylimidazolium chloride (AMICl), were used to blend the styrene-butadiene (S-SBR) and polybutadiene rubber (BR) that contained MWCNTs. Using 3 phr, AMICl-functionalized MWCNTs caused a three-fold increase in the composites' tensile strength. Despite such small quantities of MWCNTs, the sample was stretched up to 456% without mechanical failure. Therefore, it was clear that an AMICl with a double bond in the structure produced the best reinforcing activity for composites containing 3 phr of MWCNTs. Moreover, it was suggested that AMICl acted as a coupling agent between the CNTs and the rubber chains and, hence, that the twisted structure of the CNTs held a certain amount of rubber and enhanced the three-dimensional interactions of the CNTs with the elastomeric matrix. A specific interaction between the MWCNTs and the rubber matrices in the presence of AMICl was postulated. The double bond of AMICl was presumably chemically linked with the double bond of the diene rubber chains by sulfur bridges, which then interacted with the  $\pi$ -electrons of the CNTs due to delocalization of the  $\pi$ -electrons in the imidazolium cation of AMICl. Transmission electron microscopic images confirmed the improved dispersion of MWCNTs that were functionalized with AMICl in the rubber matrix. Moreover, this ionic liquid promoted the formation of MWCNT clusters with a cellular structure in the elastomeric matrix that confirmed the strong adhesion of carbon nanotubes to the rubber phase and a special bound rubber aggregation in the reported composites.

One of the most effective reinforcing fillers for rubber compounds is carbon black (CB) with the surface of graphitic structures, which possess delocalized  $\pi$ -electrons. Particles of CB can interact with ILs in a manner similar to CNTs. Kreyenschulte et al. [22] investigated the interactions of AMICl with different types of carbon black and demonstrated strong interactions between AMICl and CB, as well as an improvement of the filler's dispersion in the elastomers. CB formed a bucky gel with AMICl, and an increase in the glass transition temperature ( $T_g$ ) of ionic liquid was observed. This effect was more apparent when the CB was graphitized; thus, a larger fraction of the CB surface was coated with graphitic crystals that can interact with AMICl via cation  $\pi$ -interactions. AMICl-modified carbon blacks were applied as fillers for S-SBR/BR composites and ethylene-propylene-diene rubber (EPDM). AMICl was premixed with CB, using ethanol and an ultrasonic treatment, and then dried before mixing with elastomers. As mentioned above, Fukushima et al. have reported that CNTs are able to build so-called bucky gels by physical crosslinking of nanotube bundles by mediating the molecular ordering of imidazolium-based ILs [23]. To study this behavior, which can be caused by CB or by its mixture with AMICl, analysis of the frequency dependence of the storage modulus and the loss modulus was performed which revealed significant differences. Hydrodynamic

reinforcement of the elastomers in the presence of CB particles that were modified with ILs could not explain the differences in the frequency dependencies of the storage and the loss modulus. Therefore, it was concluded that particles of CB can form gels in the presence of ILs, similar to CNTs. AMICI appeared to react either with vulcanization systems or with the double bonds of the rubber matrix, especially for EPDM, which decreased the crosslink density and thus affected the mechanical properties of the composites. For S-SBR/BR blends with AMICI-modified CB, the elongation at break was increased slightly, but there was no influence on the rupture strength. For EPDM vulcanizates, AMICI-CB caused a huge increase in the elongation at break and a significant increase in the rupture strength compared to samples without ILs.

Silicone rubber is a special rubber with improved electrical insulation, high elasticity and flexibility, and low modulus. Xu, Wang, et al. fabricated a novel, flexible piezoresistive material by mechanical grinding and two-roll mixing of silicone-rubber (SR), conductive CB and the ionic liquid 1-hexadecyl-3-methylimidazolium bromide (HdmiBr) that was applied to improve the dispersibility of the filler in SR matrix [24]. CB and HdmiBr were effectively co-grinded in a mortar and mixed with silicone rubber. A uniform dispersion of CB particles was observed in both composites (CB/SR and CB-HdmiBr/SR), but the size of the CB particles in the SR that contained ionic liquid was much smaller. Some of the HdmiBr was distributed on the surface of the CB, and attractive interactions between the imidazolium cation of the HdmiBr and the  $\pi$ -electrons on the CB surface were reported to improve the compatibility between the SR matrix and the CB and, consequently, the extent of dispersion in the elastomer. Additionally, these composites were characterized by a lower percolation threshold compared with the composite without HdmiBr. About 5 vol.% of CB-HdmiBr filler was sufficient to obtain higher piezoresistivity, shorter time of relaxation, and better cyclic repeatability of the composites, due to the plasticizing effect of the HdmiBr which resulted in the forced motion of the CB particles in the SR elastomeric network.

ILs were also reported to interact with a specific type of filler—graphene. A perfect form of graphene consists ideally of a flat, single layer material. However, in reality, some ripples are formed due to thermal fluctuations, which along with associated waviness, may affect its ability to reinforce composite materials [25]. Generally, elastomer/graphene and graphite composites can be fabricated by solution mixing, melt blending, and in situ polymerization methods, but it is difficult to incorporate chains of rubber macromolecules directly into the interlayers of graphite. There are many surfactants that can facilitate the dispersion of graphene in polymers [26]. The increased recognition gained by ILs is due to their unique capacity of imparting surface charges to the graphene sheet and thereby increasing colloidal stability [27].

Xiong et al. demonstrated that adding modified ionic liquid graphene oxide (GO-ILs) to bromobutyl rubber (BIIR) improved the thermal stability and thermal conductivity of the BIIR [28]. The thermal stability of BIIR has always been a concern because of the double bonds, which could be generated by eliminating HBr from its backbone [29]. Suitably prepared GO was modified with 1-butyl-3-methylimidazolium hexafluorophosphate (BmiPF<sub>6</sub>) and then incorporated into a BIIR matrix. BmiPF<sub>6</sub> was successfully intercalated into the interlayer of GO, resulting in an increased degree of GO exfoliation, which consequently improved the dispersion in the BIIR matrix due to the strong interfacial interactions between GO-BmiPF<sub>6</sub> and BIIR rubber chains.



Addition of GO intercalated with BmiPF<sub>6</sub> increased the thermal stability of composites as well as the T<sub>g</sub> of BIIR, due to the attractive interactions of the elastomer chains with the large surface area of the GO-BmiPF<sub>6</sub>. Moreover, an improvement of the thermal conductivity of GO-BmiPF<sub>6</sub>/BIIR nanocomposites was observed compared with that of the unfilled BIIR.

Silica is widely used as a filler for elastomers because of its excellent mechanical properties, high thermal and chemical stability, a suitable pore structure, the presence of silanol groups on the surface and its high specific surface area [30]. ILs can be used to modify the surface of silica [31], mainly due to the  $\pi$ - $\pi$  interactions between the cations and anions of the ILs with active sites on the silica's surface [32]. Generally, nanoparticles of silica after modification with ILs are monodispersed and smooth spheres. The structure of the applied ILs significantly influences the surface and properties of modified silica nanoparticles, thereby improving the hydrophobicity to encourage the stability of dispersions and suspensions of this filler in proper dispersants [33].

ILs can be used to increase the degree of dispersion of silica fillers and vulcanization activators (zinc oxide) nanoparticles, as was reported by Maciejewska et al. [34]. The addition of ILs (salts of benzylimidazolium, alkylpyridinium, alkylpyrrolidinium, or alkylpiperidinium) produced a homogeneous dispersion of silica and zinc oxide nanoparticles in the SBR rubber. This resulted in reduced time and temperature of vulcanization and increased the crosslink density, thermal stability of vulcanizates and their aging resistance under the influence of UV radiation.

ILs with specific structures can be employed as interfacial modifiers for various silica-filled polymer composites [35]. Lei and Tang reported using 1-methylimidazolium methacrylate (MimMa) as a modifier for SBR to improve the dispersion of silica and increase the interfacial interactions between SBR and the filler [36]. MimMa was polymerized radically and grafted onto rubber chains during vulcanization, forming the graft product poly(SBR-g-MimMa), to enhance the compatibility between MimMa and SBR. As a consequence, the mechanical performance of SBR/silica composites was improved effectively. With increasing MimMa loading, the abrasion resistance, tensile strength, tear strength, and the modulus at 300% relative elongation were improved. The composites can be used as damping materials owing to increased mechanical loss under dynamic load. The strong interactions between MimMa and silica were partially linked, due to hydrogen bonding between the imidazolium cation of the MimMa and the Si-O-Si groups of silica, and partially to hydrogen bonding between the anion of the MimMa and the Si-OH groups on the silica's surface, which was well-described in [37]. SEM and TEM confirmed the improved dispersion of silica in the IL-functionalized SBR, and that agglomerates with reduced size were uniformly distributed into the SBR matrix. This was attributed to interfacial interactions that were induced by the incorporation of functional MimMa into the rubber chains. The presence of MimMa affected the vulcanization behavior of SBR compounds. With an increasing loading of MimMa, the value of minimum rheometric torque during vulcanization was consequently lowered, and the maximum torque required a maximum of 1 phr MimMa and then decreased significantly for higher content of this ionic liquid. It was expected that MimMa would cover the silica surface and reduce the adsorption of dicumyl peroxide (DCP) onto the silica, but on the other hand, it would consume a portion of the DCP during the vulcanization process.

The improved dispersion of silica nanoparticles in the SBR elastomer was confirmed by Maciejewska and Zaborski [38] for ILs with benzalkonium or didecyldimethylammonium cations and saccharinate, acesulfame, or lactate anions, which contributed to a considerable increase in the mechanical properties of the SBR composites.

Over the last two decades, the published literature regarding polymer composites with layered silicates, especially montmorillonite (MMT) and halloysite and nanoclays, has grown [39, 40]. MMT is a hydrophilic material that can be used as a filler in polymeric nanocomposites to enhance mechanical strength, modulus, heat resistance, anti-flammability, anti-gas permeability, and service life at elevated temperatures [41]. However, the key factor that is required to achieve these properties of polymer composites is ensuring a homogeneous dispersion of MMT in the polymer matrix accompanied with the exfoliation of MMT layers. The modification of clays with ILs can be considered as a green method because it does not require a solvent [42] or a melt intercalation process [43] to be successfully completed.

Fontana et al. [44] reported the use of MMT mechano-chemically co-intercalated with hexadecyltrimethylammonium bromide (HDTMA) and the ionic liquid 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl)imide (OMImTf<sub>2</sub>N) as a filler for acrylonitrile-butadiene elastomers (NBR). 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. Based on SEM analysis, it was shown that the presence of ILs was necessary to improve the dispersion of the MMT into rubber. There were numerous agglomerates in the vulcanizate with small amounts of OMImTf<sub>2</sub>N, but after increasing its loading, the dispersion of MMT became more homogeneous. Therefore, it was confirmed that the organophilization of MMT enhanced the interfacial interactions between the MMT and NBR elastomer, due to the higher compatibility of intercalated MMT with the elastomeric matrix. MMT modified with ILs added to NBR was classified as a good reinforcing filler, which improved the efficiency of the vulcanization process, and consequently, the mechanical and physical properties of the elastomer.

Halloysite nanotubes (HNTs) are naturally occurring types of mineral clays with a nanotubular structure and were studied as promising fillers for polymer composites. Overcoming the poor interfacial interactions between polymers and HNTs remains a great challenge for processing polymer/HNTs nanocomposites with desired performance [45]. Guo et al. reported that BmiPF<sub>6</sub> was strongly adsorbed onto HNT surfaces and consequently improved the strength of interfacial bonding and the dispersion of the HNTs in the elastomeric matrix [46]. It was reported that clays may adsorb ILs by an ion exchange mechanism [47]. The authors claimed that ILs may be adsorbed onto HNT surfaces by hydrogen bonding between hydrogen atoms of the imidazolium ring of the ionic liquid and the surface siloxane groups of the HNTs. The IL-coated HNTs (m-HNTs) were used as a reinforcement for SBR. The rheometric torque during vulcanization of SBR composites increased with loading of HNTs, probably due to the increase in the crosslink density of the vulcanizates and the improved interaction between SBR and m-HNTs. Moreover, using m-HNTs, the scorch time and the optimal vulcanization time of SBR compounds shortened in comparison with neat SBR. This resulted from the adsorption of IL on the surface of the HNTs, which restricted the adsorption of curing

agents on its surface, thus increasing the efficiency of vulcanization. When an IL was absorbed on the HNT, the interfacial bonding and the dispersion were improved, and consequently, the tensile strength of the SBR vulcanizates increased.

The same authors investigated two other functional ILs, 1-methylimidazolium mercaptopropionate (MimMP) and bis(1-methylimidazolium) mercaptosuccinate (BMimMS), as modifiers for tailoring the interfacial structure of SBR/HNTs composites [48]. Incorporation of functional groups, e.g., double bonds and thiol groups, into IL molecules improved the performance of rubber composites. MimMP was reported to interact with Al-O, Si-OH and Al-OH on the HNT's surface by hydrogen bonding. Hydrogen bonding between Si-O, Al-OH, or Si-OH and the imidazolium cation of BMimMS was also confirmed. With loading of functional ILs, the scorch time of SBR was reduced due to restricted adsorption of curatives on the HNT's surface. Additionally, the presence of a thiol group in the ILs could activate the vulcanization significantly by effectively lowering the activation energy of this process. Incorporation of ILs increased the maximum torque values during vulcanization, which was attributed to the filler networking into the SBR matrix and filler-rubber interfacial interactions by hydrogen bonding, as well as to increasing the vulcanizates crosslink density with ILs loading. It was also confirmed that incorporation of MimMP or BMimMS into SBR/HNTs composites effectively restrained the agglomeration of HNTs in the elastomer matrix, especially in the case of BMimMS which promoted the fine and homogeneous dispersion of filler. The addition of functional ILs improved considerably the tensile and tear strengths of the vulcanizates. Possible explanations that were proposed for this phenomenon included: the increased crosslink density of SBR, the improved dispersion of HNTs in the rubber matrix, and the strengthened interfacial interactions between HNTs and SBR. The efficiency of the described functional ILs in modifying SBR/HNTs vulcanizates was also enhanced compared with other modifiers [49].

Furthermore, it was reported that the addition of hydrophobic ILs, such as 1-hexyl-3-methylimidazolium tetrafluoroborate (HMIMBF<sub>4</sub>), 1-methyl-3-octylimidazolium hexafluorophosphate (OMIMPF<sub>6</sub>), and 1-methyl-3-methylimidazolium hexafluorophosphate (HMIMPF<sub>6</sub>), to elastomeric blends based on an ethylene-propylene copolymer (EPM), prevented the agglomeration of magnetic fillers, such as Fe<sub>2</sub>O<sub>3</sub>, and improved the degree of their dispersion. ILs were introduced with other ingredients to the pre-plasticized rubber. The elastomeric composites that were produced exhibited good magnetic and mechanical properties. Moreover, uniformly distributed particles of magnetite protected the composites against elevated temperatures and UV rays [50].

### 3. Conducting rubber composites containing ILs

Solid polymer electrolytes (SPEs) have been used in various electrochemical devices such as sensors, actuators, supercapacitors, and rechargeable batteries [51]. To improve their mechanical properties, SPEs based on elastomers, such as natural rubber (NR), NBR or SBR containing lithium salts, were developed. This is an effective process for obtaining polymer electrolytes with high tensile strength and elasticity. However, due to their high ionic conductivity, good electrochemical stability, and non-volatility, ILs could be applied successfully as novel electrolytes as an alternative to commonly used lithium salts [52].



Marwanta et al. [35] used NBR as a matrix and ILs as an ion source for SPEs. N-ethylimidazolium salts of tetrafluoroborate (EImBF<sub>4</sub>), bis(trifluoromethanesulfonyl)imide (EImTFSI) and benzenesulfonate (EImBS) were included as electrolytes. The EImTFSI was the only one miscible with NBR, which was confirmed by the single  $T_g$  present in the DSC curve. This was attributed to ion-dipole interactions between the nitrile groups of NBR and EImTFSI ions. The best miscibility of ILs with TFSI anions was confirmed by Likozar [53] for hydrogenated nitrile elastomers. In the case of other ILs, completely phase-separated composites were obtained. The  $T_g$  of NBR/EImTFSI composites decreased with increasing ionic liquid content, thereby demonstrating the plasticizing effect of ILs on the elastomeric matrix. The conductivity of NBR/EImTFSI composites increased with EImTFSI content, which resulted from both the increased carrier ion number and the low  $T_g$  of the composites. Moreover, the composites containing from 10 to 50 phr of EImTFSI exhibited good elasticity and high ionic conductivity (up to  $1.2 \times 10^{-5}$  S/cm at 30°C). The addition of lithium salts with the TFSI anion (LiTFSI) produced NBR conductive composites with even better mechanical strength than the composites without lithium salts. However, in this case, the composites revealed microscopic phase separation that was induced by the addition of a lithium salt. Li<sup>+</sup> ions in the LiTFSI should function as couplers between the NBR and the EImTFSI, since they can interact with both nitrile groups in the elastomer and the TFSI anion from the LiTFSI. As a result of microphase separation in the NBR/EImTFSI/LiTFSI composites, their ionic conductivity was approximately 100 times greater than that of composites without lithium salt, and the conductivity increased with the content of this salt up to 20 mol%.

Ion conductive elastomeric composites were also prepared by mixing NBR with lithium salts and ILs with an alkylimidazolium cation and a TFSI anion, where both cation and anion were tethered in the form of a zwitterion [54]. Addition of 9.2 wt% zwitterion enhanced the ionic conductivity approximately 8-fold compared with composites without zwitterions. The zwitterion was thought to provide additional high ion conductive paths that could improve the ionic conductivity. Moreover, zwitterions can effectively reduce the interaction between nitrile groups of the NBR and Li<sup>+</sup> ions of the lithium salt as a result of a strong interaction between zwitterions and lithium ions. The reduction of NBR/Li<sup>+</sup> interactions could increase the number of free Li<sup>+</sup> ions that can enhance the ionic conductivity of the NBR composites. No less important was microphase separation of the prepared composites, which was responsible for creating an ion conduction path. Flexible and mechanically stable NBR-based SPEs were also fabricated using BmiTFSI [55]. The highest ionic conductivity was achieved with composites that contained NBR with 40 mol% acrylonitrile. ILs were reported to act as electrolytes and plasticizers that enhanced the mobility of the elastomer chains and also increased the ionic conductivity.

Another approach that could produce a soft, flexible SPE with good dimensional stability made use of interpenetrating polymer networks (IPNs) that were formed by two crosslinked polymers, such as NBR and poly(ethylene oxide) (PEO) and the ionic liquid N-ethylmethyylimidazolium bis(trifluoromethanesulfonyl)imide (EmiTFSI) as the electrolyte [56]. EmiTFSI was chosen because of its high affinity for polymers with polar groups, which rendered it compatible with NBR and PEO [58]. Swelling of NBR/PEO IPNs with EmiTFSI produced materials with an ionic conductivity greater than  $10^{-4}$  S/cm at room temperature. Such materials could be used successfully in actuators and other electrochemical devices.

Matchawet et al. fabricated elastomeric composites with increased electrical conductivity using epoxidized natural rubber (ENR) and 1-ethyl-3-methylimidazolium chloride (EmiCl) as the ionic liquid [57]. The electrical conductivity of ENR composites increased from  $10^{-8}$  S/m (for neat ENR) to  $10^{-4}$  S/m for the composites with 7 phr of EmiCl, due to the mobility of cations and anions in the EmiCl, which served as additional charge carriers. The effect of EmiCl on both the curing behavior of ENR and its crosslink density was also reported. The scorch time and optimal vulcanization time significantly decreased for EmiCl loadings below 5 phr and then increased with the content of EmiCl due to the microphase separation of the EmiCl that was dispersed in the ENR matrix. The addition of EmiCl increased the crosslink density of ENR, probably as a result of  $\pi$ - $\pi$  and dipole interactions in the ENR with the imidazolium moiety of the EmiCl. The disadvantage of using EmiCl was the significant reduction of tensile strength and elongation at break of the ENR.

Hydrophobic ILs, such as BmiTFSI, were used to produce composites of carboxylated nitrile rubber (XNBR) that contained hydrotalcite (HT), which exhibited an increase in the ionic conductivity from  $10^{-10}$  S/cm (neat XNBR) to  $10^{-7}$  S/cm [58]. Moreover, BmiTFSI did not affect the tensile strength or elongation at break of XNBR significantly, although a plasticizing effect of BmiTFSI was confirmed. The improvement of the ionic conductivity of XNBR/HT composites resulted not only from the ionic conductivity of BmiTFSI and its concentration but was also influenced by the plasticizing effect of the ionic liquid, which increased the mobility of the rubber chain segments of the XNBR that contained BmiTFSI. Additionally, BmiTFSI improved the dispersion of HT in the elastomeric matrix.

In recent years, the use of MWCNTs has increased as a method for producing conductive elastomeric composites [21, 59, 60]. Unfortunately, because of their tendency to agglomerate due to van der Waals interactions between individual nanotubes, a fine, uniform dispersion of MWCNTs and their network formation in the elastomer is a significant challenge from a technological point of view. Different techniques have been applied to disperse MWCNTs in polymer matrices, including functionalization with the use of harmful solvents. In addition to the harmful effect of these volatile organic solvents, they also have several disadvantages, such as destruction of the  $\pi$ -electron network of MWCNTs, resulting in a reduction of their inherent electrical conductivity [61]. To preserve the  $\pi$ -electrons on the surface of MWCNTs and to maintain the inherent electrical conductivity, ILs can be used to non-covalently modify the surface of nanotubes [21, 59]. Subramaniam et al. reported the development of new elastomeric conductors that employ CR rubber and MWCNTs that were modified with ILs [59]. BmiTFSI was used for surface modification of the MWCNTs and the resultant mix was directly admixed into CR without the use of an organic solvent. The Raman spectrum confirmed the interactions between  $\pi$ -electrons of the nanotubes and cations of the BmiTFSI, or the perturbation of  $\pi$ - $\pi$  stacking of multi-walls of the nanotubes. Therefore, it was concluded that the modified MWCNTs were activated physically, without a chemical impairment of the nanotubes. The use of modified MWCNTs produced CR composites whose electrical conductivity increased with the amount of filler. Moreover, the higher the ratio of MWCNTs to BmiTFSI, the higher was the conductivity of the obtained composites. The increase in the conductivity of the CR composites was attributed to a synergistic effect of electrons and ions as well as to an improved dispersion and formation of a percolating network by the BmiTFSI-modified

MWCNTs. The dispersion of MWCNTs in the CR matrix was enhanced with an increasing proportion of BmiTFSI due to a reduction in the intertubular attraction between nanotubes in the presence of the BmiTFSI. The network formation of the exfoliated nanotubes in the elastomer matrix is destroyed with an increase in the strain amplitude in DMA measurements, as confirmed by the Payne effect.

Sabu et al. developed SBR composites that can attenuate electromagnetic radiation. To achieve this, MWCNT surfaces were modified with the 1-benzyl-3-methylimidazolium chloride (BenMIMCl) and subsequently incorporated in the SBR matrix [60]. The cation- $\pi$  interaction between the imidazolium cation of the BenMIMCl and the  $\pi$  electronic surface of the carbon nanotubes that resulted in the reduction of the size of the MWCNT agglomerates after modification, and an improvement of their dispersion in the elastomer matrix, has been reported. An increase in the dielectric constant of SBRs that contain MWCNTs was observed due to the large difference between dielectric permittivity of the elastomer matrix and the nanotubes, which caused the accumulation of charge carriers at the elastomer/carbon nanotubes interphase. Electrical percolation was determined between 3 and 5 wt% MWCNTs. At this concentration of MWCNTs, a sudden and sharp increase in the conductivity was observed, indicating the formation of an electrically conductive three-dimensional continuous network of carbon nanotubes. Moreover, SBR composites that contain MWCNTs that are functionalized with BenMIMCl exhibited the shielding effect to electromagnetic radiation, which increased with the content of the MWCNTs. After the percolation threshold, the formation of continuous networks of MWCNTs enhanced the mobility of charge carriers; as a result, the attenuation of electromagnetic radiation by absorption was observed. This was reported to be a synergistic effect of BenMIMCl that is in electrical contact with carbon nanotubes [61]. The shielding effectiveness increased with an increase of the ratio between MWCNTs and the BenMIMCl, because the ionic liquid provides additional charge carriers that increase the polarizability of the SBR composites. Therefore, the combination of ILs with MWCNTs produced a new soft rubber material that is suitable for the attenuation of electromagnetic radiation. The same authors reported developing highly conducting and mechanically durable SBR composites that contained MWCNTs that were modified with the 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide [62]. The significant increase in the dielectric constant of SBR composites was attributed to the uniform dispersion of the MWCNTs in the elastomeric matrix, resulting in the formation of micro capacitor networks of carbon nanotubes in the presence of ILs. The cation- $\pi$  interactions between ILs and MWCNTs were also confirmed.

MWCNTs pretreated with BmiTFSI were also used to produce stretchable conductive polymer nanocomposites (CPCs) of thermoplastic elastomers (polyester-based thermoplastic polyurethanes TPU) [63] that could be used as strain sensors. It was reported that entangled single-walled CNTs or MWCNTs bundles could be exfoliated into much finer bundles by grinding them with BmiTFSI, after which a gel-like material was formed. Physical interactions or the formation of chemical bonds between BmiTFSI-modified MWCNTs and TPU chains enhanced the uniform dispersion of the MWCNTs in the TPU matrix; as a result, the composites were able to withstand high strain as opposed to the TPU without BmiTFSI. The resulting CPCs exhibited a high level of strain (100%) without a noticeable degradation of the conductivity after many stretching/relaxing cycles. Their resistivity was reported to be recoverable, and the strain sensing properties were stable.

## 4. Use of ILs for crosslinking elastomers

Catalytic activity of ILs in interfacial reactions and their dispersing action could be used successfully as elastomer crosslinkers [64] or other components of crosslinking systems [37, 65–67].

Behera et al. [64] fabricated a novel ionic liquid-crosslinked flexible polyurethane elastomer using a one-pot polymerization method. Tris(2-hydroxyethyl)methylammonium methylsulfate (THMAMS) was used as a crosslinker. FT-IR analysis confirmed the presence of THMAMS in the polyurethane backbone, which significantly suppressed the hydrogen bonding interactions of the obtained polyurethane elastomer. As a result, a highly flexible and tough elastomeric material was obtained with a much lower  $T_g$  than the linear thermoplastic polyurethane elastomer (TPU) or the elastomer that was crosslinked using a non-ionic crosslinker. Moreover, THMAMS-crosslinked polyurethane elastomers exhibited significantly higher tensile strengths and elongation at break, and lower hardness, compared with conventional TPUs or elastomers prepared without THMAMS as the crosslinker. The higher tensile strength of THMAMS-crosslinked elastomers was reported to be due to the inter-ionic interaction between hard segments.

ILs with a suitably designed structure could be successfully applied as accelerators in the sulfur vulcanization of unsaturated elastomers [65–68]. These ILs consist of the 2-mercaptobenzothiazolate anion derived from the traditionally used 2-mercaptobenzothiazole (MBT) vulcanization accelerator and various organic cations, mainly benzalkonium, alkylammonium or phosphonium and alkylimidazolium. All of these are thermally stable at commonly used vulcanization temperatures (150–180°C). Benzalkonium, tetradecyltriethylphosphonium, or alkylimidazolium 2-mercaptobenzothiazolates were used in the vulcanization of silica-filled NBR as an alternative to the traditionally used MBT accelerator [66]. This resulted in a two- or even three-fold (for benzalkonium salt) reduction in the NBR vulcanization time at 160°C while maintaining the torque increase during vulcanization and a crosslink density slightly higher or comparable to that of the rubber compound crosslinked in the presence of MBT. Therefore, it was concluded that these ILs acted as vulcanization accelerators. Moreover, vulcanizates containing most of these ILs exhibited tensile strengths higher than or similar to that of NBR vulcanized with MBT. Additionally, vulcanizates with ILs exhibited an increased resistance to thermo-oxidative aging. The activity of azolanic ILs and their influence on vulcanization kinetics resulted from not only the catalytic effect of ILs but also the improvement in the degree of dispersion of curatives in the NBR composites. It is also very important that by using salts of MBT as vulcanization accelerators, approximately 30–70% less MBT was introduced into the rubber compound than by using pure MBT. The activity of benzalkonium and alkylammonium 2-mercaptobenzothiazolates as vulcanization accelerators was also studied for SBR composites that were filled with pyrogenic silica [67]. The increase in vulcanization efficiency in the presence of ILs can be attributed not only to the aforementioned factors, such as catalytic activity and the improved degree of curative dispersion in the elastomer, but also to the adsorption of ILs on the silica surface, which reduces the ability of the silica to adsorb curatives and water. Therefore, it is possible that ILs could play roles as both accelerators and shielding agents, increasing the efficiency of vulcanization. An important aspect of IL applications is the improvement in SBR resistance to thermo-oxidative aging



and long-term UV radiation that resulted from a reduction in the increase in crosslink density due to aging factors. The greatest activity, from this point of view, was exhibited by alkylammonium salts of MBT. ILs can also be applied as components of new systems that activate the sulfur vulcanization of unsaturated elastomers (SBR, NBR, and EPDM). These systems are based on the use of nanosized ZnO in combination with ILs with different cations and anions [38, 69–71]. Obtaining a homogeneous dispersion of zinc oxide nanoparticles in an elastomer is a technological challenge. Selecting the appropriate dispersing agents remains an unresolved issue. ILs could be useful in this role. Moreover, due to catalytic activity in interfacial reactions, ILs could additionally increase the crosslinking efficiency and reduce the time and temperature of vulcanization. For example, commercially available 1-ethyl-3-methylimidazolium or 1-butyl-3-methylimidazolium bromides, chlorides, tetrafluoroborates, and hexafluorophosphates with nanosized ZnO were used to activate the vulcanization of SBR filled with pyrogenic silica [69, 71]. Nanosized ZnO, despite its 60% lower content in the SBR compound than that of micro-ZnO, reduced the vulcanization time by 20 min and increased the crosslink density of the vulcanizates. ILs, especially chlorides and hexafluorophosphates, produced a further reduction in the vulcanization time to 12 min, and additionally increased the number of crosslinks in the elastomer network. Moreover, ILs decreased the onset temperature of the SBR vulcanization process by 20–30°C compared to that of rubber compounds without ionic liquids. The tensile strength of SBR vulcanizates that contain ZnO nanoparticles and alkylimidazolium salts was similar to or higher than the TS value of conventionally crosslinked vulcanizates. Furthermore, an improvement in the resistance of SBR to thermo-oxidative aging and UV radiation was achieved by reducing the intensity of the crosslinking reactions during the aging process. The activity of ILs and their influence on the useful properties of vulcanizates depends on the type of elastomer. In the case of SBR, the most significant effect was obtained with chlorides, whereas for EPDM elastomer, the most active ILs were chlorides and tetrafluoroborates. This could be a result of the superior miscibility of these ILs with SBR and EPDM elastomers, which was also observed during the preparation of rubber compounds using two roll mills.

The next area of interest of new systems for activating sulfur vulcanization is related to the application of ILs to the GRAS group (generally regarded as safe). These ILs are generally recognized as environmentally friendly and safe for human health. ILs of interest for this purpose include anions of nonnutritive sweeteners such as saccharinate and acesulfame, or pharmaceutically active anions such as lactate [72–74]. These are currently used as additives in food or pharmaceutical products and are approved by most national health agencies. Moreover, these ILs are thermally stable at vulcanization temperatures (160°C). It was observed that, similar to the ILs discussed above, these salts exhibited catalytic activity during the vulcanization process and improved the degree of dispersion of zinc oxide nanoparticles and filler (silica) in SBR [38]. It can be postulated that the IL/ZnO interactions consist of hydrogen bonding between Zn-OH or Zn-O located on the outside of the zinc oxide crystals and the anion or cation, respectively, of the ionic liquid. Similar interactions were described for Si-OH (Al-OH) or Si-O (Al-O) groups present on HNTs [48]. Hydrogen bonding in IL/ZnO results in reduced interactions between zinc oxide particles, preventing them from agglomerating. The GRAS ILs used in this research produced a 4-fold reduction in the SBR vulcanization



time with respect to that of the rubber compounds that contained micro-sized ZnO, and a two-fold reduction compared with compounds that contained nano-sized ZnO. The greatest activity in the crosslinking process was produced with didecyltrimethylammonium lactate (DDAL), which allowed for the shortest time, lowest temperature, and highest energy effect of vulcanization, thereby demonstrating the high intensity of the vulcanization process. All of the GRAS ILs that were studied improved the tensile strength of vulcanizates. They did not affect the dynamic properties of SBR at temperatures above 25°C or the resistance of SBR to thermo-oxidative aging or long-term UV radiation. A similar relationship was observed with alkylimidazolium, pyrrolidinium, piperidinium, and pyridinium salts [34, 70].

The accelerating effect of ILs on the curing process was also reported by Marzec et al. for XNBR/HT composites that contain 1-butyl-3-methylimidazolium tetrachloroaluminate ( $\text{BmiAlCl}_4$ ) [58]. This ionic liquid considerably shortened the scorch time and optimal vulcanization time of rubber compounds. Moreover, XNBR/HT composites with  $\text{BmiAlCl}_4$  exhibited higher crosslink densities than the reference without an ionic liquid, and the crosslink density increased with the concentration of the  $\text{BmiAlCl}_4$ .

The effect of the type and concentration of hydrophilic imidazolium ILs, such as 1-ethyl-3-methylimidazolium thiocyanate ( $\text{EmiSCN}$ ) and 1-methyl-3-octylimidazolium chloride ( $\text{OmiCl}$ ), on the curing kinetics of NBR filled with silica was also studied [75]. The torque values during vulcanization of rubber compounds were reported to be inversely proportional to the content of ILs due to their plasticizing action. The accelerating effect of ILs was demonstrated because their inclusion caused a reduction in the scorch time and significantly shortened the curing time of rubber compounds. However, NBR composites with high loadings of both ILs (20 and 30 phr) exhibited reversion during vulcanization. The tensile strength decreased with increasing amounts of both ILs, whereas the elongation at break was the highest for NBRs containing 30 phr of ILs, which was attributed to their plasticizing effect.

## 5. Additional applications of ILs in elastomeric composites

Apart from the main applications of ILs in elastomer composites described above, there are other interesting reports that concern additional applications of ILs in elastomer science or technology.

Tang et al. [76] utilized the phosphonium ionic liquid octadecyltriphenylphosphonium iodide ( $\text{ODtppI}$ ) in a silica-filled SBR matrix as a novel catalyst for the silanization reaction between silica and bis(3-triethoxysilylpropyl)-tetrasulfide (TESPT), a commonly used silane in the tire industry. The silanization of silica plays a vital role in enhancing the compatibility between silica and a rubber matrix, and hence the improvement of the composites' properties.  $\text{ODtppI}$  reacted with silanol groups on the silica surface to yield more nucleophilic silanolate anions, which promoted a condensation reaction with the ethoxy groups of TESPT, and as a result, improved the extent of silanization. Consequently, the dispersion of silica in the SBR matrix and the interfacial interaction between silica and rubber chains were improved. Moreover, treatment of the silica surface with  $\text{ODtppI}$  rendered it more hydrophobic; the silica surface thus

became more compatible with a nonpolar hydrocarbon rubber matrix. The SBR composites that contained silica functionalized with TESPT in the presence of an ODtppl exhibited shorter optimal vulcanization times and higher crosslink densities compared with SBR filled with pure silica or with TESPT-modified silica without ODtppl. It was confirmed that silanization prevented the adsorption of curing agents onto the silica surface. Additionally, the phosphonium cation of the ODtppl could act as a secondary accelerator, thereby increasing the curing rate and enhancing the crosslink density of the SBR. Moreover, TESPT acts as a sulfur donor that increases the amount of covalent crosslinks in the elastomer network. Finally, the resulting SBR composites exhibited greater tensile strength, abrasion resistance, or decreased energy loss during rolling of the rubber wheel.

Mouawia et al. [77] developed a process for controlling the metathetic depolymerization of NR in trihexyl-(tetradecyl)phosphonium chloride or N,N'-dioctylimidazolium bromide. This process can produce telechelic polyisoprene oligomers from waste tires. The depolymerization of NR was performed using olefin metathesis reactions in the IL phase under soft conditions, e.g., low temperature, the quantity of ILs, and short reaction times, which promoted the efficient production of telechelic oligomers with low Ru contamination. The catalytic IL phase could be recycled five times, and in each cycle, an efficient and controlled depolymerization of NR to polyisoprene oligomers occurred.

Chen et al. [78] developed highly stretchable, nonvolatile, transparent, and stable ionogels by radical polymerization of acrylic acid in the 1-ethyl-3-methylimidazolium ethylsulfate. This ionogel consisted of a three-dimensional polymer network, which provided an elastic solid form, and the IL enabled electrical conduction. The conductivity of the ionogel was adequate to fabricate electromechanical transducers when used with a dielectric elastomer. Additionally, this ionogel exhibited a low elastic modulus, a large rupturing stretch as well as good mechanical reversibility and negligible degradation after cyclic stretches of large amplitude. These studies confirmed the possibility of using ILs as nonvolatile compliant ionic conductors for dielectric elastomeric transducers.

## 6. Conclusions

Owing to their unique properties, such as thermal and chemical stability, low vapor pressure, non-flammability and high ionic conductivity, ILs have attracted much attention for applications not only in thermoplastics or resins composites, but also in elastomer technologies. An analysis of the recent literature reports indicates that ILs are widely used in elastomeric composites as dispersing agents of fillers, conductive additives, crosslinkers or components of the crosslinking system (vulcanization accelerators or activators), catalysts for the silanization reaction, solvents for the depolymerization of natural rubber, or for the production of highly stretchable ionogels. Because the structure of ILs can be designed for specific applications, it can be expected that the use of ILs in elastomeric composites will continue to increase.

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## Conflict of interest

The authors declare no conflict of interest.

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