

Multifunctional use of ionic liquids in natural rubber based compounds

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In the materials field, the use of renewable sources is the subject of increasing research efforts. Rubber based composites offer unique opportunities. In fact, natural rubber (NR), the regular head-to-tail polymer essentially made by cis-1,4-isoprene units (refs. 1-3), is the most important rubber, with increasing worldwide consumption that amounts at present to more than 12 million metric tons per year, about 40% of the global worldwide rubber consumption (ref. 4). Such an amount comes essentially from *Hevea brasiliensis* and is obtained by taking the latex from the rubber tree, and then coagulating the rubber.

The use of renewable sources makes sense if it does not have an impact on the food chain, starting building blocks are relatively available, a reasonable economic perspective can be envisaged and the effects on the environment are positive. The use of NR in place of a synthetic rubber is greatly beneficial to reduce the environmental impact. The energy consumption (in MJ/kg) for the production of NR is about 8, whereas it is about 110 for a synthetic rubber. The carbon footprint (in kg CO₂/kg) is about 0.4 for NR and about 5 for a synthetic rubber (ref. 5). Moreover, the great contribution of NR for the reduction of hysteresis of compounds that undergo demanding dynamic-mechanical applications, such as the ones for tire compounds, is widely acknowledged.

It is well known that rubber composites are made with many different ingredients other than rubber, such as fillers, coupling agents, activators, vulcanizers, processing aids and antioxidants. Most of them are oil based, and research is also conducted for their replacement with materials from renewable sources.

In this article, compounds based on NR were investigated. The objective of the work was to further reduce the environmental

impact of NR through the multifunctional use of ionic liquids. The so-called biorefinery approach was adopted. As shown in the block diagram of figure 1, the *Hevea brasiliensis* wood can be dissolved by ionic liquids, and the cellulosic materials can then be isolated by precipitation. The recovered ionic liquid (IL) can then be used for precipitating NR from the latex.

In this article, the coagulation of NR led to the preparation of masterbatches of ILs in NR. ILs were then used as accelerators. Moreover, the impact of ILs on the filler networking phenomenon in a silica based compound was preliminarily investigated.

Why use ILs? Ionic liquids (ILs) (refs. 6-12) are substances with low melting points, usually below 100°C. Some of these ions are liquid at room temperature. Interest in ionic liquids has been increasing, as they are non-flammable, non-volatile (they have a high boiling point), thermally and chemically stable and are endowed with high ionic conductivity and good electrochemical stability. They are characterized by insolubility in water and by solubility in organic solvents that can be controlled by changing their substituents. This makes possible unprecedented extractive separations, leading, for example, to the recovery of other low and high molar mass components of the plant. In most cases, ILs are non-toxic. Moreover, the high boiling point of ILs favors recycling, minimizing the amount of waste solvents. In chemical synthesis, ILs have been considered as “the solvents of the future” (ref. 12). The use of ILs for the extraction of cellulosic materials from wood has been reported (refs. 13-14).

In the field of rubber, the effect of ILs on composite properties is remarkable. Some typical organic cations of ILs, such as tetra alkyl ammonium (ref. 15) and imidazolium (ref. 16), have been used as clay modifiers. Moreover, they have shown strong affinity with sp² carbon allotropes such as carbon black (ref. 17) and carbon nanotubes (refs. 18-20), interpreted with the cation-π interaction (ref. 17). ILs are able to promote efficient dispersion of the carbon allotropes and even the debundling of the nanotubes. It has been shown that ILs and their cations (as

Figure 1 - biorefinery approach to the *Hevea brasiliensis* tree

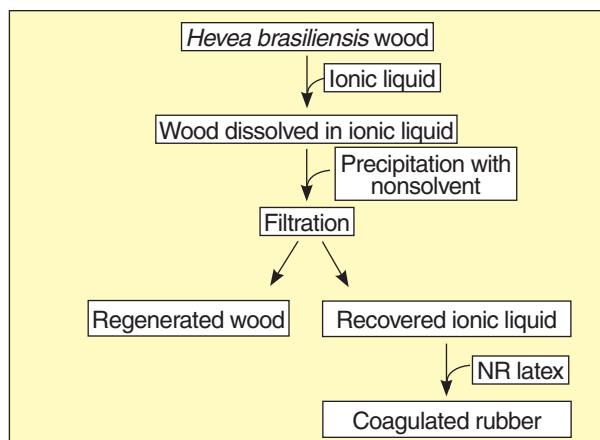
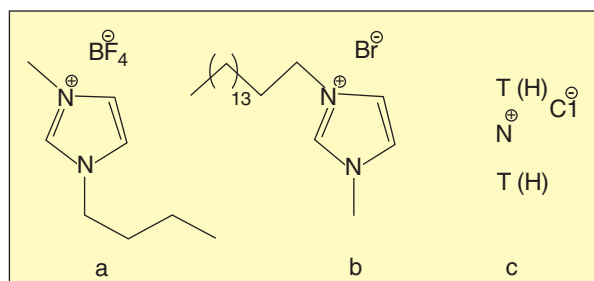


Figure 2 - chemical structures of 1-butyl-3-methyl imidazolium tetrafluoroborate (IMZ-B) (a), 1-hexadecyl-3-methyl imidazolium bromide (IMZ-O) (b) and dimethyl di(hydrogenated talloyl) chloride (2HT) (c)



clay modifiers) act as efficient accelerators (refs. 21-24). It is thus clear that ILs can have many functions in rubber compounds.

In this article, both tetra alkylammonium and imidazolium salts were used with anions such as chloride and tetraphenyl borate. They were: 1-butyl-3-methyl imidazolium tetrafluoroborate (IMZ-B), 1-hexadecyl-3-methyl imidazolium bromide (IMZ-O) and dimethyl di(hydrogenated talloyl) chloride (2HT). Their chemical structures are shown in figure 2.

Experimental section

Materials

- Reagents and chemicals: Reagents and solvents commercially available were purchased and used without further purification.

- Ionic liquids: 1-butyl-3-methyl imidazolium tetrafluoroborate (IMZ-B) and 1-hexadecyl-3-methyl imidazolium bromide (IMZ-O) were purchased from Iolitech. Di(hydrogenated tallow)-dimethylammonium chloride (2HT) was from Akzo Nobel, with Arquad HC pastilles as the trade name and 98.5 mass % as chemical purity. The alkyl chain distribution was as follows (as wt. %): bC12 = 1, C14 = 4, C16 = 31 and C18 = 64.

- Rubber samples: Natural poly(1,4-cis-isoprene) latex (NR) was Centex FA, with a solid content = 60 wt. %, pH (at 20°C) = 9 -11, density \approx 0.95 g/cm³ and partial miscibility with water. Natural rubber SMR GP, from BR-THAI, Eastern GR Thailandia - Chonburi, Lee Rubber, with 65 Mooney Units (MU). Synthetic poly(1,4-cis-isoprene) (IR) with SKI3 as trade name SKI3 and 70 Mooney units (MU) as Mooney viscosity (ML [1+4] 100°C) was from Nizhnekamskneftechim Export. Poly(styrene-co-butadiene) from solution process (S-SBR): Sprintan 4630 from Trinseo with 55 Mooney units (MU).

- Silica and silane: Silica was Zeosil 1165 (industrial grades for tire applications) from Solvay, with 165 m²/g as specific surface area, determined through nitrogen absorption (BET); bis(3-triethoxysilylpropyl) tetrasulfide (TESPT) (Si 69, Evonik).

- Compounds' ingredients: bis(3-triethoxysilylpropyl) tetrasulfide (TESPT) (Si 69, Evonik); ZnO (Zincol Ossidi); stearic acid (Sogis); sulfur (Solfotecnica); N-tert-butyl-benzothiazol-2-sulfenamide (TBBS) (Flexsys); N-N'-di-phenyl guanidine (DPG) (Rhenogran DPG80) (Rhein Chemie Additives).

- Ingredients for the preparation of organic polysulfides: Methylene chloride and Na₂S were from Aldrich.

HNR/IL masterbatches

- Preparation: The preparation of the masterbatch with IMZ-B is reported as an example. To 10 g of NR latex were added 10 g (8.2 ml) of IMZ-B, and the mixture was stirred at 25°C for five minutes. Coagulated solid rubber was separated from liquid phase and washed three times with 10 ml of acetone and finally with water. The rubber was then air dried and weighed (6.78 g). The amount of ionic liquid in HNR/IMZ-B masterbatch was evaluated by means of ¹H-NMR and was 13%.

- Characterization, NMR analysis: One-dimensional ¹H-NMR spectra were taken at 400 MHz, using a Bruker AV 400 equipped with a 5 mm multinuclear probe with reverse detection (Bruker, Rheinstetten, Germany). The solvent was deuterated 1,1,2,2-tetra-

Table 1 - formulation of composites based on SBR, NR, silica and containing ILs^a

	Without DPG	With DPG	With IMZ-B/HNR	With 2HT/HNR
SMR GP	30.0	30.0	30.0	30.0
S-SBR ^b	96.25	96.25	96.25	96.25
Silane TESPT ^c	5.2	5.2	5.2	5.2
Silica ^d	65.0	65.0	65.0	65.0
DPG	0.0	2.4	0.0	0.0
IMZ-B	0.0	0.0	2.05	0.0
2HT	0.0	0.0	0.0	5.21

^aOther ingredients: ZnO 2.5, stearic acid 2.0, 6PPD 2.0, TBBS 1.8, sulfur 1.2 ^bSprintan 4630 ^cSi 69 ^dZeosil 1165

chloroethane and the temperature was 303K. Data were processed using MestReNova. The amount of IL was determined by the ratio of integrals of rubber signals with respect to IL signals.

Compounds

- Preparation: The following procedure was adopted for the preparation of compounds whose formulations are reported in the text in table 1. A masterbatch composed of SBR and NR as the rubber, silica as the filler and TESPT as the silane, in the relative amount adopted in the formulation, was prepared in an internal mixer. Such ingredients were fed to the mixer at 60°C and masticated with rotors rotating at 75 rpm until the temperature achieved 150°C. Other ingredients (vulcanizing agents and accelerators) were added to the masterbatch by using an internal mixer. Compounds were homogenized by passing them five times on a two-roll mill at room temperature, with one roll rotating at 38 rpm and the other at 30 rpm, and 1 cm as the nip between the rolls.

- Characterization, crosslinking: Crosslinking reaction was studied at 150°C with a Monsanto oscillating disc rheometer (MDR 2000) (Alpha Technologies, Swindon, U.K.), determining the minimum modulus, ML, the maximum modulus, MH, the time t_{S1} required to have a torque equal to ML+1, the time t₉₀ required to achieve 90% of the maximum modulus MH (i.e., to achieve the optimum of crosslinking).

- Determination of the kinetic parameters and activation energy of sulfur-based crosslinking: The kinetic parameters of the curing obtained from a rheometer were determined by applying the autocatalytic model, as reported by equation (1):

$$\frac{d\alpha}{dt} = K(T)\alpha^m(1-\alpha)^n \quad (1)$$

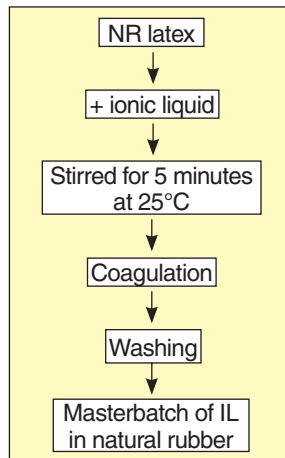
where α is the degree of curing, evaluated with equation (2), m is the autocatalytic index, n the catalytic index, and K is the kinetic constant.

$$\alpha = \frac{F_t - F_0}{F_\infty - F_0} \quad (2)$$

The values of K , n and m at the different tested temperatures were calculated through linear multiple regression analysis of the experimental data with MatLab.

The activation energy was evaluated with an Arrhenius equation. A plot of $\ln K$ versus $1/T$ gives a straight line of slope ($-E_a/RT$), where E_a is the activation energy generated during the vul-

Figure 3 - preparation of IL/HNR masterbatch by coagulation of HNR from the latex with IL



an angle of 6.98%. Curing time was 30 minutes. On crosslinked samples, a first strain sweep (0.1-25% strain amplitude) was performed at 50°C, then the sample was kept in the instrument at the minimum strain amplitude (0.1%) for 10 minutes to achieve fully equilibrated conditions. Finally, a strain sweep (0.1-25% strain amplitude) was performed with a frequency of 1 Hz.

Preparation of organic polysulfides

In a 10 mL test tube were poured in sequence Na₂S (0.100 g, 1.28 mmol), sulfur (0.328 g, 1.28 mmol) and H₂O (4 mL). The mixture was left to stir at room temperature. After this period, to the resulting natrium polysulfide mixture was added a solution of imidazolium salt (4 mL) in CH₂Cl₂. The thus obtained double phase was shaken two times and put in a separation funnel. The organic phase was dried on Na₂SO₄ and the solvent was removed. The product was imidazolium polysulfide with the sulfur chain prevailingly containing 7 and 8 sulfur atoms. The cation exchange yield was about 25% by mol.

Results and discussion

Coagulation of natural rubber from the latex, with ionic liquids

Efficient coagulation of *Hevea* latex was obtained at 25°C just mixing the latex with an equal amount or slight excess (by mass) of IL. The objective of the developed experimental procedure was the preparation of IL masterbatches in NR matrix and not the separation of “clean” HNR, free of IL. The experimental procedure is reported above in the experimental section and is summarized in the block diagram in figure 3.

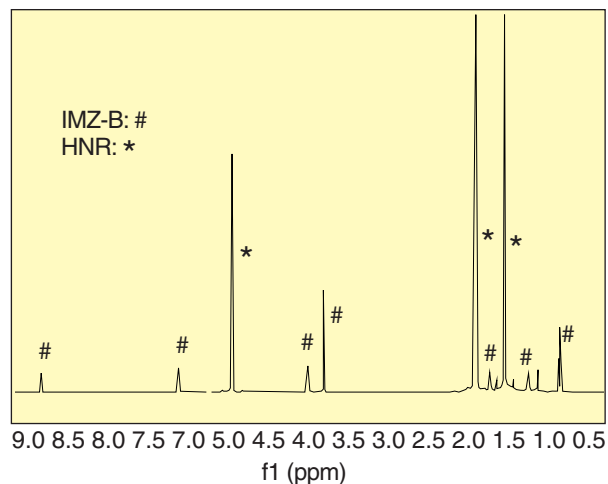
After coagulation, the excess of ILs was separated by squeezing the solid rubber and then by washing the solid with a polar solvent, such as acetone.

To determine the amount of IL in IL/HNR masterbatches, ¹H-NMR analysis was performed. The amount of IL was determined by the ratio of integrals of rubber signals with respect to IL signals. The NMR spectrum of IMZ-B/HNR masterbatch is

canization reaction, and R is the universal gas constant.

- Dynamic-mechanical measurements: They were carried out in the torsion mode with a Monsanto RPA 2000 rheometer. A first strain sweep (0.1-25% strain amplitude) was performed at 50°C on uncrosslinked samples to cancel their thermomechanical history. The samples were then kept in the instrument at the minimum strain amplitude (0.1%) for 10 minutes to achieve fully equilibrated conditions. A strain sweep (0.1-25% strain amplitude) was then performed with a frequency of 1 Hz. Curing was carried out at 150°C with a frequency of 1.67 Hz and

Figure 4 - ¹H-NMR spectrum of HNR/IMZ-B masterbatch



shown in figure 4.

The amount of IMZ-B in the masterbatch was estimated to be about 13% by mass, whereas the amount of 2HT was about 15% by mass.

Ionic liquids as secondary accelerators in silica based compounds

Composites were prepared based on S-SBR and NR as the rubbers, and silica as the filler. The objective was to investigate the efficiency of ILs as secondary accelerators. In the field of silica based compounds, the role of guanidines as secondary accelerator is known. In particular, diphenyl guanidine (DPG) is largely used at the industrial scale. In spite of the great efficiency of DPG, research is conducted in order to replace it, as DPG presents issues from the point of view of health and safety. In the literature, particularly in patents, ionic liquids are used in place of DPG (refs. 25-26). Comparison with diphenyl guanidine was thus performed. Recipes are shown in table 1.

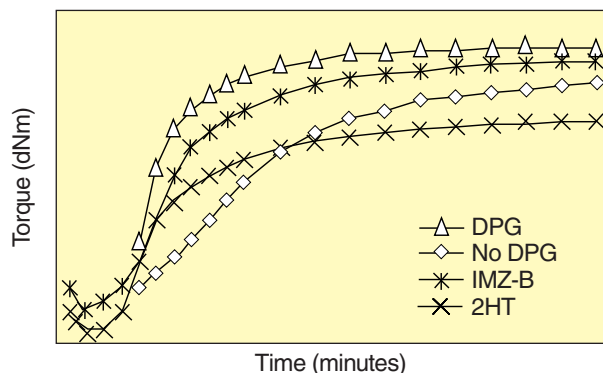
Vulcanization was performed at 170°C for 10 minutes. Curves are shown in figure 5, and data from the rheometric curves are in table 2.

From the curves in figure 5 and from the data in table 2, it is evident that ionic liquids are efficient secondary accelerators when they are used as NR coagulating agents. Particularly interesting is the imidazolium salt, as it allows one to achieve larger values of MH with respect to the tetra alkylammonium salt. This

Table 2 - data from rheometric curves of composites based on SBR, NR, silica and containing ILs

	Without DPG	With DPG	With IMZ-B/HNR	With 2HT/HNR
t _{S1} (min.)	3.5	2.67	2.64	2.81
T ₉₀ (min.)	18.98	10.21	13.95	13.66
ML (dNm)	2.65	2.11	2.66	1.42
MH (dNm)	14.36	16.14	15.45	12.35

Figure 5 - rheometric curves of composites based on SBR, NR, silica and containing ILs vulcanized at 170°C for 10 minutes (formulations of the composites are in table 1)



is probably due to the presence in 2HT of long chain alkyl substituents that act as a plasticizer.

In the literature, to justify the positive effect of ammonium cations on vulcanization, two explanations are proposed. The cationic part of an ammonium salt is seen as a thermal generator of redox active neutral species such as tertiary amines (ref. 21), and is also considered (ref. 22) to take part in the inter-phase transfer reactions occurring in the course of vulcanization. In particular, it can work as an activator, increasing the mobility of sulfur accelerating anionic species. In the case of IMZ, the presence of a basic nitrogen atom in position 3 of the imidazolium ring should also be considered. IMZ could thus be particularly effective in promoting faster vulcanization reactions. In the literature, a good number of data are available for the ammonium cations (ref. 21), in particular when they are the compensating cations of clays, such as the smectites. To the best of our knowledge, reports on vulcanization reaction of isoprene rubbers are not yet available for imidazolium salts. Hence, to acquire more information on the behavior of ammonium and imidazolium salts, further experiments were performed. It

Table 3 - formulation of composites based on IR and containing ILs^a

	With 2HT	With IMZ
IR	100.0	100.0
2 HT	5.21	0.00
IMZ-O	0.0	3.78

^aOther ingredients: ZnO 4.0, stearic acid 2.0, sulfur 2.0, CBS 1.0

was decided to use a different type of IMZ, 1-hexadecyl-3-methyl imidazolium bromide (for the chemical structure, see figure 1). IMZ-O presents two main differences with respect to IMZ-B, including the counterion, bromide, in place of tetrafluoroborate, and the long alkyl chain substituent of the nitrogen atom in position 1 that could give easier solubility in the rubber matrix. Composites, whose formulations are

shown in table 3, were prepared. In order to exclude any effect on vulcanization of the non-rubber components of NR, for example proteins, synthetic poly(1,4-cis-isoprene) was used.

Kinetics of vulcanization were investigated by means of differential scanning calorimetry, an analytical tool that allows the determination of the energy involved in the vulcanization reaction. In such analysis, it is assumed that the heat of the reaction is only due to a single curing reaction, and is proportional to the extent of the reaction. Data arising from DSC analysis were elaborated, as described in the experimental section. In particular, E_a values were obtained through the Arrhenius equation and were calculated to be 117.5 and 71.9 for vulcanizations in the presence of 2HT or IMZ-O, respectively.

It is confirmed that an imidazolium salt is able to promote faster sulfur based vulcanization reactions. In the frame of the adopted experimental conditions, the activation energy of crosslinking reaction is lower with IMZ-O than with 2HT. The role that the basic nitrogen atom of the IMZ ring could play was mentioned above. To investigate the ability of 2HT and IMZ-O to form nitrogenous bases via thermal degradation during vulcanization, their thermal stability was investigated by means of thermogravimetric analysis. Figure 6 shows TGA traces of IR, 2HT and IMZ-O. They clearly show that IMZ-O degradation begins at a temperature higher than the one adopted in vulcanization. Hence, nitrogenous

Figure 6 - TGA traces of IR (a), IMZ-O (b) and 2HT (c)

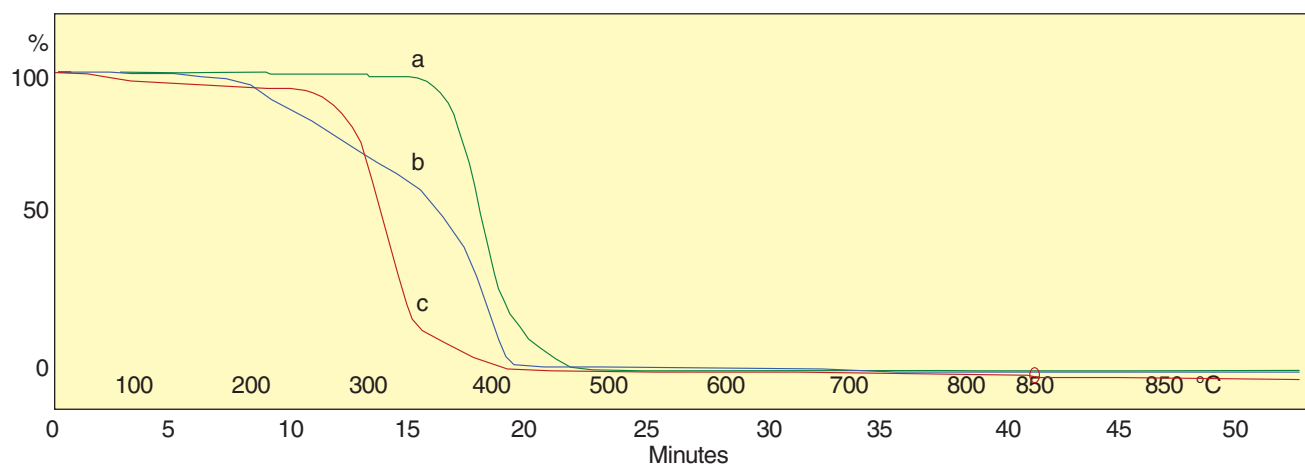
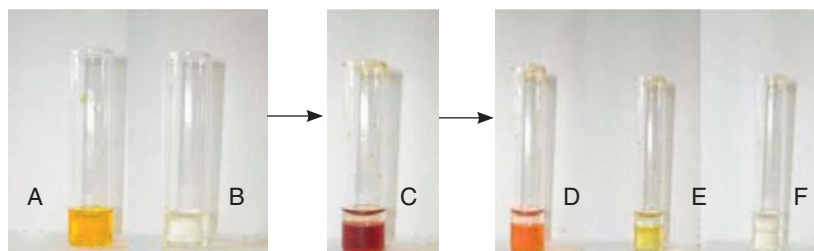


Figure 7 - (A): water solution of Na₂S and S₈, (B) CH₂Cl₂ solution of IMZ-O, (C) biphasic system obtained by adding Sol. B to Sol. A (the lower dark red solution is based on CH₂Cl₂ and contains organic polysulfides), (D, E, F) CH₂Cl₂ solution turns colorless in the time range from five to 20 minutes



bases are not formed by IMZ degradation during the crosslinking reaction.

The above mentioned hypothesis of the increased mobility of sulfur accelerating anionic species promoted by IMZ cations was investigated by performing the experiment reported in the experimental section. In this article, such an experiment is preliminarily described, and detailed data will be reported in a future paper. In brief, a water solution of Na₂S and S₈ was prepared at room temperature. After a few minutes of stirring, sodium polysulfide was formed and a dark yellow transparent solution was obtained, indicated as solution A in figure 7. IMZ-O was dissolved at room temperature in CH₂Cl₂, obtaining a colorless transparent solution, solution B in figure 7, that was then added to the sodium polysulfide solution. A biphasic system was obtained. By shaking it, the lower higher density phase, based on CH₂Cl₂, acquired an intense dark red color, typical of an organic polysulfide, that was verified to be IMZ polysulfide. The red color was observed to vanish after about five minutes, and the solution turned colorless after about 20 minutes, as can be observed in figure 7 (solutions D, E and F).

This experiment suggests the validity of the investigated hypothesis on the increased mobility of sulfur accelerating anionic species. Such mobility should be reasonably considered to occur in the presence of both ammonium and imidazolium cations.

Conclusions

It is widely acknowledged that NR provides a great contribution for reducing the impact on the environment as a rubber from renewable resources that favors the reduction of compound hysteresis in demanding dynamic-mechanical applications. This work was in the frame of research aimed at further reducing the impact on the environment of NR based compounds. The approach was to develop a multifunctional use of a single ingredient. Ionic liquids, such as dimethyl di(hydrogenated talloyl) chloride (2HT) and 1-hexadecyl-3-methyl imidazolium bromide (IMZ-O), were used to coagulate NR and as secondary accelerators in silica based compounds. From the results reported here, the accelerating effect of 2HT and IMZ salts can be justified, taking into consideration: (1) the presence of nitrogenous bases in both types of salts, in the imidazolium ring and after thermal degradation occurring in vulcanization in 2HT, and (2) the increased mobility of sulfur anionic species.

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