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The impact of imidazolium ionic liquids on the properties of nitrile rubber composites

Anna Marzec [a,*], Anna Laskowska [a], Gisele Boiteux [b], Marian Zaborski [a], Olivier Gain [b], Anatoli Serghei [b]

[a] Institute of Polymer & Dye Technology, Technical University of Lodz, Stefanowskiego 12/16, 90924 Lodz, Poland
[b] Ingénierie des Matériaux Polymères,University of Lyon, Université Claude Bernard Lyon 1, UMR CNRS 5223, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne, France

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ABSTRACT

The purpose of this work was to investigate the influence of hydrophilic imidazolium ionic liquids on the curing kinetics, mechanical, morphological, thermal and conductive properties of acrylonitrile–butadiene rubber (NBR) composites. NBR/SiO_2/IL composites were prepared by the conventional melt mixing method. It was found that 1-ethyl-3-methylimidazolium thiocyanate (EMImSCN) and 1-methyl-3-octylimidazolium chloride (OMImCl) improved the ionic conductivity of NBR composites. Moreover, both ionic liquids strongly influenced the rheometric data and mechanical properties (static and dynamic). NBR – based composites displayed elastomeric properties and high tensile strength up to 19 MPa when 10 phr EMImSCN was added. The presence of 30 phr EMImSCN in the composite resulted in an increase in its conductivity from 10^{-11} S/cm (NBR/SiO_2) up to approximately 10^{-5} S/cm (NBR/SiO_2/EMImSCN30) at room temperature. Thermal analysis showed that the T_g of NBR/SiO_2/IL systems, decreased as a function of increasing ionic liquid content due to a plasticizing effect, particularly for samples containing OMImCl.

1. Introduction

Room temperature molten salts, ionic liquids (ILs), have received a great deal of interest due to their unique characteristics, such as high polarity, non-volatility, non-flammability, high thermal stability and high ionic conductivity [1–6]. The increasing interest in the ILs field in the last decade has led to advance both in fundamental knowledge and in technological applications [7]. ILs have been considered as solvents for reactions, as absorption media for gas separations, as separating agents in extractive distillation [8], as reagents for processing biomass [9] and for electrochemical applications such as solar cells [10,11]. In early publications, ionic liquids were considered as processing additives in rubber compound formulations. Commonly, ionic liquids are used in the field of elastomers for improving the dispersion of nanofillers, such as carbon nanotubes or carbon black, in the rubber matrix as well as for enhancing ionic conductivity and the thermal and mechanical properties of polymer composites [12–18]. The combination of elastic polymer and ionic liquids is expected to generate a semi-conductive elastomeric material with excellent mechanical properties. Due to their flexibility, rubbers in combination with ionic liquids are used for the production of specialty materials, such as solid-state polymer electrolytes or electroactive polymers (EAP) [19,20]. In Marwanta's investigations, a NBR composite with an ionic liquid content of 50 wt% had an ionic conductivity of 1.21×10^{-5} S/cm at 30 °C [21]. A high content of ionic liquid was necessary to obtain the desired properties, including conductivity. It has been already

* Corresponding author. Tel.: +48 42 631 32 09; fax: +48 42 636 25 43.
E-mail address: marzec.anna@hotmail.com (A. Marzec).

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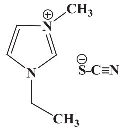
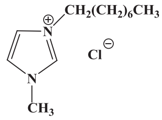
reported that imidazolium ionic liquids may affect the crosslinking behavior of the rubber composites in sulfur based-system. Their presence in rubber composites contributed to a considerable decrease of vulcanization time, an increase in crosslinking efficiency as well as improvement of vulcanizate tensile properties. It was concluded that ionic liquid improved dispersion of curatives particularly zinc oxide in polymer matrix, what is an important factor determining the efficiency of vulcanization [22]. Sulfur and organic accelerators are widely used to crosslink unsaturated rubber, such as the NBR, due to the presence of double bonds (C=C) in diene rubber structure. In previous studies researchers avoided vulcanization of elastomers in the presence of high levels of ionic liquids (e.g., 20 and 30 phr) by immersion already cured composite in a solvent/IL solution [14,19]. In the literature there is no information about the impact of a high ionic liquid content on crosslinking process in the presence of sulfur cure system. We examined the effect of the hydrophilic imidazolium salts 1-ethyl-3-methylimidazolium thiocyanate (EMImSCN) and 1-methyl-3-octylimidazolium chloride (OMImCl), on the curing kinetics of acrylonitrile–butadiene rubber (NBR) where silica was used as a reinforcing filler. In this study, NBR composites were prepared by the conventional melt mixing method. The influence of these types of imidazolium salts on the mechanical, morphological, thermal and ionic conductivity properties of NBR/SiO_2/IL composites was investigated in detail. NBR was employed as a matrix and ionic liquids as ions source for the polymer electrolyte.

2. Experimental

2.1. Materials

Acrylonitrile–butadiene rubber NBR (Perbunan 28-45F) containing 28 wt% of acrylonitrile was obtained from Lanxess, GmbH. Mooney viscosity was (ML1 + 4(100 °C):45). NBR rubber was cured using a conventional sulfur (Siarkpol, Poland) based crosslinking system in the presence mercaptobenzithiazole (MBT) as an accelerator (Lanxess, GmbH). Znic oxide (Lanxess, GmbH) and stearic acid (Sigma Aldrich, GmbH) were used as activators in sulfur vulcanization. Hydrophilic fumed silica Aerosil 380, supplied by Evonik Degussa, GmbH, was used as a reinforcing filler. The ionic liquids: 1-ethyl-3-methyl imidazolium thiocyanate (EMImSCN) and 1-methyl- 3-octylimidazolium chloride (OMImCl) were provided by Sigma Aldrich (Table 1).

Table 1
Molecular mass and chemical structure of ionic liquids.

Chemical name	Molecular mass ($gmol^{-1}$)	Chemical structure
1-Ethyl-3-methylimidazolium thiocyanate (EMImSCN) - hydrophilic	169.25	
1-Methyl-3-octylimidazolium chloride (OMImCl) – hydrophilic	230.78	

2.2. Preparation of NBR composites

The rubber mixture consisted of the following: NBR rubber (100 phr), sulfur (2 phr), mercaptobenzothiazole (2 phr), zinc oxide (5 phr), stearic acid (1 phr), Aerosil 380 (30 phr) and ionic liquid at different loadings (10, 20, and 30 phr). The preparation of rubber mixes was performed by following a two-step procedure. Homogenization of rubber and SiO_2 filler mixed with ionic liquid was carried out an internal mixer (Brabender Measuring Mixer N50). The rubber compounds were processed at a rotor speed of 50 rpm and at 50 °C initial temperature. Subsequently 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 resulting films were approximately 1 mm thick.

3. Measurment methods

3.1. Rheometric study

The study was conducted in a moving die 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 (M_H–M_L). The time required to reach 90% of (M_H–M_L) is termed as the optimum cure time (t_{90}). The scorch time t_{02} was defined as the time for an increase of 2 units above the minimum viscosity (M_H). The mixed stocks were cured in a standard hot press at 160 °C and for an optimum cure time (t_{90}) of the samples.

3.2. Mechanical properties

The stress–strain tests were performed with 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. Tensile strength, modulus at 100% and 300% elongation and elongation at break were measured at room temperature.

3.3. Morphological analysis

The morphology of the elastomer matrix containing ionic liquids was estimated using scanning electron microscopy with a Zeiss SEM microscope equipped with ES2 and EBS detectors. The NBR vulcanizates were broken down in liquid nitrogen, and the fracture surfaces of the vulcanizates were examined. Prior to the measurements, the samples were coated with carbon.