



# An efficient highly flexible strain sensor: Enhanced electrical conductivity, piezoresistivity and flexibility of a strongly piezoresistive composite based on conductive carbon black and an ionic liquid



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## ARTICLE INFO

### Keywords:

A. Polymer-matrix composites (PMCs)  
B. Electrical properties  
B. Mechanical properties  
Piezoresistivity

## ABSTRACT

Flexible strain sensors based on conductive carbon black (CB) filled styrene-butadiene rubber were developed. The use of ionic liquid (IL) allows improvement of the filler dispersion, rubber-filler interaction and flexibility of the sample that finally enhances the piezoresistive performance and the sensibility. At filler loading close to the percolation threshold, the electrical conductivity increases by two orders of magnitude when the IL/CB ratio is increased from 0 to 1.5. In contrast to the use of normal plasticisers, the loss in piezoresistivity at low strains is overcome. The sensitivity at 2.5% strain using an IL/CB ratio of 1.5 is about 600% higher compared with the sample without IL. Also, the response consistency becomes better with higher IL/CB ratios. Moreover, the use of IL allows the composites to be deformed more easily while still providing high responsivity to small strains. This enables the construction of better flexible strain sensors with long-term stability.

## 1. Introduction

Conductive rubber composites (CRCs) based on electrically conductive fillers, such as carbon black and carbon nanotubes dispersed in an insulating rubber matrix, have found a wide range of applications [1–5]. Strong strain-dependent conducting networks make the composite suitable for strain sensor applications [1,2,4]. In order to develop a good strain sensor [3,6,7], a large change in resistance caused by a small change in strain is required. This sensitivity depends on the type and concentration of the conductive fillers, and also on the extent of breakdown in the conducting networks during deformation. Compared with high aspect ratio carbon nanotubes, carbon black provides greater sensitivity because of the smaller filler particle dimensions [8,9]. This makes it easier to lose the conducting networks when the sample is deformed. With such fillers, at a given strain, the highest sensitivity is achieved when the amount of the conductive filler is close to the percolation threshold (or critical filler concentration) [6,10,11]. A significant breakdown of the conducting networks is achieved when the rubber-filler interactions are high [7].

Having a high level of filler dispersion is one way to increase the rubber-filler interactions and so the sensitivity of the CRCs [4,12]. This also increases the number of conducting components as well as the particle distribution, leading to the formation of many conducting networks throughout the whole matrix. For a system containing a high aspect ratio filler, such as carbon nanotubes, a high filler dispersion may enhance the electrical conductivity since the carbon nanotube bundles become more expanded and then interpenetrate each other [13]. On the contrary, there will be a negative effect in those systems with low aspect ratio filler such as carbon black. In this case, carbon black agglomerates (and also aggregates) are separated from each other, and become more surrounded by the electrically insulating bound rubber [14–16]. So, in the carbon black filled CRCs, even though high filler dispersion can promote higher sensitivity, it decreases the overall electrical conductivity [12,14,17]. That creates a difficulty in flexible strain sensor applications [9,18,19]. The conflicting requirements are that the CRCs have to be stretched or deformed easily, but need to remain highly piezoresistive to the small change in strain (or the associated stress). Unfortunately, in the fabrication of carbon black

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filled CRCs for soft/flexible strain sensors, the conventional addition of a plasticiser or processing oil to soften the composite causes loss of sensitivity at low strain, and sometimes increases the resistance of the unstrained specimen [3,10,20–22]. These are the significant problems in sensor applications. Recently, it has been shown that, for composites containing high aspect ratio carbon nanotube fillers, an ionic liquid (IL) can act as plasticiser, increasing the flexibility and pliability of the composites [23,24]. Moreover, the use of IL can improve the filler dispersion, the local conductive filler contacts and so the electrical conductivity [4,25,26]. However, these works did not cover the piezoresistive behaviour, especially when using carbon black filler.

In the present study an attempt has been done to investigate the application of IL not only as plasticiser to improve flexibility and filler dispersion, but also as conductor to reduce the effect of the electrically insulating barrier of the bound rubber layer. This, then, improves both the electrical conductivity and the piezoresistivity.

## 2. Experimental

### 2.1. Composite preparation

Oil extended styrene-butadiene rubber (SBR) (Buna® VSL 5025-2 HM, Lanxess, Germany) with 25% styrene content and TDAE oil content of 27.3% (or 37.5 phr) was used in this study. Conductive carbon black (CB) (Printex XE 2-B, DBP adsorption value of 350–410 ml/100 g and BET surface area of 1002 m<sup>2</sup>/g, Orion Engineered Carbons, Germany) was used as filler. The ionic liquid (IL) used was 1-decyl 3-methyl imidazolium chloride (DMIC) received from Sigma-Aldrich, Germany. The CB/SBR conductive composites were prepared in an internal mixer (Haake Rheomix OS 600p, Germany) with the following mixing condition: initial chamber temperature of 70 °C; rotor speed of 70 rpm and fill factor of 0.75.

The amounts of filler and additives were varied as parts per hundred of rubber (phr). The amounts of IL used, as a ratio to the mass of CB, were 0, 0.5, 1.0 and 1.5. In use, for convenience, the compounds were named according to this ratio. These are 0-IL/CB, 0.5-IL/CB, 1.0-IL/CB and 1.5-IL/CB. The compositions of these different filled compounds are shown in Table 1.

Raw SBR was masticated for 1 min. Then, the premix of CB and IL with 3 phr *N*-(1,3-dimethylbutyl)-*N*'-phenyl-*p*-phenylenediamine (6PPD) (abc r GmbH & Co.KG, Germany), 1 phr stearic acid (Fisher chemical, UK) and 3 phr ZnO (ACROS Organics, Spain) was added. The mixing was continued for 20 min. After that, 2 min prior to discharging, 1.75 phr sulphur (ACROS Organics, Belgium) and 1.38 phr *N*-tert-butyl-2-benzothiazolesulfenamide (TBBS) (Rhein Chemie Rheinau GmbH, Germany) were charged into the mixing chamber. The curing process of the rubber compounds (vulcanisation) was conducted using a hot-press at 160 °C with the optimum cure time (*t*<sub>c90</sub>; i.e., the time required to reach the 90% state of cure as per ISO 6502) which was predetermined from data generated by the rubber process analyser (Scarabaeus V-50, Germany).

### 2.2. Compound and vulcanisate characterisations

The bound rubber content (BRC), a measurement of rubber-filler

**Table 1**  
Composition of differently filled IL/CB/SBR compounds.

Compounds	Ingredient (phr)		
	SBR	CB	IL
0-IL/CB	137.5	11.07	0
0.5-IL/CB	137.5	11.07	5.54
1.0-IL/CB	137.5	11.07	11.07
1.5-IL/CB	137.5	11.07	16.60

interaction [27], was measured by immersing approximately 0.1 g compound in 60 ml toluene at room temperature for 3 days. Subsequently, to remove the ionic liquid [25], 40 ml ethanol were added to the solution. After 5 days, the rubber-filler gel was taken out and then dried at 70 °C for 24 h. The BRC was calculated using Eq. (1).

$$\text{Bound rubber content (\%)} = \frac{W_{fg} - W [m_f / (m_f + m_p)]}{W [m_p / (m_f + m_p)]} \times 100\% \quad (1)$$

where  $W_{fg}$  is the weight of rubber-carbon black gel,  $W$  is the weight of the test specimen before extraction,  $m_f$  is the weight of filler in the compound, and  $m_p$  is the weight of polymer in the compound. Filler dispersion of the vulcanisates was quantified in terms of the dispersion index according to ISO 11345 using dispersion grader (disperGRADER α view, Alpha Technologies, USA). The agglomerate size distribution was also provided. The macro-dispersion of the composite (cut surface) was qualitatively observed using an optical microscope (Nikon, Japan). The resistivity/conductivity of highly resistive composites ( $> 10^7 \Omega\text{m}$ ) was measured using a Keithley 8009 (a plate measuring device) in combination with a Keithley electrometer 6517A (Keithley Instruments Inc., USA). Test specimens were circular with a diameter of 60 mm and thickness of 1 mm. The low resistive composites ( $< 10^7 \Omega\text{m}$ ) were measured on stripes (10 mm × 30 mm × 2 mm) using a 4-point test fixture. The distances between the inner and outer electrodes were 10 mm and 16 mm. Uniaxial and cyclic piezoresistance tests were performed on DIN S2 dumbbell specimens using an in-house developed instrument, as described in previous work [10]. The resistances of the composite were measured as a function of applied strain with a constant cross-head speed of 50 mm/min. The stress, strain and resistance measured in real-time (0.5 s intervals) were monitored and recorded by a PC [10]. The normalized change of electrical resistance was used to represent the piezoresistive response to strain, as shown in Eq. (2).

$$\text{Piezoresistive response} = \frac{\Delta R}{R_0} = \frac{R(\epsilon) - R_0}{R_0} \quad (2)$$

where  $\Delta R$  is the resistance difference,  $R(\epsilon)$  is the resistance of the specimen for the applied strain  $\epsilon$ , and  $R_0$  is the resistance of the unstrained specimen. Hardness of the vulcanisates was measured as per ISO 7619-1 using Shore A durometer (Digi test, Bareiss, Germany). For the dynamic mechanical analyses (DMA), temperature sweep tests were carried out using a mechanical spectrometer (GABO EPLEXOR 150N, Germany) at 0.5% dynamic strain, 2 K/min heating rate and 10 Hz frequency. The amplitude sweep tests were performed with a dynamic mechanical analyser (GABO EPLEXOR 2000N, Germany) at 10 Hz, 20 °C and 60% of pre-strain. The difference in storage moduli ( $E'$ ) between low (0.16%) and high (20%) strains, the Payne effect, was used as a measure of the filler-filler interactions [3]. Tensile tests were performed with the universal mechanical tester (Zwick 8195.04, Germany) according to DIN 53504 S2 with a cross-head speed of 200 mm/min.

## 3. Results and discussion

### 3.1. Determination of percolation threshold

In order to determine the percolation threshold, the composites were prepared with different loadings of CB from 0 phr to 20 phr (without addition of IL). The conductivities as a function of volume fraction of CB are shown in Fig. 1(a).

The unfilled vulcanisate displays the lowest conductivity in the order of  $10^{-13} \text{ S/m}$ . The results show that the conductivities increase slightly as the filler volume fractions increase up to 0.030. A sharp increase in conductivity is found at a filler volume fraction around 0.035–0.040. Based on the classical percolation theory [4], the electrical conductivity is very dependent on the CB concentration in the composite, as shown by the scaling law equation, Eq. (3).

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