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Effect of Styrene-Butadiene Rubber Electrolytes Modified with $BaCl_2$, $MoCl_2$ and Active Carbon

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Styrene-butadiene rubber (SBR), as a solvent and repository of electric charges, gain these properties after adding to methanolic solution of $BaCl_2$ or $MoCl_2$ and active carbon by styrene-butadiene rubber. Electrical conductivity of SBR-active carbon system with added $BaCl_2$ or $MoCl_2$ equals to 10^{-5} to 10^{-6} S cm^{-1} at 293 K and a frequency of 10 kHz. The examined electrolytes were tested for the frequency range of 1 to 25 KHz. These polymer electrolyte systems may find their application as materials for anticorrosive and antielectrostatic protection of fuel or hazardous material tanks.

Key Words: Polymer electrolytes, Styrene-butadiene rubber, $BaCl_2$, $MoCl_2$, Active carbon (900 m^2 g^{-1} type).

INTRODUCTION

At present, there are a number of publications containing the examples of conductive polymer application. Polymers modified with lithium compounds[1-7], which are widely used as electrolytes in the production of polymer batteries[8,9], can be included among one of the greatest achievements. Polymer composites are also obtained with copper compounds[10], magnesium compounds[11], silver compounds[12] and sodium compounds[13-34], but to a lesser degree when compared with lithium compounds.

In the present paper, a method is presented for obtaining polymer electrolytes from styrene-butadiene rubber. As a factor inducing electrical conductivity of polymer systems, $BaCl_2$ or $MoCl_2$ (manufactured by Chempur®, Poland) were used as well as active carbon (also manufactured by Chempur®, Poland) with a 900 m^2 active surface per one gram of active carbon.

For research purposes, styrene-butadiene rubber as a 1,4-*cis* and -*trans* mixture composed of 77 % butadiene and 23 % styrene (these values being expressed as molar fractions) was selected due to its good quality and low price, manufactured by the Dwory Chemical Plant S.A. near Oswiecim. This rubber was obtained in the process of low-temperature emulsion copolymerisation, No. KER® 1507.

EXPERIMENTAL

Synthesis of the system: SBR + $BaCl_2$ or $MoCl_2$ + active carbon

Stage-1: Dissolution of styrene-butadiene rubber (SBR) with active carbon addition: Styrene-butadiene rubber is well-soluble in toluene. Toluene (40 mL), is added to 3 g of fine-cut SBR. After 3 d of leaving it at room temperature, the polymer becomes an oily substance. Such a dissolved rubber was supplemented with active carbon (powdery form) in the amount of 0.5, 1, 1.5, 2 and 2.5 g.

Stage-2: Synthesis of polymer electrolyte: Before obtaining a rubber electrolyte with active carbon addition, a maximum amount (5 g) of $BaCl_2$ or $MoCl_2$ possible for adding was determined. The tests executed to increase the conductivity by adding bigger quantities $BaCl_2$ or $MoCl_2$ to the rubber demonstrated that the polymer dissolved in toluene is not precipitated as homogenous gel, but is broken into small, inhomogeneous forms of particles. $BaCl_2$ or $MoCl_2$ (5 g) dissolved in 40 mL methanol and added to the SBR solution prepared earlier with addition of active carbon.

After stirring, rubber electrolyte precipitated from the solution almost at once. Such a rubber electrolyte system is left for 1 d after removal from the solution. After 1 d, the rubber system is subjected to electrical conductivity testing (Fig. 1).

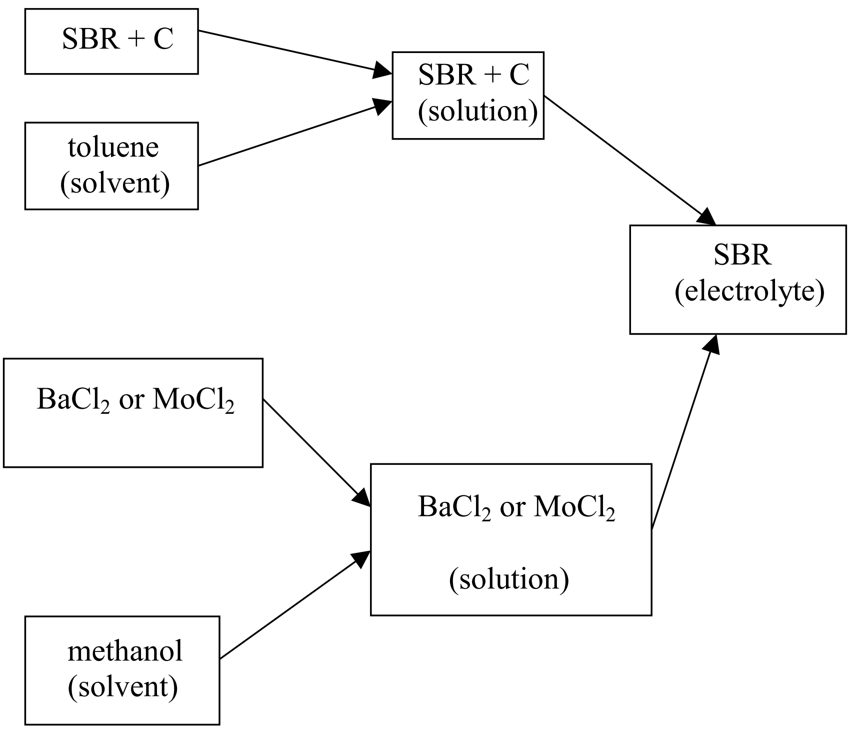

Fig. 1. Preparation of conductive styrene-butadiene rubber (SBR)

Methods for measurements of polymeric electrolytes: To determine the electrolytic conductivity, the system obtained was subjected to testing using a variable current with a frequency varying between 1 Hz and 25 KHz. The following testing equipment was used for this purpose (Fig. 2).

(a) A Hewlett Packard's Alternator 33120A 15 MHz, A Function/Arbitary Waveform Generator; (b) An Agilent 3458A 8 ½ Digit Multimeter; (c) A Hewlett Packard's Infinium Oscilloscope 500 Mhz, 1 Gigasample-per-second.

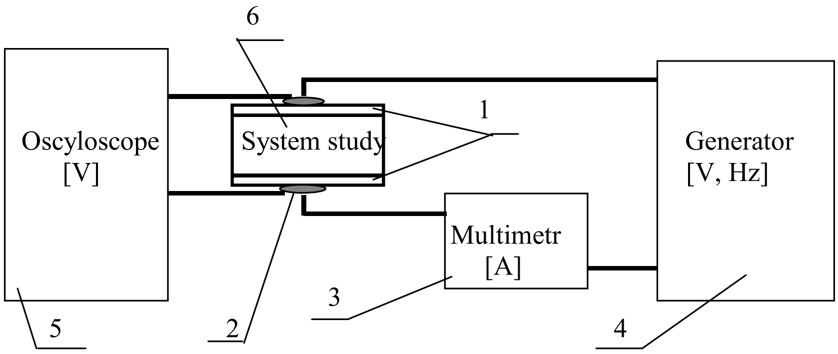

Fig. 2. Measuring diagram of the conductivity of the polymer system being tested: 1 = Copper plates, 2 = Junction of a conductor with a copper plate, 3 = Multimeter, 4 = Alternator, 5 = Oscilloscope, 6 = Polymeric electrolyte

Tables 1 and 2 present the amounts which were added to rubber for a constant concentration of 3 g SBR per 40 mL toluene and a variable amount of active carbon in a temperature ranging from 273 to 313 K. For each temperature, electrical conductivity was determined of the obtained rubber electrolytes with addition of active carbon and of the added electrolytes in methanol: $BaCl_2$ or $MoCl_2$.

TABLE-1
ELECTRICAL CONDUCTIVITY OF RUBBER ELECTROLYTE AT TEMPERATURE RANGING FROM 273-313 K FOR SBR + $BaCl_2$ + ACTIVE CARBON SYSTEM

Quantity of active carbon (g)	Temperature 273 K (S cm^{-1})	Temperature 283 K (S cm^{-1})	Temperature 293 K (S cm^{-1})	Temperature 303 K (S cm^{-1})	Temperature 313 K (S cm^{-1})
0.5	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-7}
1.0	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-7}
1.5	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}
2.0	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}
2.5	1.5×10^{-5}	1.5×10^{-5}	1.5×10^{-5}	1.6×10^{-5}	1.7×10^{-5}

The polymers of the good conductivity are such polymers, which conductivity is bigger than 10^{-3} S cm^{-1}, whereas for the protective finishes used as the materials for the anti-corrosive and anti-static protections, such a high conductivity is not required, but above 10^{-5} S cm^{-1}.

TABLE-2
ELECTRICAL CONDUCTIVITY OF RUBBER ELECTROLYTE AT TEMPERATURE RANGING FROM 273-313 K FOR SBR + $MoCl_2$ + ACTIVE CARBON SYSTEM

Quantity of active carbon (g)	Temperature 273 K (S cm^{-1})	Temperature 283 K (S cm^{-1})	Temperature 293 K (S cm^{-1})	Temperature 303 K (S cm^{-1})	Temperature 313 K (S cm^{-1})
0.5	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-7}
1.0	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-7}
1.5	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-7}
2.0	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}
2.5	8.3×10^{-6}	8.3×10^{-6}	9.1×10^{-6}	1.0×10^{-5}	1.1×10^{-5}

RESULTS AND DISCUSSION

Rubber electrolyte systems after adding $BaCl_2$ or $MoCl_2$ causes the whole system to become a conductive system. After adding $BaCl_2$ or $MoCl_2$ to SBR with active carbon, the electrical conductivity of such systems ranges from 10^{-5}–10^{-6} S cm^{-1}. For these four systems of rubber electrolytes, an optimum amount of the added $BaCl_2$ or $MoCl_2$ equals to 5 g.

It results for each rubber electrolyte system tested for its electrical conductivity that such rubber systems have low conductive properties. Such systems, however, show inconsiderable changes of electrical conductivity in a temperature ranging from 273 to 313 K. Such rubber systems are stable in variable temperatures, although they have low values of electrical conductivity.

Fig. 3 showed a diagram of container coating with conducting material. Metal container is covered with oily conductive rubber. After 2 d, when conductive rubber has been cross-linked with atmospheric oxygen, it is being protected with bituminous coating with the same or lower hardness.

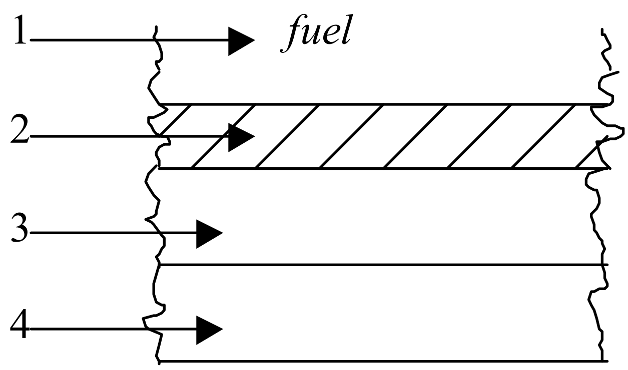

Fig. 3. Scheme of anti-static and anti-corrosion protection by the conductive polymer composite consisting in: 1 = Fuel, 2 = Metallic container, 3 = Polymer electrolytes system: SBR + $BaCl_2$ or $MoCl_2$ + active carbon, 4 = Bitumen coating

Except for the conducting properties, this polymer changes its colour from the transparent-yellow insulator into the colour of the conducting, non-transparent gel. It is caused by adding $BaCl_2$ or $MoCl_2$ in the form of ions to the polymer. Except for the conducting properties of such rubber electrolyte, it has also features of a viscous gel, which allows cover the external surface of a tank hermetically. However, such a system has a negative feature. The ageing time period of the electrolyte is very fast. It is caused by oxidation of the conducting system. The oxidised system of the rubber electrolyte starts being brittle and breakable and hardly adhesive to the surface of the tank. Eliminating of this disadvantageous phenomenon is executed by protection of the electrolyte surface with the layer of the bituminous finish.

Conclusion

Such systems can find their application as materials for anticorrosive and antielectrostatic protection of tanks with flammable and hazardous materials, as electrical conductivity of the tested systems changes inconsiderably in a variable temperature.

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