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Styrene-Butadiene Rubber Electrolytes Modified with $CaCl_2$, $CdCl_2$, $CuCl_2$, $MnCl_2$ and Active Carbon

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Styrene-butadiene rubber (SBR), as a solvent and repository of electric charges, starts to gain these properties after adding to SBR $CaCl_2$, $CdCl_2$, $CuCl_2$ or $MnCl_2$ in methanol solution with addition of active carbon. Electrical conductivity of such an SBR-active carbon system with added $CaCl_2$ or $CdCl_2$ or $CuCl_2$ or $MnCl_2$ equals to 10^{-6} to 10^{-5} S cm^{-1} at a room temperature (293 K) and a frequency of 10 KHz. The electrolytes were tested for the frequency range of 1 Hz 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, Active carbon.

INTRODUCTION

At present, there are a good 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[13-20], but to a lesser degree when compared with lithium compounds.

In the present work, a method is presented of obtaining polymer electrolytes from styrene-butadiene rubber. As a factor inducing electrical conductivity of polymer systems, $CaCl_2$, $CdCl_2$, $CuCl_2$ and $MnCl_2$ (manufactured by Chempur®, Poland) were used as well as active carbon (also manufactured by Chempur®, Poland) with a 900 m^2 active surface per 1 g 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 copolymerization, No. KER® 1507.

EXPERIMENTAL

Synthesis of the system: Styrene-butadiene rubber + $CaCl_2$ or $CdCl_2$ or $CuCl_2$ or $MnCl_2$ + active carbon

Stage-1: Dissolution of styrene-butadiene rubber with active carbon addition: Styrene-butadiene rubber is well-soluble in toluene. Toluene, in the amount of 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, 1.0, 1.5, 2.0 and 2.5 g.

Stage-2: Synthesis of polymer electrolyte: Before obtaining a rubber electrolyte with active carbon addition, a maximum amount of $CaCl_2$ or $CdCl_2$ or $CuCl_2$ or $MnCl_2$ possible for adding was determined.

This amount was assayed and it equaled to 5 g of $CaCl_2$ or $CdCl_2$ or $CuCl_2$ or $MnCl_2$. After adding a larger amount than 5 g of $CaCl_2$ or $CdCl_2$ or $CuCl_2$ or $MnCl_2$, problems related to precipitation of rubber electrolytes in the form of gel from this solution occurred in all systems. These problems consisted in a non-homogenous form of gel (Fig. 1).

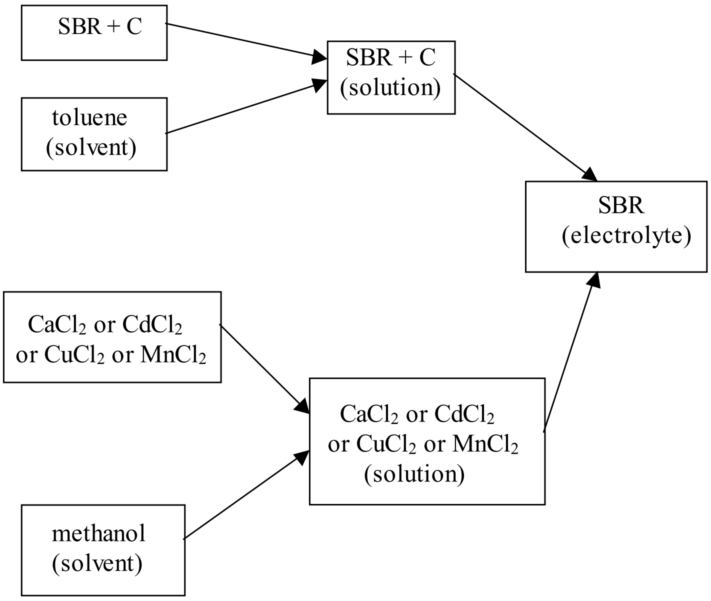

Fig. 1. Preparation of conductive styrene-butadiene rubber (SBR)

$CaCl_2$ or $CdCl_2$ or $CuCl_2$ or $MnCl_2$ in the amount of 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 one day, the rubber system is subjected to electrical conductivity testing.

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 Hewlett Packard's alternator 33120A 15 MHz
  A Function/Arbitary
  Waveform Generator
- An Agilent 3458A 8 ½ Digit Multimeter
- A Hewlett Packard's infinium oscilloscope 500 MHz 1Gsa/s.

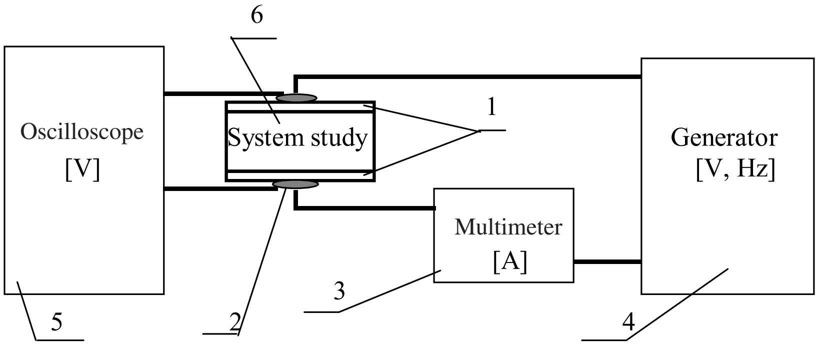

Fig. 2. Measuring diagram of the conductivity of the polymer system being tested: 1= copper plates, 2 = junction of a conductor with a copper plate, 3 = multimeter, 4 = alternator, 5 = oscilloscope, 6 = polymeric electrolyte

RESULTS AND DISCUSSION

Table-1 presented the amounts of active carbon in methanol, 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: $CaCl_2$, $CdCl_2$, $CuCl_2$ or $MnCl_2$.

Rubber electrolyte systems after adding $CaCl_2$, $CdCl_2$, $CuCl_2$ or $MnCl_2$ causes the whole system to become a conductive system. After adding $CaCl_2$, $CdCl_2$, $CuCl_2$ or $MnCl_2$ to SBR with active carbon, the electrical conductivity of such systems ranges from 10^{-6}-10^{-5} S cm^{-1}. For these four systems of rubber electrolytes, an optimum amount (5 g) of the added $CaCl_2$, $CdCl_2$, $CuCl_2$ or $MnCl_2$.

TABLE-1
ELECTRICAL CONDUCTIVITY (S cm^{-1}) OF RUBBER ELECTROLYTE IN A TEMPERATURE RANGING FROM 273 TO 313 K

Quantity of active carbon (g)	Temperature (K)				
	273	283	293	303	313
For SBR + $CaCl_2$ + Active carbon system					
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	1.7×10^{-6}	1.7×10^{-6}	1.7×10^{-6}	1.8×10^{-6}	1.8×10^{-6}
For SBR + $CdCl_2$ + Active carbon system					
0.5	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-7}
1.0	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}
1.5	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}
2.0	10^{-5}	10^{-5}	10^{-5}	10^{-5}	10^{-5}
2.5	2.5×10^{-5}	2.5×10^{-5}	2.7×10^{-5}	2.8×10^{-5}	2.9×10^{-5}
For SBR + $CuCl_2$ + Active carbon system					
0.5	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-7}
1.0	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}
1.5	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}
2.0	10^{-5}	10^{-5}	10^{-5}	10^{-5}	10^{-5}
2.5	5.0×10^{-5}	5.0×10^{-5}	5.2×10^{-5}	5.3×10^{-5}	5.5×10^{-5}
For SBR + $MnCl_2$ + Active carbon system					
0.5	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}
1.0	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}
1.5	10^{-5}	10^{-5}	10^{-5}	10^{-5}	10^{-5}
2.0	2.7×10^{-5}	2.8×10^{-5}	2.8×10^{-5}	2.7×10^{-5}	2.6×10^{-5}
2.5	6.2×10^{-5}	6.2×10^{-5}	6.6×10^{-5}	6.6×10^{-5}	7.1×10^{-5}

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. It is suggested that such rubber systems are stable in a variable temperature, 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.

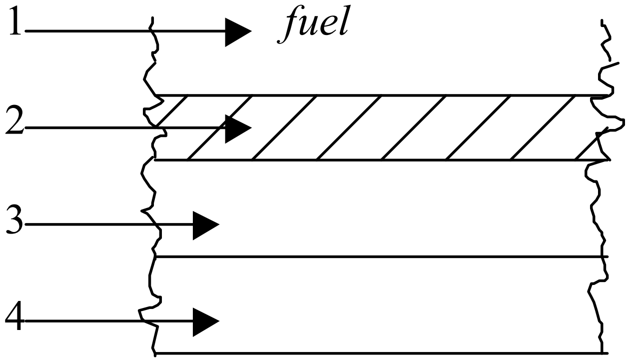

Fig. 3. Scheme of antistatic and anticorrosion protection by the conductive polymer composite consisting in: 1 = fuel, 2 = metallic container, 3 = polymer electrolytes system: styrene-butadiene rubber + $CaCl_2$, $CdCl_2$, $CuCl_2$ or $MnCl_2$ + carbon active, 4 = bitumen coating

Conclusion

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

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