Rubber electrolytes on the basis: styrene–butadiene rubber with an addition of $CoCl_2$ or $FeCl_2$ and active carbon

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Styrene-butadiene rubber (SBR) becomes conducting material after addition of $CoCl_2$ or $FeCl_2$ in the methyl alcohol solution active carbon. Electrical conductivity of such an SBR-active carbon system with added $CoCl_2$ or $FeCl_2$ equals to $5{,}3 \cdot 10^{-5}$ to $4{,}1 \cdot 10^{-5}$ $S \cdot cm^{-1}$ at a room temperature of 293 K and a frequency of 10 kHz. The examined electrolytes were tested for the frequency range of 1 kHz 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, SBR, $CoCl_2$, $FeCl_2$, active carbon (900 $m^2 \cdot g^{-1}$)*

Elektrolity kauczuku butadienowo-styrenowego z dodatkiem $CoCl_2$ albo $FeCl_2$ i węgla aktywnego

Kauczuk butadienowo-styrenowy (SBR) po dodaniu $CoCl_2$ lub $FeCl_2$ w postaci roztworu w alkoholu metylowym i węgla aktywnego, zaczyna wykazywać właściwości przewodzące. Przewodność właściwa (konduktywność) takiego układu wynosi od $5{,}3 \cdot 10^{-5}$ do $4{,}1 \cdot 10^{-5}$ $S \cdot cm^{-1}$ w temperaturze 293 K i przy częstotliwości 10 Hz. Przewodność uzyskanych elektrolitów badano w zakresie częstotliwości od 1 do 25 Hz. Takie elektrolity polimerowe mogą być stosowane do antykorozyjnej i antyelektrostatycznej ochrony zbiorników paliwa i materiałów niebezpiecznych.

Słowa kluczowe: *elektrolity polimerowe, SBR, $CoCl_2$, $FeCl_2$, węgiel aktywny (typu: 900 $m^2 \cdot g^{-1}$)*

1. Introduction

At present, there are a lot 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 [13-28], but to a lesser degree when compared with lithium compounds.

In the present paper, a method is presented of obtaining polymer electrolytes from styrene-butadiene rubber. As a factor inducing electrical conductivity of polymer systems, $CoCl_2$ or $FeCl_2$ (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 (KER® 1507), was selected due to its good quality and low price, manufactured by the Chemical Plant of Dwory near Oświęcim, Poland.

2. Experimental procedure

2.1. Preparation of the system: SBR + $CoCl_2$ or $FeCl_2$ + active carbon

- ***Stage 1 – dissolution of styrene-butadiene rubber with active carbon addition***

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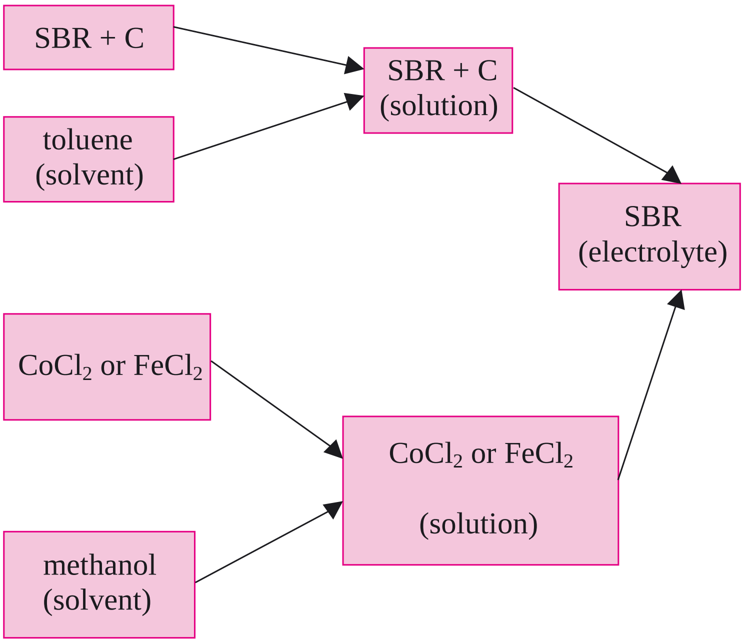

Figure 1. *Preparation of conductive styrene-butadiene rubber (SBR)*
Rysunek 1. *Preparatyka przewodzącego kauczuku butadienowo-styrenowego (SBR)*

Styrene-butadiene rubber is well-soluble in toluene. Toluene, in the amount of 40 cm^3, is added to 3 grams of fine-cut SBR. After three days 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 g, 1 g, 1.5 g, 2 g and 2.5 g.

- ***Stage 2 – synthesis of polymer electrolyte***

Before obtaining a rubber electrolyte with active carbon addition, a maximum amount of $CoCl_2$ or $FeCl_2$ possible for adding was determined. This amount was assayed and it equaled to 5 grams of $CoCl_2$ or $FeCl_2$. After adding a larger amount than 5 grams of $CoCl_2$ or $FeCl_2$, problems related to precipitation of rubber electrolytes in the form of gel from this solution was occurred in all systems. These problems consisted in a non-homogenous form of gel.

$CoCl_2$ or $FeCl_2$ in the amount of 5 grams dissolved in 40 cm^3 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 one day after removal from the solution. After one day, the rubber system is subjected to electrical conductivity testing (Figure 1).

3. Methods for evaluation 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 (Figure 2):

- A HEWLETT PACKARD's alternator 33120A 15 MHz
- A FUNCTION / ARBITARY WAVEFORM Generator

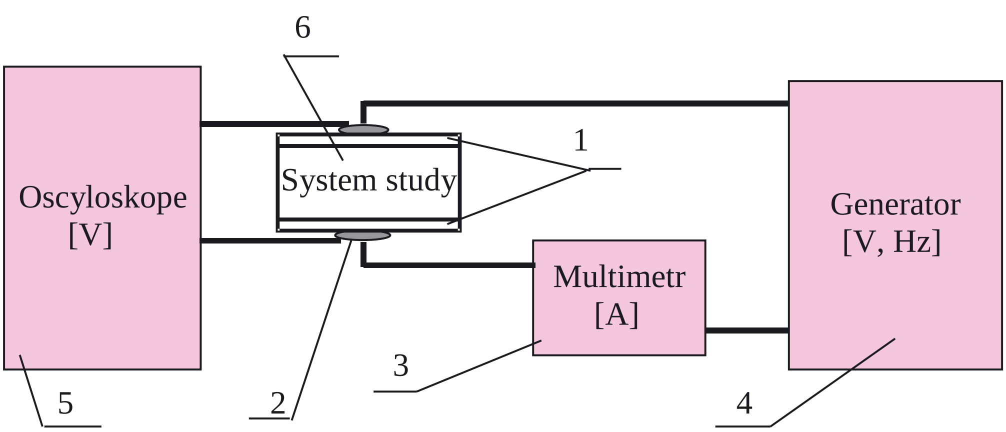

Figure 2. *Measuring diagram of the conductivity of the polymer system being tested: 1 – copper plates, 2 – junction of a conductor with a copper plate, 3 – multimeter, 4 – alternator, 5 – oscilloscope, 6 – polymer electrolytes system*
Rysunek 2. *Schemat pomiarowy przewodnictwa badanego układu polimerowego: 1 – płytki miedziane, 2 – miejsce złączenia przewodu z płytką miedzianą, 3 – multimetr, 4 – generator prądu zmiennego, 5 – oscyloskop, 6 – elektrolit polimerowy*

- An AGILENT 3458A 8 $^{1}/_{2}$ DIGIT MULTIMETER
- A HEWLETT PACKARD's infinium oscilloscope 500 MHz 1Gsa/s

4. Test results

In table 1 and 2 are presented the amounts which were added to rubber for a constant concentration of 3 g SBR per 40 cm^3 toluene and a variable amount of active carbon in a temperature ranging from 273 K 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: $CoCl_2$ or $FeCl_2$.

5. Discussion

Rubber electrolyte systems consisted $CoCl_2$ or $FeCl_2$ causes the whole system to become a conductive system. After adding $CoCl_2$ or $FeCl_2$ to SBR with active carbon, the electrical conductivity of such systems ranges from $5{,}3\cdot10^{-5}$ to $4{,}1\cdot10^{-5}$ $S\cdot cm^{-1}$ at a room temperature of 293 K and a frequency of 10 kHz. For these four systems of rubber electrolytes, an optimum amount of the added $CoCl_2$ or $FeCl_2$ equals to 5 grams.

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 K to 313 K. One may think thus that such rubber systems are stabile in variable temperature, although they have low values of electrical conductivity.

In Figure 3 is showed a diagram of container coating with conducting material. Metal container is covered with oily conductive rubber. Next, it is being protected with bituminous coating with the same, or lower, hardness.

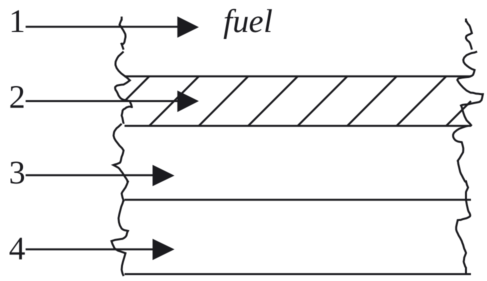

Figure 3. *Scheme of anti-static and anti-corrosion protection by the conductive polymer composite consisting in: 1 – fuel, 2 – metallic container, 3 – polymer electrolytes system: styrene-butadiene rubber + $CoCl_2$ or $FeCl_2$, + active carbon, 4 – bitumen coating*

Rysunek 3. *Schemat zabezpieczenia antystatycznego i antykorozyjnego przewodzącym kompozytem polimerowym: 1 – paliwo, 2 – metalowy zbiornik, 3 – polimer przewodzący typu: kauczuk butadienowo-styrenowy + $CoCl_2$ lub $FeCl_2$ + węgiel aktywny, 4 – powłoka bitumiczna*

Table 1. *Electrical conductivity of rubber electrolyte in different a temperature ranging from 273 K to 313 K for SBR + $CoCl_2$ + active carbon system*

Tabela 1. *Konduktywność elektrolitu kauczukowego w zakresie temperatury od 273 K do 313 K; układ: SBR + $CoCl_2$ + węgiel aktywny*

Quantity of active carbon	Temperature 273 K [$S\cdot cm^{-1}$]	Temperature 283 K [$S\cdot cm^{-1}$]	Temperature 293 K [$S\cdot cm^{-1}$]	Temperature 303 K [$S\cdot cm^{-1}$]	Temperature 313 K [$S\cdot cm^{-1}$]
0,5 g	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-7}
1 g	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}
1,5 g	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}
2 g	10^{-5}	10^{-5}	10^{-5}	10^{-5}	10^{-5}
2,5 g	$5{,}2\cdot10^{-5}$	$5{,}3\cdot10^{-5}$	$5{,}3\cdot10^{-5}$	$5{,}4\cdot10^{-5}$	$5{,}5\cdot10^{-5}$

Table 2. *Electrical conductivity of rubber electrolyte in different temperature ranging from 273 K to 313 K for SBR + $FeCl_2$ + active carbon system*

Tabela 2. *Konduktywność elektrolitu kauczukowego w zakresie temperatury od 273 K do 313 K; układ: SBR + $FeCl_2$ + węgiel aktywny*

Quantity of active carbon	Temperature 273 K [$S\cdot cm^{-1}$]	Temperature 283 K [$S\cdot cm^{-1}$]	Temperature 293 K [$S\cdot cm^{-1}$]	Temperature 303 K [$S\cdot cm^{-1}$]	Temperature 313 K [$S\cdot cm^{-1}$]
0,5 g	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-7}
1 g	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-7}
1,5 g	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}
2 g	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}
2,5 g	$3{,}9\cdot10^{-5}$	$4{,}0\cdot10^{-5}$	$4{,}1\cdot10^{-5}$	$4{,}3\cdot10^{-5}$	$4{,}6\cdot10^{-5}$

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 inserting $CoCl_2$ or $FeCl_2$ in the form of ions to the polymer. Except for the conducting properties of such caoutchouc 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 oxidized system of the caoutchouc 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.

6. Conclusions

Such systems can find their 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.

References

1. *Khorassani A. and West A.R., Solid State Ionics (1982), 7, 1-8*
2. *Finn W. Poulsen, Solid State Ionics (1981), 2, 53-57*
3. *Kamphorst J.G. and Hellstrom E.E., Solid State Ionics (1980), 1, 187-1979*
4. *Ostrovskii D., Torell L.M., Appeteccchi G.B. and Scrosati B., Solid State Ionics (1998), 106, 19-24*
5. *Deepa M., Sharma N., Agnihotry S.A., Solid State Ionics (2002), 152-153, 253-258*
6. *Glasse M.D., Idris R., Latham R.J., Linford R.G., Schlindwein W.S., Solid State Ionics (2002), 147, 289-294.*
7. *Idris R., Glasse M.D., Latham R.J., Linford R.G., Schlindwein W.S., Jurnal of Power Sources (2001), 94, 206-211.*
8. *Nashiura M., Kono M., Namegaya N., Matsuda Y., Solid State Lett. 1 (1998), 1, 246-248*
9. *Kim D., Journal of Power Sources (2000), 87, 78-83*
10. *Lewandowski A., Stepniak I., Grzybkowski W., Solid State Ionics (2001), 143, 425-432*
11. *Vito de Noto, Vittadello M., Solid State Ionics (2002), 147, 309-316*
12. *Gargarczyk J.E., Machowski P., Wasiucionek M. and Jakubowski W., Solid State Ionics (2003), 157, 269-273*
13. *Himba T., Solid State Ionics (1983), 9-10, 1101--1105*
14. *Gomes Correia S.M., de Zea Bermudez V., Silva M.M., Solid State Ionics (2003), 156, 85-93*
15. *Borowski T., Fuels, oils and greases in exploatation, (2003), 115, 8-10*
16. *Borowski T., Karczmarek J., Kwaśniewski J., Oleksy M., Chemik, (2004), 11, 447-450.*
17. *Borowski T., Karczmarek J., Kwaśniewski J., Oleksy M., Hryniewicz T., Przem. Chem. (2005), 8, 607--610*
18. *Borowski T., Sienicki W., Mat. II Conference Polymers, Poznań 2003*
19. *Borowski T., Sienicki W., Mat. XLVI Congress Science PSC, Lublin 2003, p. 700.*
20. *Borowski T., Hryniewicz T., Mat. VII Conference Polish Academy Science, Słupsk 2004, (2004) 79-124.*
21. *Hryniewicz T., Borowski T., International Conference on Vehicles Alternative Fuel Systems and Environmental Protection, Dublin, Ireland 2004, No. 182*
22. *Borowski T., IX International Conference on Frontiers of Polymers and Advanced Materials, Cracow (Poland), 8-12 July 2007, p. 328*
23. *Borowski T., Fifteenth Annual International Conference on Composites/Nano Engineering (ICCE--15), July 15-21, 2007, Haikou, Hainan, China, p. 100-101*
24. *Borowski T., Journal of Power Sources (2007) 172, 988 – 990*
25. *Borowski T., Materials Letters (2008), 62, 1382 – 1384*
26. *Borowski T., Asian Journal of Chemistry Vol. 20, No.4 (2008), 3083*
27. *Borowski T., Science and Engineering of Composite Materials (2008), Vol.15, No. 2, 159 – 164*
28. *Borowski T., Molecular Crystals & Liquid Crystals (2008), Vol. 484, Issue 1, 127[493]-133[499]*