Effect of Natural Rubber Electrolytes Modified with CoCl$_2$, FeCl$_2$, SrCl$_2$, ZnCl$_2$ and Active Carbon

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Natural rubber (NR), as a solvent and repository of electric charges, starts to gain these properties after adding to NR $CoCl_2$ or $FeCl_2$ or $SrCl_2$ or $ZnCl_2$ in the form of methanol solution with addition of active carbon. Electrical conductivity of such a NR – active carbon system with added NR $CoCl_2$ or $FeCl_2$ or $SrCl_2$ or $ZnCl_2$ equals to 10^{-6} to $10^{-5}\,S \cdot cm^{-1}$ 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.

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 [13–29], but to a lesser degree when compared with lithium compounds.

In the present article, a method is presented of obtaining polymer electrolytes from natural rubber. As a factor inducing electrical conductivity of polymer systems, CoCl₂, FeCl₂, SrCl₂ and ZnCl₂ (manufactured by Chempur®, Poland) were used as well as active

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carbon (also manufactured by Chempur®, Poland) with a $900\,m^2$ active surface per one gram of active carbon.

Natural rubber (*Hevea brasiliensis*), which was used for obtaining polymer electrolytes, originated from a Para rubber tree plantation in Ranni, Kerala State, southwestern India. Natural rubber (NR) was collected and taken down from a Para rubber tree and imported to Poland in June 2006.

2. EXPERIMENTAL PROCEDURE

2.1. Synthesis of the System: NR + CoCl$_2$ or FeCl$_2$ or SrCl$_2$ or ZnCl$_2$ + Active Carbon

2.1.1. Stage 1 – Dissolution of Rubber Latex with Active Carbon Addition

Natural rubber is found in the form of rubber latex and oxidates quickly in the air, producing an elastic and stretchy caoutchouc (India-rubber). In order to avoid this process (since India-rubber dissolves more easily in the form of rubber latex), it was immediately added to toluene (99% pure). Toluene (manufactured by Spectrum Chemicals, Edayar, Cochin-683 502, India, Code: T 0105) was bought straight before collection of natural rubber in India. Natural rubber latex, preserved this way, was imported to Poland.

To work out a method of natural conductive rubber synthesis, it required in the first stage to precipitate rubber latex from toluene and to dissolve it again in toluene in order to make strictly specific mass recalculations. For precipitating the rubber latex, methanol (98%, manufactured by Chempur®, Poland) was used. Rubber latex can be dissolved in petrol or benzene, but it best dissolves in toluene. For this purpose, toluene (99.5%, manufactured by Chempur®, Poland) was used. Proportions of rubber latex dissolution are as follows: 3 grams of natural rubber were added to $40\,cm^3$ of toluene.

Such a rubber solution was left for 12 hours, shaking it from time to time. After 12 hours, natural rubber was again dissolved in toluene of a known concentration and of white oily consistency. Such a natural rubber solution 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.

2.1.2. Stage 2 – Synthesis of Polymer Electrolyte

Before obtaining a rubber electrolyte with active carbon addition, a maximum amount of CoCl$_2$ or FeCl$_2$ or SrCl$_2$ or ZnCl$_2$ possible for adding was determined. This amount was assayed and it equaled to

5 grams of $CoCl_2$ or $FeCl_2$ or $SrCl_2$ or $ZnCl_2$. After adding a larger amount than 5 grams of $CoCl_2$ or $FeCl_2$ or $SrCl_2$ or $ZnCl_2$, 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.

$CoCl_2$ or $FeCl_2$ or $SrCl_2$ or $ZnCl_2$ in the amount of 5 grams dissolved in $40\,cm^3$ methanol and added to the NR 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.

3. 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. 1)

- A HEWLETT PACKARD's alternator 33120 A 15 MHz A FUNCTION/ ARBITARY WAVEFORM Generator
- An AGILENT 3458 A 8½; DIGIT MULTIMETER
- A HEWLETT PACKARD's infinium oscilloscope 500 MHz 1 Gsa/s
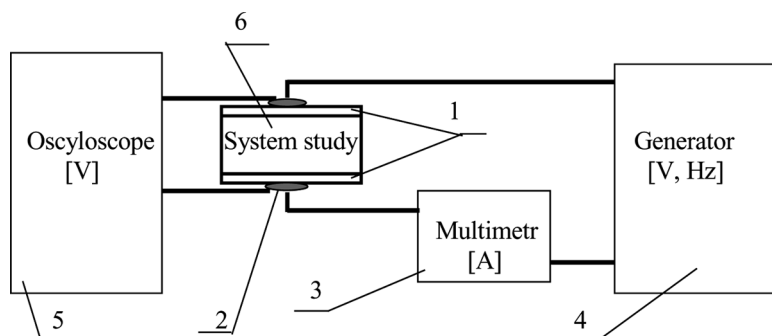
FIGURE 1 Measuring diagram of the conductivity of the polymer system being tested: 1 – copper plates, 2 – junction of a conductor with a copper plate, 3 – multimeter, 4 – alternator, 5 – oscilloscope, 6 – polymeric electrolyte.

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4. SUMMARY FINDINGS

In Tables 1, 2, 3 and 4 are presented the amounts of active carbon in methanol, which were added to natural rubber for a constant concentration of 3 g NR per 40 cm^3 toluene and a variable amount of active

TABLE 1 Electrical Conductivity of Rubber Electrolyte in a Temperature Ranging from 273 K to 313 K for NR + CoCl$_2$ + Active Carbon System

Quantity of active carbon	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 g	10^{-8}	10^{-8}	10^{-8}	10^{-8}	10^{-8}
1 g	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-7}
1,5 g	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-7}
2 g	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}
2,5 g	$9,6 \cdot 10^{-6}$	$9,6 \cdot 10^{-6}$	$9,7 \cdot 10^{-6}$	$9,8 \cdot 10^{-6}$	$9,9 \cdot 10^{-6}$

TABLE 2 Electrical Conductivity of Rubber Electrolyte in a Temperature Ranging from 273 K to 313 K for NR + FeCl$_2$ + Active Carbon System

Quantity of active carbon	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 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	$6,6 \cdot 10^{-5}$	$6,7 \cdot 10^{-5}$	$6,7 \cdot 10^{-5}$	$6,8 \cdot 10^{-5}$	$7,0 \cdot 10^{-5}$

TABLE 3 Electrical Conductivity of Rubber Electrolyte in a Temperature Ranging from 273 K to 313 K for NR + SrCl$_2$ + Active Carbon System

Quantity of active carbon	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 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	$4,5 \cdot 10^{-5}$	$4,6 \cdot 10^{-5}$	$4,7 \cdot 10^{-5}$	$4,7 \cdot 10^{-5}$	$4,9 \cdot 10^{-5}$

TABLE 4 Electrical Conductivity of Rubber Electrolyte in a Temperature Ranging from 273 K to 313 K for NR + ZnCl$_2$ + Active Carbon System

Quantity of active carbon	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 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	$7,3 \cdot 10^{-5}$	$7,3 \cdot 10^{-5}$	$7,4 \cdot 10^{-5}$	$7,5 \cdot 10^{-5}$	$7,6 \cdot 10^{-5}$

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$_2$, FeCl$_2$, SrCl$_2$, and ZnCl$_2$.

5. DISCUSSION

Rubber electrolyte systems after adding CoCl$_2$ or FeCl$_2$ or SrCl$_2$ or ZnCl$_2$ causes the whole system to become a conductive system. After adding CoCl$_2$ or FeCl$_2$ or SrCl$_2$ or ZnCl$_2$ to NR 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 of the added equals to 5 grams.

It results for each rubber electrolyte system tested for its electrical conductivity that such rubber systems have low conductive properties.
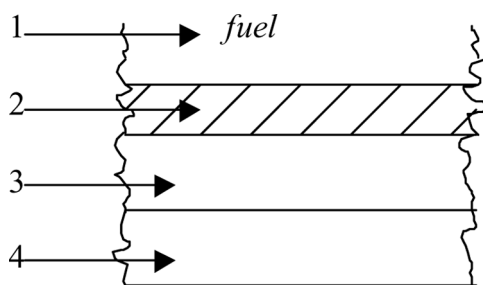
FIGURE 2 Scheme of anti-static and anti-corrosion protection by the conductive polymer composite consisting in: 1 – fuel, 2 – metallic container, 3 – polymer electrolytes system: natural rubber + CoCl$_2$ or FeCl$_2$ or SrCl$_2$ or ZnCl$_2$, 4 – bitumen coating.

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Such systems, however, show inconsiderable changes of electrical con-
ductivity in a temperature ranging from 273 K to 313 K. One may
think thus that such rubber systems are stabile in a variable tempera-
ture, although they have low values of electrical conductivity.

In Figure 2 is showed a diagram of container coating with conduct-
ing material. Metal container is covered with oily conductive rubber.
Next, after two days, when conductive rubber has been cross-linked
with atmospheric oxygen, it is being protected with bituminous
coating with the same, or lower, hardness.

6. CONCLUSIONS

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

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