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Effect of Natural Rubber Electrolytes Modified with $CuCl_2$, $NiCl_2$ and Active Carbon

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Natural rubber, as a solvent and repository of electric charges, starts to gain these properties after adding to natural rubber $CuCl_2$ or $NiCl_2$ in the form of methanol solution with addition of active carbon. Electrical conductivity of such a natural rubber-active carbon system with added natural rubber $CuCl_2$ or $NiCl_2$ equals to 3.5×10^{-6} to 3.8×10^{-6} S 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 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, Natural rubber, $CuCl_2$, $NiCl_2$, 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 of obtaining polymer electrolytes from natural rubber. As a factor inducing electrical conductivity of polymer systems, $CuCl_2$, $NiCl_2$, (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.

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

EXPERIMENTAL

Synthesis of the system: Natural rubber + $CuCl_2$ or $NiCl_2$ + active carbon

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 Indian-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 g of natural rubber were added to 40 mL of toluene.

Such a rubber solution was left for 12 h, shaking it from time to time. After 12 h, 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, 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 $CuCl_2$ or $NiCl_2$ was added. This amount was assayed and it equaled to 5 g of $CuCl_2$ or $NiCl_2$. After adding a larger amount than 5 g of $CuCl_2$ or $NiCl_2$, 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.

$CuCl_2$ or $NiCl_2$ in the amount of 5 g dissolved in 40 mL methanol and added to the natural rubber 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.

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 33120A 15 MHz; a function/arbitary waveform generator. • An AGILENT 3458A 8 ½ digit multimeter; • A Hewlett Packard's infinium oscilloscope 500 MHz 1 Gsa/s.

Tables 1 and 2 represent the amounts of active carbon in methanol, which were added to natural rubber for a constant concentration of 3 g natural rubber 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 $CuCl_2$ and $NiCl_2$ in methanol.

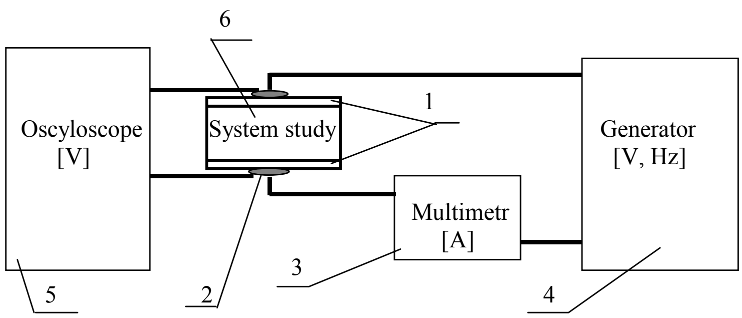

Fig. 1. Measuring diagram of the conductivity of the polymer system being tested: 1 = copper plates, 2 = junction of a conductor with a copper plate, 3 = multimeter, 4 = alternator, 5 = oscilloscope, 6 = polymeric electrolyte

TABLE-1
ELECTRICAL CONDUCTIVITY OF RUBBER ELECTROLYTE IN TEMPERATURE RANGING FROM 273 TO 313 K FOR NATURAL RUBBER + $CuCl_2$ + ACTIVE CARBON SYSTEM

Quantity of active carbon (g)	Temperature K (S cm^{-1})				
	273	283	293	303	313
0.5	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-7}
1.0	10^{-6}	10^{-6}	10^{-6}	10^{-6}	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	3.5×10^{-6}	3.7×10^{-6}	3.8×10^{-6}	3.9×10^{-6}	4.0×10^{-6}

TABLE-2
ELECTRICAL CONDUCTIVITY OF RUBBER ELECTROLYTE IN TEMPERATURE RANGING FROM 273 TO 313 K FOR NATURAL RUBBER + $NiCl_2$ + ACTIVE CARBON SYSTEM

Ilosc wegla aktywnego	Temperature K (S cm^{-1})				
	273	283	293	303	313
0.5	10^{-8}	10^{-8}	10^{-8}	10^{-8}	10^{-8}
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	3.4×10^{-6}	3.5×10^{-6}	3.5×10^{-6}	3.5×10^{-6}	3.6×10^{-6}

RESULTS AND DISCUSSION

Rubber electrolyte systems after adding $CuCl_2$ or $NiCl_2$ causes the whole system to become a conductive system. After adding $CuCl_2$ or $NiCl_2$ to natural rubber with active carbon, the electrical conductivity of such systems ranges from 3.5×10^{-6} - 3.8×10^{-6} S cm^{-1}. For these four systems of rubber electrolytes, an optimum amount of the added 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. One may think thus that such rubber systems are stable in a variable temperature, although they have low values of electrical conductivity.

Fig. 2 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.

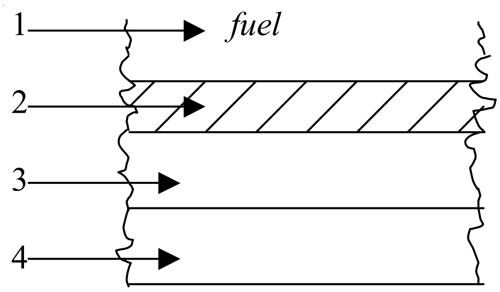

Fig. 2. Scheme of anti-static and anti-corrosion protection by the conductive polymer composite consisting in: 1 = fuel, 2 = metallic container, 3 = polymer electrolytes system: natural rubber + $CuCl_2$ or $NiCl_2$, 4 = bitumen coating

Conclusion

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.

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