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Synthesis and Conductivity of Natural Rubber, Butadiene Rubber and Butadiene-co-styrene Rubber Solutions Containing $NaClO_4$ and Active Carbon

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Natural rubber (NR), butadiene rubber (BR) and styrene-co-butadiene rubber (SBR) dissolved in toluene as solvents gains electrolytic properties after the addition of $NaClO_4$. Active carbon was also added to this polymer in order to improve its conductivity. The conductivity of the NR system with $NaClO_4$ and active carbon is equal to 4×10^{-6} S cm^{-1}, while that of the BR system with $NaClO_4$ and active carbon is equal to 5.8×10^{-5} S cm^{-1}; however, the conductivity for the SBR system with $NaClO_4$ and active carbon is 7.7×10^{-5} S cm^{-1} at a temperature of 293 K and a frequency of 10 kHz. The electrolytes were tested within a conductivity range of 1 to 25 kHz. These polymer electrolyte systems can find application as materials for anticorrosive and antielectrostatic protection in tanks designed for fuel and inflammable liquids.

Key Words: Polymer electrolytes, Natural rubber, Butadiene rubber, Styrene-co-butadiene rubber, $NaClO_4$, Active carbon.

INTRODUCTION

In present days, there are several publications containing the examples of conductive polymer applications. Polymers modified with lithium compounds[1-7], which are used in many applications, including electrolytes for polymer batteries[8], could be rated among the greatest achievements. Polymer composites with copper compounds[9], magnesium compounds[10], silver compounds[11] and sodium compounds[12-21] are also produced, but to a lesser extent.

The method for manufacturing polymer electrolytes from natural and styrene-butadiene rubber and the comparison of their conductive properties are presented in this paper. $NaClO_4$ and active carbon (both manufactured by Chempur®, Poland), with a 900 m^2 active surface area per one gram of active carbon, were used as a factor making polymer systems to be conductive.

Natural rubber (*Hevea brasiliensis*), used for manufacturing polymer electrolytes, was obtained from a rubber-tree plantation in Ranni, India. Rubber latex was collected from rubber trees by the author himself, after tapping them earlier. Thereafter, it was brought to Poland in July 2006.

The butadiene rubber, as a mixture of 1,4-*cis* and -*trans* and the styrene-co-butadiene rubber, as a mixture of 1,4-*cis* and -*trans*, composed of 77 % butadiene and 23 % styrene (values expressed in molar fractions) manufactured by the Dwory S.A. Chemicals, Poland, were selected for comparison, taking into account their good quality and a low price. These rubbers were obtained in the process of low-temperature emulsion copolymerization (Code No. KER® 1507).

EXPERIMENTAL

Synthesis of NR + $NaClO_4$ system

Stage-1: Rubber latex solution: Natural rubber in the form of rubber latex oxidizes immediately in the air, forming a flexible and tensile rubber. To avoid this process, since rubber in the form of latex is readily soluble, it was introduced straight away to toluene (99.5 % purity, Spectrum Chemicals, India), directly before collecting the rubber. The natural rubber preserved this way was delivered to Poland. To develop the synthesis of natural conductive rubber, it was necessary in the first stage to precipitate latex from toluene and then to re-dissolve it in toluene in order to carry out the strictly specified mass calculations. Ethanol (99.5 %, Chempur®, Poland) is soluble in petrol or benzene, but it is the most readily soluble in toluene. For this purpose, toluene (99.5 %, Chempur®, Poland) was used. 3 g of rubber latex was dissolved in 40 mL of toluene. This rubber solution specimen was then left for 12 h and held agitated from time to time. After 12 h, the rubber was again dissolved in toluene of a given concentration, to the consistency of white mineral oil.

Stage-2: Synthesis of polymer electrolyte: To obtain the electrolytic solution, $NaClO_4$ was dissolved in 40 mL of toluene (99.5 %). The concentration of $NaClO_4$ ranged from 1 to 5 g. The rubber solution prepared in Stage-1 was supplied with an adequate concentration of $NaClO_4$ and methanol and after thorough mixing it formed a uniform composite material. The rubber electrolyte precipitated almost at once in the form of gel. Such an electrolytic system with natural rubber, after drying in the air for 24 h was subjected to cross-linking with atmospheric oxygen (at the concentration exceeding 5 g of $NaClO_4$ per 3 g of natural rubber, it is not possible to precipitate polymeric electrolyte in a uniform mass). After that time, it was possible to test the electrolytic conductivity as given in Table-1.

TABLE-1
ELECTRICAL CONDUCTIVITY OF RUBBER ELECTROLYTE WITH CONCENTRATIONS OF $NaClO_4$ FROM 1 TO 5 g WITHIN THE TEMPERATURE RANGE FROM 273 TO 313 K FOR NR + $NaClO_4$ SYSTEM

Concentration of $NaClO_4$ in ethanol	Temperature (K) [S cm^{-1}]				
	273	283	293	303	313
1 g	10^{-8}	10^{-8}	10^{-8}	10^{-8}	10^{-8}
2 g	10^{-8}	10^{-8}	10^{-8}	10^{-8}	10^{-8}
3 g	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-7}
4 g	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-7}
5 g	7.7×10^{-7}	7.8×10^{-7}	7.8×10^{-7}	7.9×10^{-7}	7.9×10^{-7}

Synthesis of NR + $NaClO_4$ + active carbon system: This synthesis is analogous to the synthesis of NR + $NaClO_4$ system. It differs from the previous one merely in adding the active carbon to the system. The solution in the synthesis of NR + $NaClO_4$ system in Stage-1, after dissolving the natural rubber in toluene (after 12 h) was supplied with active carbon in an amount of 0.5-2.5 g. The electrical conductivity of the system is given in Table-2.

TABLE-2
ELECTRICAL CONDUCTIVITY OF RUBBER ELECTROLYTE FOR A CONSTANT CONCENTRATION OF 3 g NR IN 40 cm^3 OF TOLUENE AND VARIABLE AMOUNTS OF ACTIVE CARBON WITHIN THE TEMPERATURE RANGE FROM 273 K TO 313 K FOR NR + $NaClO_4$ + ACTIVE CARBON SYSTEM

Quantity of active carbon	Temperature (K) [S cm^{-1}]				
	273	283	293	303	313
500 mg	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-7}
1.0 g	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-7}
1.5 g	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}
2.0 g	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}
2.5 g	3.8×10^{-6}	4.0×10^{-6}	4.0×10^{-6}	4.2×10^{-6}	4.2×10^{-6}

Synthesis of BR and SBR + $NaClO_4$ system

Stage-1: Butadiene and styrene-co-butadiene rubber solution: Styrene-co-butadiene rubber is readily soluble in toluene. Toluene in the amount of 40 mL was added to 3 g of fine-cut BR and SBR. The polymer left at room temperature for 3 d became an oily substance. At the concentration exceeding 5 g of $NaClO_4$ per 3 g of butediene and styrene-co-butadiene rubber, it is not possible to precipitate polymeric electrolyte in a uniform mass.

Stage-2: Polymeric electrolyte synthesis: The preparation of $NaClO_4$-ethanol solution and the synthesis of polymeric electrolyte with BR and SBR are analogous to the procedures as described earlier. The polymeric gel precipitates almost immediately for BR and SBR + $NaClO_4$ system. After short-drying, it was ready for testing the conductivity. The polymer modified this way is flexible and similar to the pure one. The amounts of $NaClO_4$ being added are compiled in Tables 3 and 4.

TABLE-3
ELECTRICAL CONDUCTIVITY OF RUBBER ELECTROLYTE WITH CONCENTRATIONS OF $NaClO_4$ FROM 1 TO 5 g WITHIN THE TEMPERATURE RANGE FROM 273 TO 313 K FOR BR + $NaClO_4$ SYSTEM

Concentration of $NaClO_4$ in ethanol	Temperature (K) [S cm^{-1}]				
	273	283	293	303	313
1 g	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-7}
2 g	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-7}
3 g	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-7}
4 g	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}
5 g	4.5×10^{-6}	4.5×10^{-6}	4.7×10^{-6}	4.7×10^{-6}	5.0×10^{-6}

TABLE-4
ELECTRICAL CONDUCTIVITY OF RUBBER ELECTROLYTE WITH CONCENTRATIONS OF $NaClO_4$ FROM 1 TO 5 g WITHIN THE TEMPERATURE RANGE FROM 273 TO 313 K FOR SBR + $NaClO_4$ SYSTEM

Concentration of $NaClO_4$ in ethanol	Temperature (K) [S cm^{-1}]				
	273	283	293	303	313
1 g	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-7}
2 g	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-7}
3 g	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}
4 g	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}
5 g	6.2×10^{-6}	6.2×10^{-6}	6.6×10^{-6}	6.6×10^{-6}	7.1×10^{-6}

Synthesis of BR and SBR + $NaClO_4$ + active carbon system: This synthesis is analogous to the one for BR and SBR + $NaClO_4$ + active carbon system. The amounts of carbon being added and the measurement results are presented in Tables 5 and 6.

TABLE-5
ELECTRICAL CONDUCTIVITY OF RUBBER ELECTROLYTE FOR A CONSTANT CONCENTRATION OF 3 g BR IN 40 cm^3 OF TOLUENE AND VARIABLE AMOUNTS OF ACTIVE CARBON WITHIN THE TEMPERATURE RANGE FROM 273 TO 313 K FOR BR + $NaClO_4$ + ACTIVE CARBON SYSTEM

Quantity of active carbon	Temperature (K) [S cm^{-1}]				
	273	283	293	303	313
500 mg	10^{-6}	10^{-6}	10^{-6}	10^{-5}	10^{-5}
1.0 g	10^{-5}	10^{-5}	10^{-5}	10^{-5}	10^{-5}
1.5 g	10^{-5}	10^{-5}	10^{-5}	10^{-5}	10^{-5}
2.0 g	10^{-5}	10^{-5}	10^{-5}	10^{-5}	10^{-5}
2.5 g	5.5×10^{-5}	5.5×10^{-5}	5.8×10^{-5}	5.8×10^{-5}	5.8×10^{-5}

TABLE-6
ELECTRICAL CONDUCTIVITY OF RUBBER ELECTROLYTE FOR A CONSTANT CONCENTRATION OF 3 g SBR IN 40 cm^3 OF TOLUENE AND VARIABLE AMOUNTS OF ACTIVE CARBON WITHIN THE TEMPERATURE RANGE FROM 273 TO 313 K FOR SBR + $NaClO_4$ + ACTIVE CARBON SYSTEM

Quantity of active carbon	Temperature (K) [S cm^{-1}]				
	273	283	293	303	313
500 mg	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}
1.0 g	10^{-5}	10^{-5}	10^{-5}	10^{-5}	10^{-5}
1.5 g	10^{-5}	10^{-5}	10^{-5}	10^{-5}	10^{-5}
2.0 g	10^{-5}	10^{-5}	10^{-5}	10^{-5}	10^{-5}
2.5 g	7.1×10^{-5}	7.1×10^{-5}	7.7×10^{-5}	7.7×10^{-5}	7.7×10^{-5}

Methods of measuring polymeric electrolytes: To determine the electrolytic conductivity, the system obtained was subjected to testing by using a variable current with a frequency varying between 1 Hz and 25 kHz.

Collective measuring results: In order to obtain the largest value of electrolytic conductivity possible, an optimum concentration of $NaClO_4$ in ethanol, which was added to the dissolved rubber needed to be determined. Tables 1, 3 and 4 present the concentration of $NaClO_4$ in ethanol, which was added to rubber. They also include the electrical conductivity of rubber electrolytes. Tables 2, 5 and 6 show the amount of active carbon added, as well as the computed values of resistance and electrical conductivity of rubber electrolytes.

RESULTS AND DISCUSSION

The addition of $NaClO_4$ to rubber electrolytic systems caused the whole system to be conductive. After adding $NaClO_4$ to NR, BR and SBR, the optimum conductivity fluctuated within the range 10^{-7}-10^{-6} S cm^{-1}. The optimum amount of $NaClO_4$ added to these two rubber electrolytic systems is equal to 5 g. After adding $NaClO_4$ in the amount exceeding 5 g, the precipitation of rubber electrolytes in a gel form started to be hampered. This difficulty results from the heterogeneous form of gel.

After adding active carbon to the rubber systems, the whole system improves its conductive properties. For the system made of natural rubber, its value amounts to 4×10^{-6} S cm^{-1} with optimum dose of active carbon being equal to 2.5 g. In case of the BR and SBR systems with active carbon, their conductivity increases respectively to 5.8×10^{-5} and 7.7×10^{-5} S cm^{-1} with optimum dose of active carbon being equal to 2.5 g.

For each of the rubber electrolytic systems tested, the value of their conductivity changed to a small extent within the temperature range from 273 to 313 K. Although these rubber systems have small values of conductivity, they can be considered as stable at variable temperatures (Figs. 1 and 2).

A diagram of a container coated with a conducting material is shown in Fig. 3. Metal container is covered with oily conductive rubber. Then, after 2 d, when conductive rubber was cross-linked with atmospheric oxygen, it is being protected with a bituminous coating of the same or lower hardness.

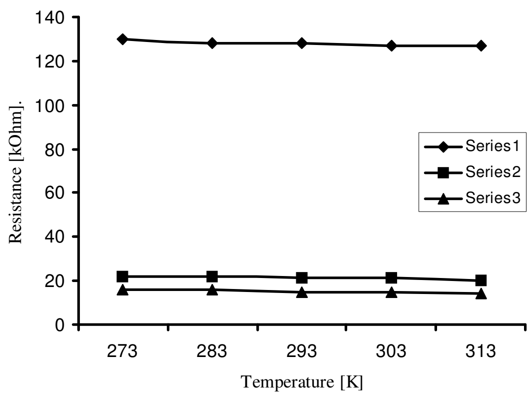

Fig. 1. Comparison of conductivity values within the temperature range from 273 to 313 K for the systems tested: Series 1 = NR + $NaClO_4$, Series 2 = BR + $NaClO_4$, Series 3 = SBR + $NaClO_4$

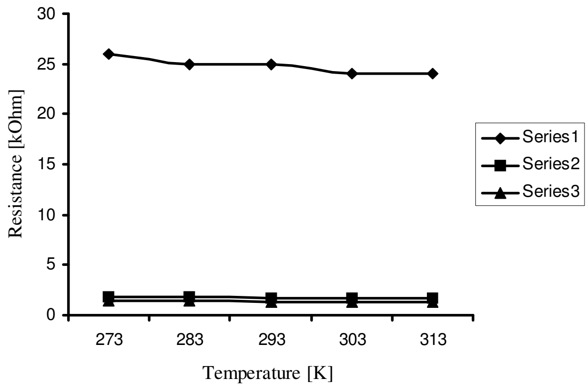

Fig. 2. Comparison of conductivity values within the temperature range from 273 to 313 K for the systems tested: Series 1 = NR + $NaClO_4$ + active carbon, Series 2 = BR + $NaClO_4$ + active carbon, Series 3 = SBR + $NaClO_4$ + active carbon

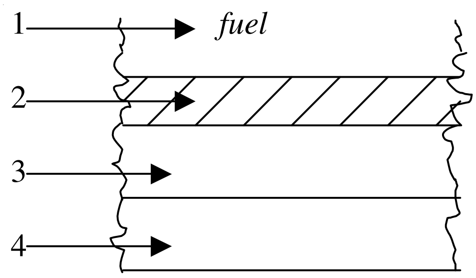

Fig. 3. Schematic drawing of anti-static and anti-corrosion protection by conductive polymer composite consisting of: 1 = fuel, 2 = metallic container, 3 = polymer electrolyte system: NR + $NaClO_4$ or BR + $NaClO_4$ or SBR + $NaClO_4$ or NR + $NaClO_4$ + active carbon or BR + $NaClO_4$ + active carbon or SBR + $NaClO_4$ + active carbon, 4 = bituminous coating

Conclusion

The rubber electrolytic systems are characterized by small conductivity values. However, such a system can find application as a material for anti-corrosive and antielectrostatic protection in tanks designed for inflammable materials. The rubber electrolyte made of natural rubber is characterized by favourable properties. Such a system is cross-linked but after depositing on a paricular material, it is being intrinsically cross-linked with atmospheric oxygen.

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