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THE THERMAL STUDY OF PSEUDOHOMOGENEOUS ION-EXCHANGE MEMBRANES

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Derivatograph was used to investigate pseudohomogeneous ion-exchange membranes. Two membrane types were examined: a) a membrane obtained from polyethylene film modified with the copolymer of styrene and DVB; and b) membrane AMF C-311 obtained on a film of fluorinated polymeric material.

Although differential thermal analysis (DTA) has been used in the investigation of polymers only recently, a large number of papers concerning different problems in this field have already appeared. Only a few of these papers, however, have been devoted to cross-linked polyelectrolytes and more exclusively to ion-exchange resins [1 – 5], i.e. "homogeneous" polyelectrolytes. Up to date no publication dealing with "pseudohomogeneous" ion-exchange membranes has appeared. The pseudohomogeneous membrane is a system of two phases: a polymer film (polyethylene is most often used as matrix), with a cross-linked acid (e.g.polystyrenesulphonic acid) dispersed in the polymer film. The present investigation was undertaken to find the correlation between the thermal curves of a pseudohomogeneous cation-exchange membrane and the thermal properties of both phases of the membrane.

Experimental

Two types of these membranes were examined: a) a membrane obtained from polyethylene film modified with the copolymer of styrene and DVB; this membrane was synthesized at Wrocław Polytechnic School; b) membrane AMF C-311 (American Machine and Foundry Co.) obtained on a film of fluorinated polymeric material.

The examination of other polymers was performed to explain endo- and exothermic effects occurring in the DTA curves of pseudohomogeneous ion-exchange membranes. These polymers were: the initial polyethylene film (PE); the polyethylene film modified with the copolymer of styrene and DVB (before sulphonation); the ethylene – styrene copolymer; the PE and PS homopolymer physical mixture; and the mixture of PE and polystyrenesulphonic acid ion-exchangers with different degrees of cross-linking.

The thermal studies were carried out using a Derivatograph [6, 7]. Samples of the air-dried membranes were well ground (to 20 μm); 110 mg was taken. The examinations were performed with heating rates of 2.5 and 5° per minute up to 450° in a 20 l per hour argon stream.

Results and discussion

As known from the literature, the DTA curves in the temperature range 111–500° for low-density polyethylene and 136°–500° for high-density polyethylene show no thermal effects when the heating is performed in vacuum [8] or in an inert atmosphere (e.g. nitrogen) [9]. With heating under nitrogen, a small endothermic peak occurred at about 410° prior to depolymerisation. This peak has been attributed to the rupture of the weaker bonds of the polymer macromolecules [9], and investigations have proved that it does not disturb the interpretation of the DTA curves of the membranes.

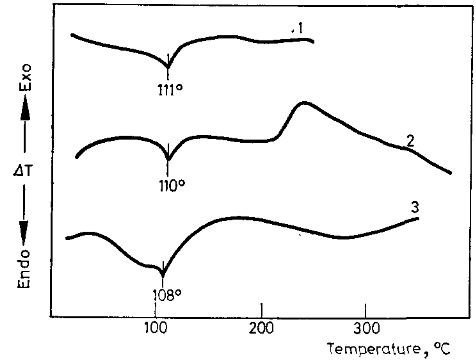

Fig. 1. DTA curves of the initial polyethylene film (1), the polyethylene film modified with the copolymer of styrene and DVB (before the sulphonation) (2) and cation exchange membrane obtained of the polyethylene film (3), in argon atmosphere

On the basis of the DTA curves obtained it was possible to determine the phase transition, i.e. melting point, of the PE matrix. For the film modified with the St/DVB copolymer it is 110°. When cross-linked polystyrol was introduced into the PE film, new thermal effects appeared in the temperature range studied.

The melting point of the matrix (PE) in the pseudohomogeneous ion-exchange membrane is about 108°. Compared with pure PE there is a small decrease of about 3–5° (Fig. 1). The appearence of exo- and endothermic effects in the temperature range 136–500° can be assigned to the dispersed phase of the polyelectrolyte which is the cross-linked polystyrenesulphonic acid.

This provides a reason, therefore, for using this method to study the thermal properties of the cross-linked polyelectrolyte phase in pseudohomogeneous ion-exchange membranes. Analysis of thermal curves obtained with the Derivatograph gives valuable information about the structure of the phase and the influence of the cross-linking agent (DVB). Since thermal decomposition of the cross-linked polyelectrolyte takes place, many gaseous products are formed, and they must all diffuse through the matrix phase (PE). In the case of the membranes considered, thermal decomposition of the dispersed phase of the cross-linked polyelectrolyte proceeds in the visco-flowing state.

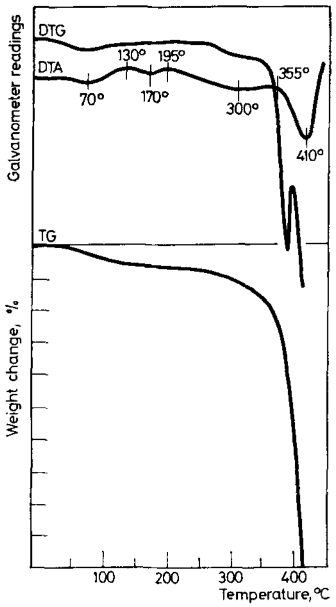

Fig. 2. Thermal curves of the ion exchange membrane AMF C-311, in argon atmosphere

In order to determine the influence of the physical state of the matrix on the thermal decomposition of cross-linked polystyrenesulphonic acid, the graft copolymer membrane AMF C-311 synthesized on a fluorinated polymeric backboneing was also investigated by DTA. Fig. 2 shows DTA curves of this membrane. A very high melting point of the matrix (410°), higher than the decomposition temperature of the sodium salt of polystyrenesulphonic acid (330°) [10], is the reason why the thermal decomposition of the polyelectrolyte in the AMF C-311 membrane occurs under quite different conditions when the matrix is in the visco-elastic state. Comparison of the thermal decomposition processes of the cross-linked polyelectrolyte in the PE matrix and in the matrix of the fluorinated polymer reveals some differences. These differences can be explained, for example, by the different technologies of preparation of the membranes.

The investigations of pseudohomogeneous ion-exchange membranes were performed by DTA in the oxidizing atmosphere of air. They formed the basis of conclusions on the thermooxidative destruction of polystyrenesulphonic acid and its salts, when the destruction takes place in a polymer matrix in different physical states.

The investgations performed indicate that the thermal curves of the pseudohomogeneous ion-exchange membranes express the heat and mass effects describing the process of thermal decomposition of the cross-linked polyelectrolyte phase. Thus, we can conclude that differential thermal analysis (DTA) combined with thermogravimetric analysis may be useful in investigations of pseudohomogeneous ion-exchange membranes. Further more detailed investigations are being carried out.

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