

Physicochemical Investigation of Radiation-Grafted Poly(acrylic acid)-*graft*-Poly(tetrafluoroethylene–ethylene) Copolymer Membranes and Their Use in Metal Recovery from Aqueous Solution

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ABSTRACT: ET-*g*-PAAc membranes were obtained by radiation grafting of acrylic acid onto poly(tetrafluoroethylene–ethylene) copolymer films using a mutual technique. The ion selectivity of the grafted membranes was determined toward K^+ , Ag^+ , Hg^{2+} , Co^{2+} , and Cu^{2+} in a mixed aqueous solution. The ion-exchange capacity of the grafted membranes was measured by back titration and atomic absorption spectroscopy. The Hg^{2+} ion content of the membrane was more than that of either the K^+ or Ag^+ ions. The presence of metal ions in the membranes was studied by infrared and energy-dispersive spectroscopy measurements. Scanning electron microscopy of the grafted and metal-treated grafted membranes showed modification of the morphology of the surface due to the adsorption of K^+ and Ag^+ ions. No change was observed for the surface of the membrane that was treated with Hg^{2+} ions. The thermal stability of different membranes was improved more with Ag^+ and Hg^{2+} ions than with K^+ ions. It was found that the modified grafted membranes possessed good hydrophilicity, which may make them promising candidates for practical applications, such as for cation-exchange membranes in the recovery of metals from an aqueous solution. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2692–2698, 2002

Key words: ion-exchange capacity; grafting membrane; morphology; thermal stability

INTRODUCTION

Radiation-induced graft polymerization is an attractive method to prepare cation-exchange membranes for use in various electrochemical applications,^{1–3} such as in battery separators and in the field of complexed membranes.⁴ Also, these grafted membranes are proposed to remove heavy metal ions from industrial effluents.⁵ Synthetic

polymeric membranes play a very important role in several separation techniques, in either alkali or transition metals. Fluoropolymers are appropriate materials in preparing membranes for the separation process because of their good thermal and chemical resistance. Irradiation of the base polymers by ionizing radiation generates free-radical sites, which are capable of initiating a polymerization reaction with vinyl monomers such as acrylic acid (AAc) molecules to form poly(acrylic acid) (PAAc) graft copolymers by a simultaneous or preirradiation grafting process.^{6–12} Moreover, several articles have also been pub-

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lished on radiation grafting of AAc onto hydrocarbon polymers such as polyethylene (PE), which investigated the structural, morphological, and phase peculiarities of grafted copolymers.^{13–15} To the best of our knowledge, the present investigation is the first to demonstrate the adsorption of Hg²⁺ ions from an aqueous solution on the ET-*g*-PAAc copolymer.

In this article, a grafted poly(tetrafluoroethylene–ethylene) with acrylic acid (ET-*g*-PAAc) copolymer was prepared and reacted with K⁺, Ag⁺, and Hg²⁺ ions in aqueous solutions. The characterization was carried out by infrared (IR), ultraviolet-visible (UV/vis), energy-dispersive spectroscopy (EDS), scanning electron microscopy (SEM), thermogravimetry (TG), and ionic conductivity of grafted and metal ion-treated grafted membranes. The main objective was to study the selectivity of the grafted membranes toward metal ions (K⁺, Ag⁺, Co²⁺, Cu²⁺, and Hg²⁺) in an aqueous solution.

EXPERIMENTAL

Materials

Poly(tetrafluoroethylene–ethylene) (ET) films of 100- μ m thickness (Hoechst, Germany) were used as a polymeric substrate. AR reagent-grade acrylic acid (AAc) with a purity of 99% (Merck, Germany) was used as supplied. The other solvents were also AR reagent-grade products of Merck.

Grafting Procedure^{6,16}

The graft copolymers were prepared by a simultaneous irradiation method of aqueous AAc onto ET films under atmospheric pressure and ambient temperature. Mohr's salt (ammonium ferrous sulfate solution, 2.5 wt %) was added to minimize homopolymerization of the monomer during the radiation-grafting process. The reaction mixture obtained was kept in glass ampules, which were deaerated by bubbling nitrogen for 5 min, then sealed and subjected to 30 kGy of γ -radiation from a ⁶⁰Co source at a dose rate of 0.07 Gy/s. After grafting, the nonreacted monomer and homopolymers were removed with hot water and, subsequently, with methanol. The ET-*g*-PAAc membrane was then dried in a vacuum oven at 50°C for 24 h. The grafting yield was calculated as follows:

$$\text{Degree of grafting (\%)} = [(W_g - W_0)/W_0] \times 100$$

where W_g and W_0 denote the weights of grafted and ungrafted ET films, respectively.

Ion Selectivity

The ET-*g*-PAAc membrane (71 wt %, which gave the most homogeneous grafting) was immersed in a mixture containing a 0.1M aqueous solution of KNO₃, AgNO₃, Co(NO₃)₂, Cu(NO₃)₂, and HgCl₂ at room temperature for 24 h. The ionic selectivity of the metal-treated membranes was determined using EDS measurements. Meanwhile, the physical properties, such as the swelling behavior in water and dimensional change, were studied previously.⁸

Determination of Ion-exchange Capacity

The ion-exchange group content was determined from measurement of the total ion-exchange capacity of K⁺ and Ag⁺ ions by a back-titration method. Atomic absorption spectroscopy (AAS) was used to determine the content of Hg²⁺ ions, employing a Perkin–Elmer 5000 pc spectrometer (USA).

Ion-exchange Capacity of K⁺ Ion

The grafted membrane was immersed in a 0.1M KOH aqueous solution at room temperature for 24 h, and the excess base was titrated with a 0.06M HCl aqueous solution.

Ion-exchange Capacity of Ag⁺ Ion

The grafted membrane was immersed in a 0.1M AgNO₃ solution at room temperature for 24 h, and the excess AgNO₃ was titrated with 0.05M NaCl using Mohr's method.

Ion-exchange Capacity of Hg²⁺ Ion

The grafted membrane was immersed in a 0.05M HgCl₂ solution at room temperature for 24 h, and the excess Hg²⁺ (mg/L) was determined using AAS.

Infrared Spectroscopy

Infrared spectra of the trunk, grafted, and metal-treated ET membrane with the Hg²⁺ ion were measured using a Shimadzu 5000 FTIR spectrometer (Japan).

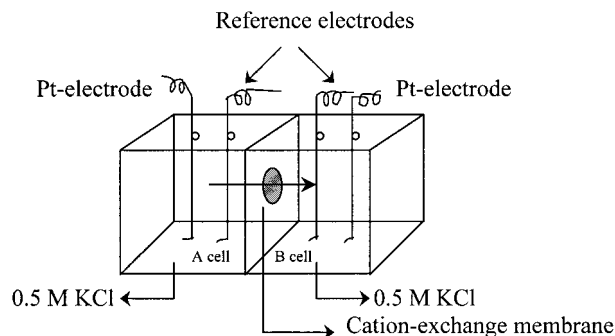


Figure 1. The apparatus for the measurement electric resistance of cation-exchange membrane

EDS

EDS chemical area mapping of various metal-treated membranes was performed with a LINK'S exl II energy-dispersive spectrometer (Oxford Instruments, UK) attached to a scanning electron microscope to measure the ion selectivity of the membrane.

Ionic Conductivity Measurements

Measurements of the ionic conductivity of the K^+ ion via ET-g-PAAc were carried out using a Keithley 220 programmable current source (as d.c. constant current), The Pt electrode, Ag electrode (as the reference electrode), and a multimeter (electrometer) are shown in Figure 1. The electric resistance of the grafted membrane was measured in a 0.5M KCl solution at 25°C. The electric resistance, R (Ω), was calculated by

$$R = (R_{\text{soln+membr}} - R_{\text{soln}})$$

where $R_{\text{soln+membr}}$ denotes the electric resistance of the KCl solution in the presence of the membrane, and R_{soln} , the electric resistance of the KCl solution without the membrane. The ionic conductivity, σ ($\Omega^{-1} \text{ cm}^{-1}$) was calculated by

$$\sigma = \frac{1}{R} \times \frac{T}{S}$$

where S denotes the surface area (cm^2) of the membrane, and T , the thickness (cm) of the membrane.

TG

TG was carried out in a dynamic atmosphere of pure nitrogen gas using a Shimadzu DSC 50 an-

alyzer (Japan) set at a heating rate of 20°C/min and the temperature range of 25–500°C.

SEM

The grafted and metal-treated grafted membranes (with K^+ , Ag^+ , and Hg^{2+} ions at room temperature) were examined in a JEOL Model JSM-6300 scanning electron microscope (Japan) at 20 kV.

RESULTS AND DISCUSSION

Ion Selectivity

Figure 2 shows EDS of a mixture consisting of K^+ , Ag^+ , Hg^{2+} , Co^{2+} , and Cu^{2+} solutions. It can be seen that the Hg^{2+} ion is selectively taken up by the membranes due to the presence of carboxylic groups, which absorb the Hg^{2+} ion from an aqueous solution. However, the phenomenon of Co^{2+} and Cu^{2+} ions not being absorbed via grafted membranes from an aqueous solution may be due to the lower ionic radii of these species compared to those of the K^+ , Ag^+ , and Hg^{2+} ions.¹⁷ Furthermore, the capacity of the Hg^{2+} ions was higher than that of the K^+ or Ag^+ ions at the same conditions.

IR Spectroscopy

Figure 3 shows spectra of the original ET copolymer (spectrum a), ET-g-PAAc (spectrum b), and a

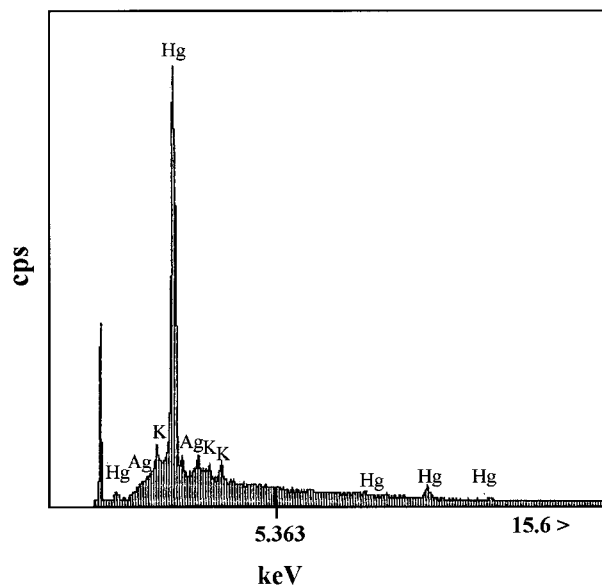


Figure 2 EDS of grafted ET copolymer treated with 1.0 wt % of Hg^{2+} , K^+ , and Ag^+ solutions.

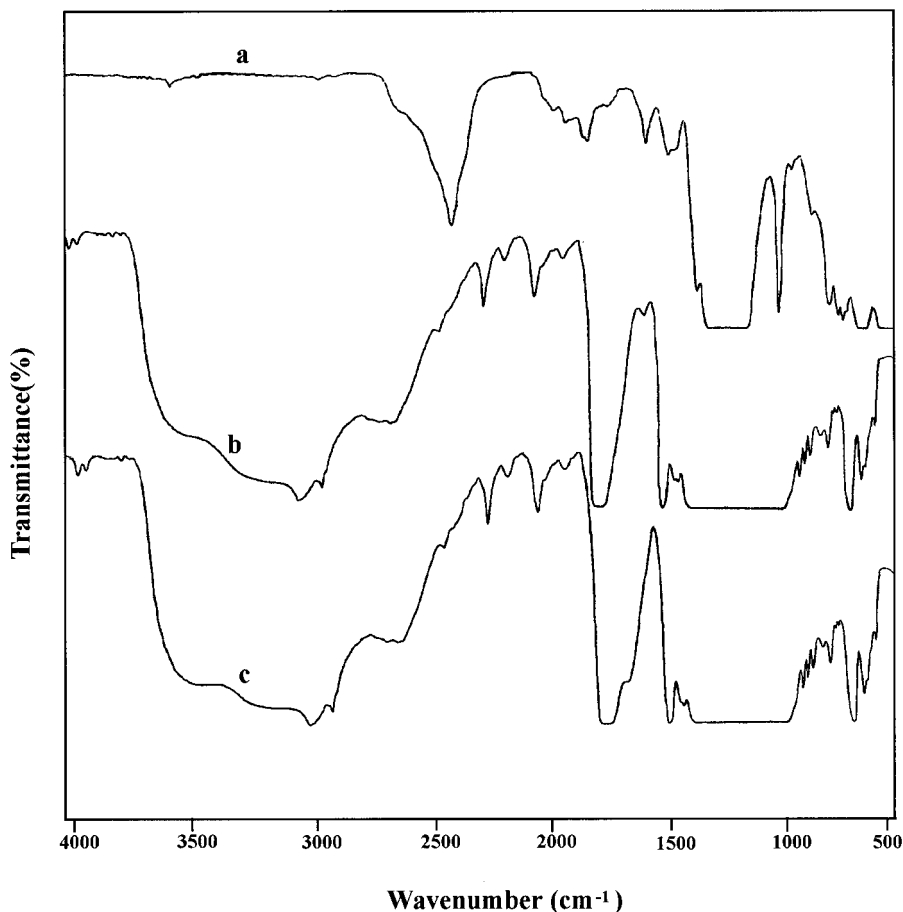


Figure 3 IR spectra of (a) original ET, (b) ET-*g*-PAAc, and (c) ET-*g*-PAAc treated with the Hg^{2+} ion, all having the same degree of grafting (9 wt %).

copolymer complex of the Hg^{2+} ion of the treated membrane (spectrum c). Both grafted and complexed membranes have the same degree of grafting (9.0 wt %). A careful comparison between spectra (b) and (c) gives insight about the coordination sites of the copolymer with the Hg^{2+} ion. Spectrum (b) shows two bands: One is broad at $3500\text{--}2800\text{ cm}^{-1}$, which is assigned to free and associated $\nu(\text{OH})$ of the carboxylic group and $\nu(\text{CH})$, while the other is strong, lying at 1720 cm^{-1} , which is characteristic for $\nu(\text{C}=\text{O})$. The only difference between spectra (b) and (c) is the splitting of a new band at 1620 and 1530 cm^{-1} , which may imply group formation of carboxylate ions. The other bands remain more or less at the same position. It is, therefore, evident that some $-\text{COOH}$ groups interact with the metal ions while some remain unreacted.^{18,19}

Ionic Conductivity

Figure 4 shows the relationship between ionic conductivity and the degree of grafting of the

membranes at room temperature. It can be seen that the ionic conductivity increases with increasing of the grafting yield. This may be due to increase in the number of carboxylic groups. The initial conductivity shows a sharp increase, and at a certain degree of grafting (≈ 60 wt %), it tends to level off. This can be explained by taking the distribution of the carboxylic group grafts in the membrane into consideration. It was reported that the grafting of AAc onto ET film starts at the surface of the film and continues to the middle by progressive diffusion of the monomer through the grafted layers.^{3,20} Therefore, the ionic conductivity increases as the degree of grafting increases in the membrane beyond 60%.

The results suggest that the higher the grafting yield, the higher is the permeability and the porosity; consequently, the ionic conductivity via membranes increases. Therefore, ET-*g*-PAAc membranes have acceptable electrochemical capabilities to be used as cation-exchange membranes.

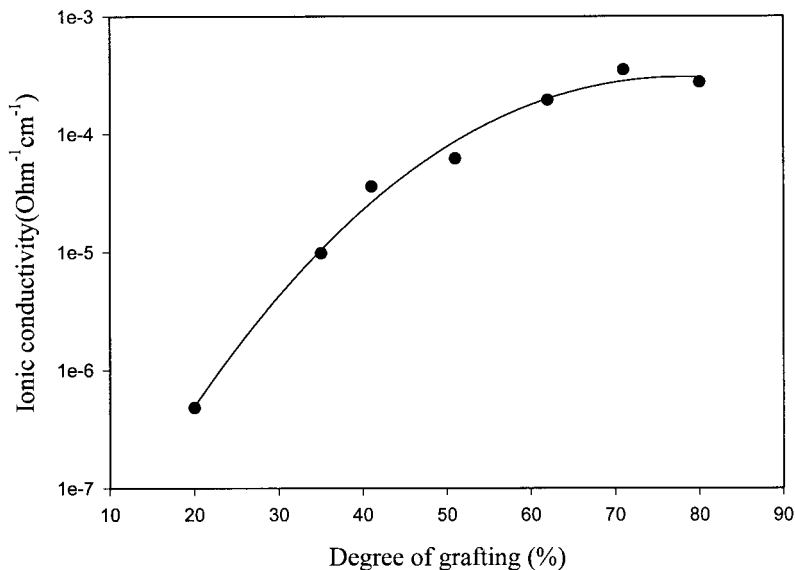


Figure 4 Ionic conductivity of K^+ ions via grafted membranes as a function of the degree of grafting.

Ion-exchange Capacity

Figure 5 shows the ion-exchange capacity of membranes toward K^+ , Ag^+ , and Hg^{2+} ions as a function of the degree of grafting. It is shown that the ion-exchange capacity of the metal ions increases with an increasing the degree of grafting. The ion-exchange capacity of the Hg^{2+} ion is more than that of either K^+ and Ag^+ ions. Because the membrane was preconditioned with a KOH solution overnight,

the carboxylic groups of the graft chains were completely changed to carboxylate, $-COOK$, while the reaction between the $AgNO_3$ solution and the grafted chains may form a silver complex on the grafted membrane. Also, the $HgCl_2$ solution reacted with the carboxylic groups of the grafted membranes to give a Hg complex, which may be absorbed inside the layer of grafted membranes without change of the morphology of the surface.

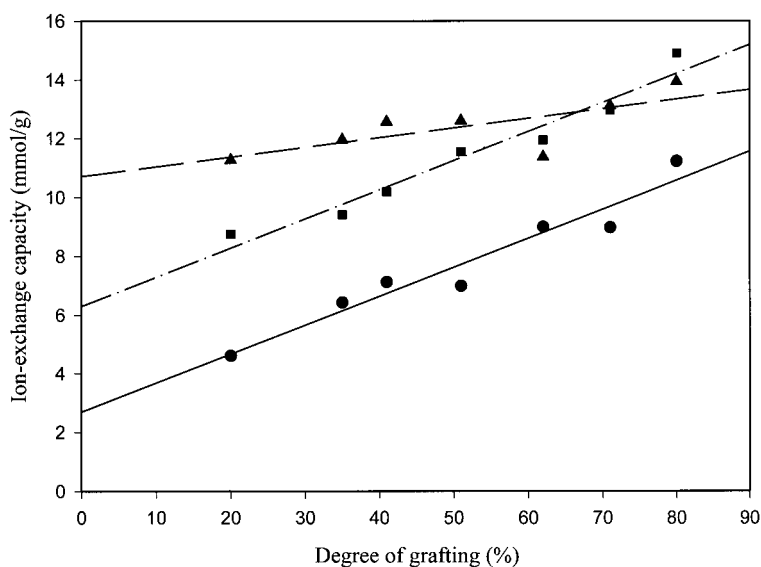


Figure 5 Ion-exchange capacity of the ET-g-PAAc membrane with (\blacktriangle) Hg^{2+} , (\blacksquare) K^+ , and (\bullet) Ag^+ as a function of the degree of grafting.

Table I TGA of the Grafted and Modified ET-*g*-PAAc Membranes Grafted with K⁺, Ag⁺, and Hg²⁺ Ions at 71 wt% Grafting

Sample	Weight Loss (%)					Total Weight Loss (%)
	25–100°C	100–200°C	200–300°C	300–400°C	400–500°C	
ET- <i>g</i> -PAAc	—	4.20	9.78	10.70	34.43	59.11
ET- <i>g</i> -PAAc-K	—	11.50	2.39	6.91	28.43	49.24
ET- <i>g</i> -PAAc-Ag	—	2.96	8.67	10.38	15.74	37.75
ET- <i>g</i> -PAAc-Hg	—	3.80	11.42	9.86	17.82	42.82

The results suggest that the ion-exchange capacity of the Hg²⁺ ion is higher than that of either the K⁺ and Ag⁺ ions due to its low ionic radius. This may enhance the Hg²⁺ ion to more easily penetrate through the grafted layer than can the other ions. Also, the process of the ion-exchange capacity may depend on the nature of the metal ions. To test the ion-exchange nature of the process, metal-treated membranes were washed with an acid solution (HCl) and regeneration of membrane carboxylic groups was confirmed.

Thermogravimetry

The thermal stability of the radiation-grafted ET membranes was measured by TG at the range of 100–500°C (under a nitrogen atmosphere). The samples tested include grafted and metal-treated grafted membranes (with K⁺, Ag⁺, and Hg²⁺ ions) having the same degree of grafting (71 wt %). Table I indicates that the weight loss of the first stage starting at a temperature range between 100 and 200°C of 4.2% for ET-*g*-PAAc is due to the removal of water bound to hydrophilic carboxylic groups present in the membranes during the initial heating. The persistence of some water at a temperature higher than 100°C may be due to hydrogen bonding between some water molecules and —COOH groups through the grafted or grafted membrane treated with K⁺, Ag⁺, and Hg²⁺ ions or may be due to water coordinated to the metal ions. The highest value observed for K⁺-treated membranes (11.50%) may be attributed to a greater amount of surrounding water, since K⁺ is more hydrophilic than are the other ions.³ The massive degradation of PAAc through the membrane starts at 200°C, in which the ET matrix begins to decompose with a weight loss of more than 8%. The second decomposition of the grafted membranes occurs at the range from 300 to 500°C. The results illustrate the efficiency of the metal ions toward the stabilization of the mem-

brane compared with the grafted one. The sequence of the stability of various membranes is as follows: —Ag⁺ ≥ —Hg²⁺ > —K⁺ > —COO[−]. Such a sequence seems to be reasonable, from the viewpoint of the effective ionic radii of the investigated ions.

Structural and Morphological Investigation

The micrographs of (a) ET-*g*-PAAc and (b) ET-*g*-PAAc complexed with K⁺ ions, (c) complexed with Ag⁺ ions, and (d) complexed with Hg²⁺ ions recorded at room temperature are shown in Figure 6, which all have the same degree of grafting (71 wt %). On close examination of the micrograph [Fig. 6(a)], it can be concluded that the grafted phase of PAAc is distributed on the polymer surface as some granular formations of pores and chaps on the surface of the grafted layer. The scanning electron micrograph depicted in Figure 6(b) shows that the modified grafted ET with K⁺ ions cause some change on the surface of the grafted layers due to the interaction of metal ions with carboxylic groups on the surface of the membranes, that is, the metal ions aggregate on the grafted chains. This aggregation on the grafted layers forms small globules, which increase in number and size with an increasing degree of grafting. The micrograph in Figure 6(c), which is due to the treated membranes of grafted ET with Ag⁺ ions, gives a clearly smooth and translucent shape due to complete adsorption of Ag⁺ on the surface. However, the micrograph of grafted ET complexed with Hg²⁺ ions [Fig. 6(d)] is very similar to the grafted one [Fig. 6(a)], that is, the interactions with the Hg²⁺ ion do not give a new phase but granular formations are still present without any surface change.

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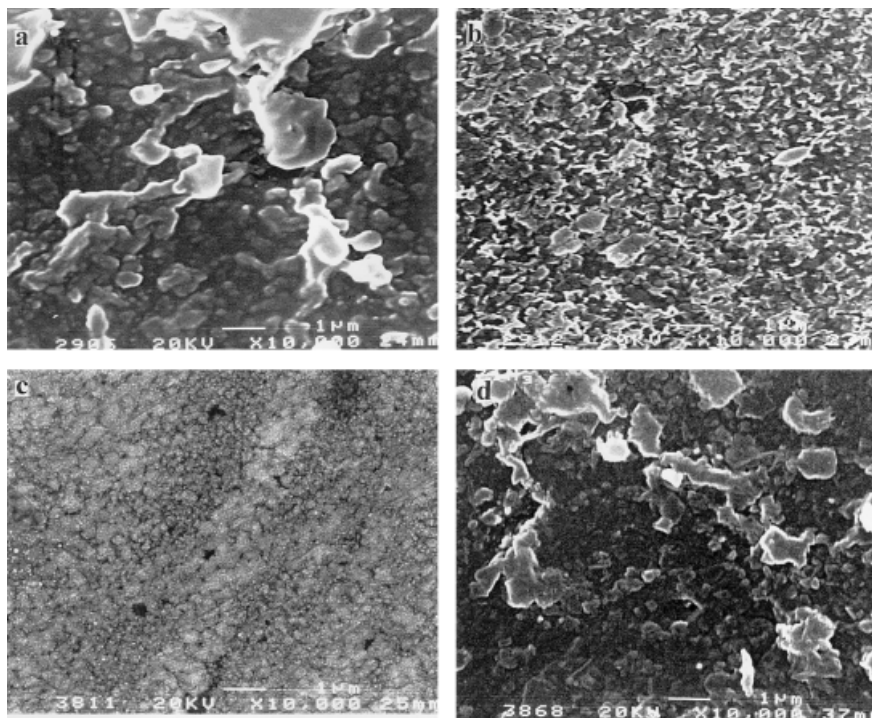


Figure 6 Scanning electron micrographs of (a) ET-*g*-PAAc and (b) ET-*g*-PAAc modified with K^+ , (c) Ag^+ , and (d) Hg^{2+} at room temperature.

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