

Iron(III) Complexed with Radiation-Grafted Acrylic Acid onto Poly(tetrafluoroethylene-co-perfluorovinyl ether) Films

Naem M. El-Sawy, Z. I. Ali

National Center for Radiation Research and Technology (NCRRT), Nasr City, Cairo, Egypt

Received 29 August 2006; accepted 11 September 2006

DOI 10.1002/app.25493

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: To introduce functional moieties to a poly-32#(tetrafluoroethylene-co-perfluorovinyl ether) film, graft copolymerization of vinyl monomers such as acrylic acid was attempted by a simultaneous technique in aqueous solution using γ -irradiation. The graft copolymers were complexed with the Fe(III) in aqueous solution. The grafted copolymer-metal complexes were examined by infrared (IR), ultraviolet/visible, energy-dispersive X-ray spectroscopy, and electron spin resonance techniques. The effect of temperature on the trunk copolymer, untreated grafted, and treated grafted copolymer films was investigated by IR and thermogravimetric analysis. The overall results sug-

gest octahedral structure for Fe(III) and revealed the high stability of the obtained ligand-metal complexes. Furthermore, scanning electron microscope investigation of the grafted and modified films, both unheated and heated (200°C), showed changes in the structure and surface morphology. Promising results were achieved enhancing the practical applications of modified grafted membranes in the recovery of metal ions from aqueous systems. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 4065–4071, 2007

Key words: graft copolymer; octahedral structure; ligand-metal complexes; membranes; surface morphology

INTRODUCTION

Radiation-induced grafting of acrylic and vinyl monomers onto fluorine-containing polymers is an attractive way to prepare and develop the membranes by using direct method or preirradiation grafting techniques.^{1–7} The presence of carboxylic groups in the grafted layers leads to the formation of metal acrylate complex by a treatment with salt solutions of transition metals such as Iron(III) chloride. The coordination reaction of a polymer ligand to metal ions or to metal complexes and the structure of the resulting polymer-metal complex are studied mainly by spectrophotometry.^{1,2,8–10} Furthermore, the metal introduced into a polymer chain causes improvement of the polymer behavior and changes the surface morphological structure.^{11,12} The formation and structure of an interpolymer complex have been shown to depend on several factors such as chemical structure and environment conditions of pH and temperature.¹³

The present work was designed to take advantage of the evident complexing tendency of graft copolymers toward metal ions and to explore their utilities

in the field of heavy and rare metal waste treatment for the metal recovery. Therefore, the graft poly(tetrafluoroethylene-co-perfluorovinyl ether) film with acrylic acid (PFA-g-PAAc) copolymer was prepared by the direct method and then reacted with aqueous solution of FeCl₃. The characterization was carried out by infrared (IR), ultraviolet/visible (UV/vis), energy-dispersive X-ray spectroscopy (EDX), electron spin resonance (ESR), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

Poly(tetrafluoroethylene-co-perfluorovinyl ether) (PFA) film of 100 μm thickness (Hoechst, Germany) was used as a polymeric substrate. Acrylic acid with a purity of 99% (Analar reagent-grade, Merck, Germany) was used as supplied. The other solvents were Analar reagent-grade products of Merck.

Graft copolymerization

The graft copolymers were prepared by the simultaneous irradiation technique in which the polymer (PFA) and monomer solution (acrylic acid/water, AAc/H₂O, 20/80 wt % for 8.7% grafting yield and 50/50 wt % for 44% one) were subjected to ionizing radiation under atmospheric pressure and ambient

Correspondence to: N. M. El-Sawy (naemelsawy@yahoo.co.uk).

temperature. Mohr's salt (ammonium ferrous sulfate solution, 2.5 wt %) was added to minimize the homopolymerization of monomer during the irradiation-grafting process. The glass ampule containing the monomer solution and films was deaerated by bubbling nitrogen gas for 5–7 min and then sealed. The glass ampules were then subjected to 20 kGy Co-60 γ -rays at a dose rate of 1.88 Gy/s. After grafting, the nonreacted monomer and homopolymers were washed thoroughly with hot distilled water and soaked overnight in water to extract the residual monomer and the homopolymer occluded in the graft films. The PFA-g-PAAc membranes were dried in a vacuum oven for 24 h at 50–60°C and weighed. Percentage add-on was calculated as follows:

$$\% \text{ Add - on} = (W_1 - W_0/W_0) \times 100$$

where W_0 and W_1 are the weights of the initial and grafted films after complete removal of the homopolymer.

Synthesis of graft copolymer-Fe(III) complexes

The graft copolymers of PFA with PAAc were refluxed with 1.0 wt % of aqueous ferric chloride solution for 2 h (8.7 and 44% grafting). The treated films were then dried in a vacuum oven at 50°C and weighed.

Infrared spectroscopic analysis

Infrared spectra of the trunk, grafted, and complexed PFA-g-PAAc membranes with Fe(III) ion were analyzed using a Fourier transform infrared (FTIR) spectrometer (ATI Mattson, Genesis series I, USA made). The FTIR spectrometer was used for measuring and scanning the IR absorption spectra of samples under investigation with a resolution of 4 cm^{-1} , over the range $400\text{--}4000 \text{ cm}^{-1}$. The FTIR analysis of samples was carried out at room temperature and at 200°C, using a variable automatic temperature controller cell (cryostat) of type Greasby/Specac P/N/12573 (made in England). High signal-to-noise spectra were obtained by the collection of 100 scans for each sample.

Ultraviolet/visible spectrophotometric investigation

UV2 double beam Unicam ultraviolet/visible (UV/vis) spectrometer (England made) was used for scanning the absorption spectra in the range from 190 to 1000 nm wavelengths and measuring the optical density at λ_{max} for sample under investigation.

Energy-dispersive X-ray analysis

EDX chemical area mapping of Fe(III)-treated film was performed with a LINK's exl II energy-disper-

sive spectrometer (Oxford Instruments, UK) attached to a scanning electron microscope to measure the metal ion through the film.

Electron spin resonance analysis

The ESR spectra were recorded on a Bruker, ELEXSYS E-500 spectrometer, operating at X-band frequency. The unheated and heated (200°C) polymer films were cut into strips, introduced in the sample tube, and then analyzed at room temperature (no vacuum was employed). The stretching direction of the films was either parallel or perpendicular to the axis of the magnetic field.

Thermogravimetric analysis

The TGA curves were obtained on heating the polymeric samples at heating rate of 20°C/min in a dynamic atmosphere (30 cc/min) of pure nitrogen gas by means of Shimadzu DSC 50 analyzer (Japan).

Scanning electron microscope investigation

The surface morphology of the trunk, grafted, and modified grafted copolymers at room temperature and at 200°C was seen by SEM technique. The micrographs were taken with a JSM-5400 instrument by JEOL (Japan). The investigated samples were kept for 1 h in liquid nitrogen prior to fracture. A sputter coater was used to precoat conductive gold onto the fracture surface before observing the microstructure at 15 kV.

RESULTS AND DISCUSSION

FTIR investigation

Figure 1 shows the spectra of the original PFA copolymer (curve a), PFA-g-PAAc (curve b), and a copolymer complex of the Fe(III) ion (curve c) at room temperature, respectively. Both grafted and complexed films have the same degree of grafting (8.7 wt %). It can be seen from curve b that there is an absorption band at $3500\text{--}2800 \text{ cm}^{-1}$, which is assigned to the stretching vibration of free and associated carboxylic groups, while the IR band lying at 1720 cm^{-1} , which is characteristic for $\nu(\text{C}=\text{O})$. Both these two IR bands are characterizing the PAAc structure.^{2,11} It can be seen from curve c that the IR bands appear at 1700 and 1560 cm^{-1} , which may arise from the formation of carboxylate ions $\nu(\text{COO}^-)$. This is due to the ionization effect of Fe(III) with PFA-g-PAAc copolymer.^{3,14} It is, there-

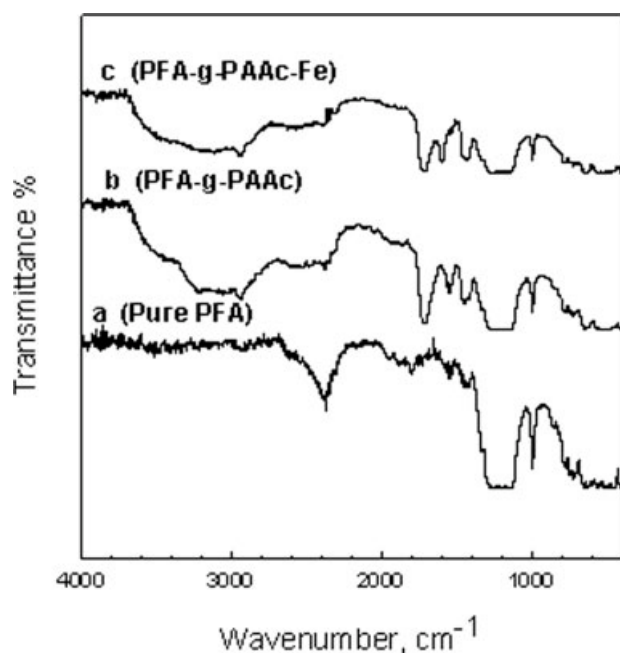


Figure 1 FTIR spectra of trunk PFA (curve a), PAAc-graft-PFA (curve b), and complexed grafted PFA with Fe(III) (curve c) having the same grafting yield (8.7 wt %).

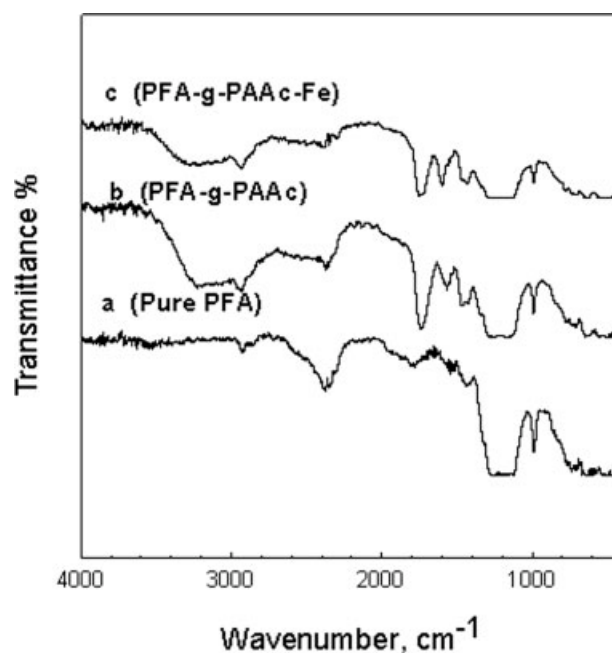
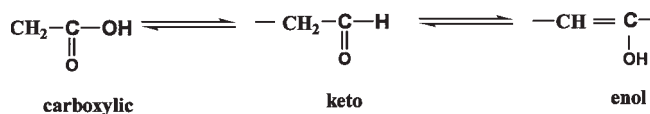


Figure 2 FTIR spectra of heated samples at 200°C. (a) Trunk PFA, (b) PAAc-graft-PFA, and (c) complexed grafted PFA with Fe(III) having the same grafting yield (8.7 wt %).

fore, evident that some $-\text{COOH}$ groups interact with metal ions giving rise to a COO^- ion group, whereas other $-\text{COOH}$ groups remain unreacted. The after-mentioned peaks are absent in the IR spectrum of the original PFA films (curve a).

Effect of temperature on the grafted and complexed copolymers

Figure 2 shows the spectra of trunk PFA (curve a), PFA-g-PAAc film (curve b), and its complex with Fe(III) ions (curve c) heated at 200°C, having the same degree of grafting (8.7 wt %). The heating of the grafted film at 200°C (curve b) brought about the decrease of the hydroxyl group band and the appearance of a new band at about 1736 cm^{-1} , which may be due to conversion of carboxylic groups, $-\text{COOH}$, into aldehydic groups, $-\text{CHO}$. Meanwhile, the heating of a complexed film at 200°C (curve c) brought about the slight band of the hydroxyl group, with the appearance of band at $\approx 1745\text{ cm}^{-1}$, which may be due to the formation of an aldehydic group, $-\text{CHO}$. The appearing IR band in the range of $1745\text{--}1600\text{ cm}^{-1}$ may indicate the presence of carboxylate ions, $-\text{COO}^-$, coming from moderate degradation of $-\text{COO-M}$ bonds. The presence of hydroxyl groups either in grafted or complexed one after heating at 200°C due to the formation of keto-enol form of the unstable aldehydic groups, $-\text{CHO}$, is as follows:



Ultraviolet/visible measurements

Figure 3 shows the relative absorbance as a function of wavelength (nm) for an aqueous solution of FeCl_3 (curve a), which exhibits a UV band at about 294 nm before the reaction with PFA-g-PAAc films at 44 wt %

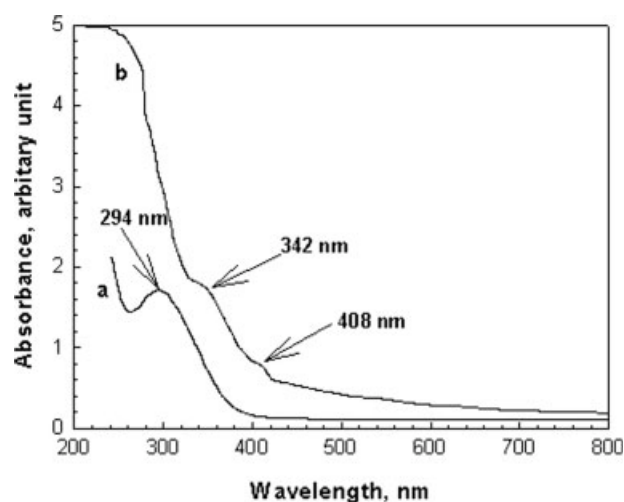


Figure 3 Change in the relative absorbance with wavelength (nm) for (a) FeCl_3 in aqueous solution, and (b) PAAc-grafted-PFA with Fe(III) complex films having a grafting yield of 44 wt %.

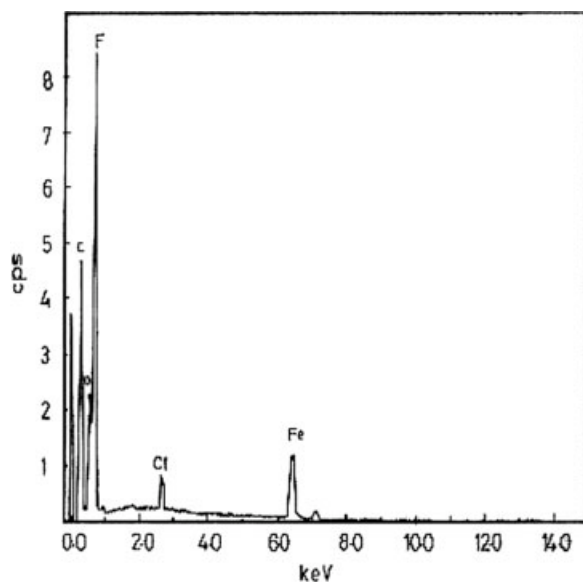


Figure 4 Energy-dispersive X-ray spectroscopy of PAAC-grafted PFA copolymer, treated with FeCl_3 solution.

grafting. Meanwhile, Figure 3 (curve b) shows the change in the relative absorbance as a function of wavelength (nm) for the complexed grafted polyacrylic acid chains onto PFA films at 44 wt % grafting. The shoulder band that appeared at around 342 nm may be due to the charge transfer, whereas the appeared band at 408 nm is attributed to the absorption of Fe(III) ions resulting from the complexation of metal ions with carboxylic groups ($-\text{COOH}$) of the grafted chains.¹⁵

Energy-dispersive X-ray analysis

Figure 4 gives the energy-dispersive X-ray spectroscopy (EDX) of a PAAC-grafted PFA film complexed with Fe(III) ions, showing the appearance of iron at 6.5 keV on the scale. The relative atomic abundance of different constituents of polymeric substrates, given in Table I, accounts for the different atomic abundance of C, F, O, Fe, and Cl present in the uppermost surface layers of the investigated grafted complexed substrate. The analytical data obtained from EDX (cf. Table I) indicated that the Fe(III) is obtained during the complex formation between PAAC-grafted PFA and Fe(III) ions. Furthermore, the Fe(III) ions appeared as K_α (2.43%) in the complex film with some traces of chloride ion, Cl^- (0.48%), which may be introduced in the geometrical structure of grafted-metal complex.

Electron spin resonance investigation

The ESR spectra of the graft copolymer- Fe(III) complex samples before and after heating at 200°C were investigated (Fig. 5). The spectrum of the graft copoly-

TABLE I
EDX Analysis Data of the Grafted Film Complexed with Fe(III) at 44% Grafting Yield

Element	Line	Atom (%)
C	K_{ser}	24.74
F	K_{ser}	56.33
O	K_{ser}	16.02
Fe	K_α	2.43
Cl	K_{ser}	0.48

mer- Fe complex exhibits a signal at $g = 2.03$ (Fig. 5a). This result reflects octahedral structure and gives strong evidence that metal ions interact with the graft copolymer. This is consistent with the above electronic and IR spectral data.

Figure 5b, the Fe(III) still exist even after heating at 200°C . In this case of Fe(III) there are two groups of signals, the first group is lying around $g = 2.003$ and the second appears around $g = 4.3$. Therefore, the Fe(III) exists in distorted symmetry evidenced by the appearance of a signal at $g = 4.3$ and at $g = 2.003$, which shows axial symmetry environment.¹⁶ In addition, small sharp signal at $g = 2.003$ appears indicating the presence of some free radical species resulted from some degradation of the grafted chains in the polymeric material.

In the present study, Fe(III) is chelated with PAAC onto PFA films. The proposed structure of the polymer-metal complex formed by inter and intramolecular crosslinking in the polymer matrix is as follows:

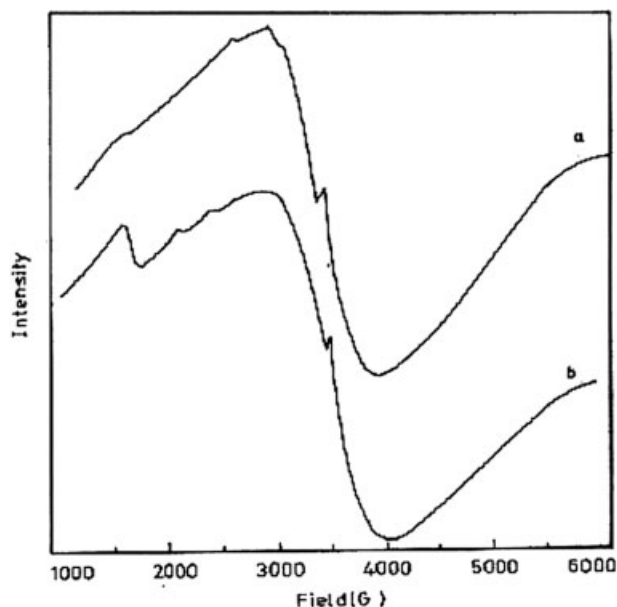
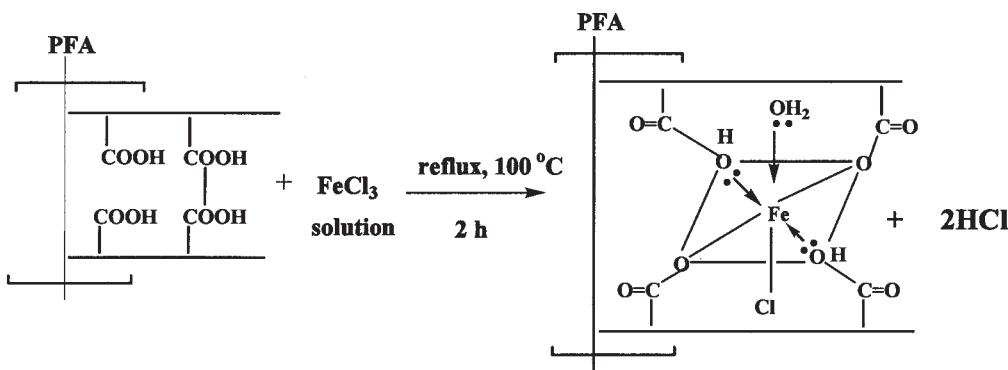
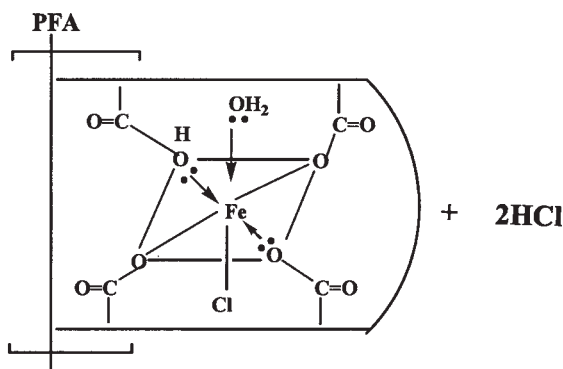


Figure 5 ESR spectra of Fe(III) complex of PFA-graft-PAAC at room temperature (curve a) and its complexes with Fe(III) at 200°C (curve b) having the same degree of grafting (44 wt %).



Intermolecular crosslinking as octahedral structure

and / or



Intramolecular crosslinking as octahedral structure

Moreover, the traces of chloride ions may be removed upon the degradation process as HCl gas at the elevating temperature and also may be given some compounds such as Fe_2O_3 after the degradation of the structure with increasing temperature.

Thermogravimetric analysis

Figure 6 shows the TGA curves of the original PFA (curve a), PAAc-grafted PFA complexed with Fe(III) (curve b), and PAAc-grafted PFA copolymer (curve c). It can be observed that the decrease in the thermal stability of PFA film occurred upon grafting of PAAc chains. This decrease could be attributed to the departure of physisorbed water (100–200°C), dehydration of grafted PAAc (200–400°C), and decarboxylation of PAAc grafted onto PFA (400–500°C). The weight loss accompanying these processes attained 2.077, 15.762, and 15.125, respectively (cf. Table II). This finding proves that the chains of the grafted film degraded at elevated temperature. This result is in a good agreement with those

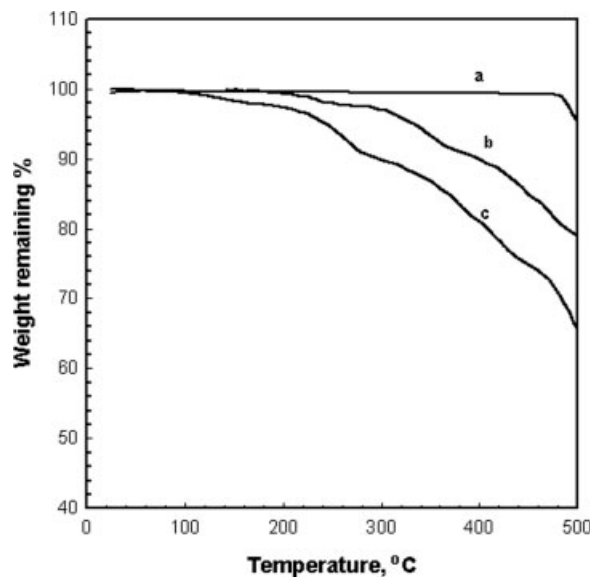


Figure 6 TGA thermograms of (a) trunk PFA, (b) PAAc-grafted PFA complexed with Fe(III), and (c) PAAc-grafted PFA copolymer films.

TABLE II
Thermogravimetric Analysis Data of the Grafted Copolymer and Grafted Copolymer complexed with Fe(III) Ions at 44% Grafting Yield

Sample	Weight loss % at different temperature ranges					Total weight loss %
	25–100°C	100–200°C	200–300°C	300–400°C	400–500°C	
PFA-g-PAAc	–	2.077	7.408	8.354	15.125	32.964
PFA-g-PAAc-Fe	–	1.918	3.838	6.396	10.272	22.424

reported by other investigators.^{12,17} Moreover, the total weight loss of Fe(III) complexed with grafted PFA via PAAc chains has a lower value during heating than that of the grafted ones. In other words, Fe(III) complexed with grafted PFA film is thermally more stable than the grafted PFA one. This result clearly suggested that the degradation was some-

what difficult due to the complexation process of metal with $-\text{COOH}$ of PAAc chains. However, the trunk copolymer PFA (curve a) should be thermally stable up to $\approx 450^\circ\text{C}$ at which it has a total weight loss % (5.559%) and this is because it did not contain grafted layer of PAAc, which undergoes the decomposition with increasing temperature.

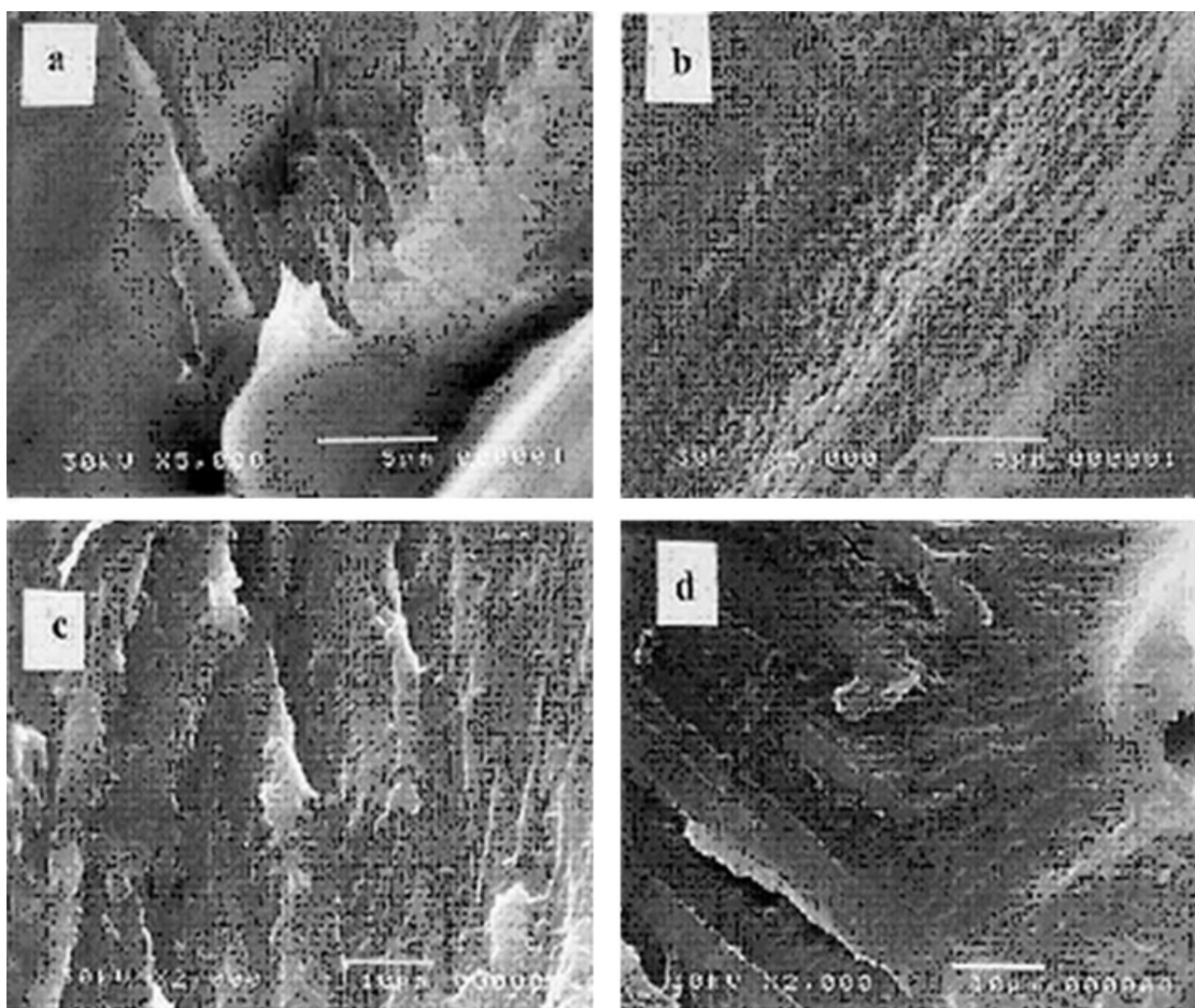


Figure 7 Scanning electron micrographs of (a) PAAc-grafted PFA at room temperature, (b) PAAc-grafted PFA at 200°C , (c) PAAc-grafted PFA complexed with Fe(III) at room temperature, and (d) PAAc-grafted PFA complexed with Fe(III) at 200°C .

Morphological investigation

The micrographs of (a) unheated PFA-g-PAAc, (b) its grafted heated at about 200°C, (c) unheated PFA-g-PAAc complexed with Fe(III), and (d) its complex heated at 200°C are shown in Figure 7, which all have the same degree of grafting (44 wt %). On close examination of the micrograph [Fig. 7(a)], it can be concluded that the grafted phase of PAAc is distributed on the polymer surface as some big granular formations. The micrograph in Figure 7(b) for the heated membrane of the grafted PFA with PAAc gives a clearly smooth and translucent shape due to some degradation and the rearrangement of the grafted layer at 200°C. The scanning electron micrograph depicted in Figure 7(c) shows that the modified grafted PFA with Fe(III) at room temperature causes the change on the surface morphology of film due to the complexation of metal ions throughout the interaction of metal ions with carboxylic groups of grafted chains. The complexed grafted membrane was degraded after heating at 200°C as illustrated in Figure 7(d). The complex structure and the surface became rough and probably contain HCl gas, H₂O, or form a new compound such as Fe₂O₃ due to the decomposition of the geometrical structure. Therefore, the heating of the grafted or complexed films may cause some rearrangement via structural changes and degrade layer of the polymeric substrate. Also, the heated film exhibited partial porosity, which is probably important in the application of membranes.

CONCLUSIONS

The grafting of AAc onto PFA films and its complexation grafted films has been studied. From the discussion of the experimental results, the following may be concluded:

1. The presence of hydroxyl groups after heating (200°C) of grafted or complexed films is due to the formation of the ket-enol form.
2. The Fe(III) ions appeared with some traces of chloride ion, which may be introduced in the

geometrical structure of the complexed grafted film.

3. The two groups of signals in the ESR spectra appeared in the complexed film after heating at 200°C and the presence of some free radical species due to some degradation of the grafted chains.
4. The introduction of Fe(III) in the grafted film gives more thermal stability than the grafted one.
5. The modified grafted film with Fe(III) causes the change on the surface morphology due to complexation of metal ions.
6. The present work was designed to take advantage of the evident complexing tendency of grafted copolymers in the field of metal recovery.

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