

Effects of Cobalt and Potassium Doping on Thermal Stability and Electrical Properties of Radiation Grafted Acrylic Acid Onto Poly(Tetrafluoroethylene Ethylene) Copolymer Films

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ABSTRACT: Grafted copolymer of poly(tetrafluoroethylene ethylene) (ET) with acrylic acid (AAc) was prepared by direct radiation method. The obtained films were modified by treating with small amounts of Co²⁺ and K⁺ ions (1.0 wt %). The effects of such treatment on the thermal stability and electrical conductivity of these films were studied. Cobalt treatment did not much affect the thermal degradation of the films. The results obtained revealed that k⁺ treatment enhanced the thermal degradation of ET-g-PAAc, which started 273 K lower than that observed in the case of the untreated and Co²⁺-treated films. Potassium and cobalt

treatment of the investigated films increased their electrical conductivity (σ) and decreased the activation energy ΔE_{σ} . The increase in σ values was, however, more pronounced in the case of K⁺-treated film. These results were discussed in terms of the effective increase in the hydrophilicity of the films, especially those treated with potassium. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 867–871, 2005

Key words: grafting; modification; electrical conductivity; mobility; thermal stability

INTRODUCTION

Fluoropolymers have drawn much attention in the past and gained wide practical use because of their excellent thermal and chemical resistance because of the high carbon fluorine bond strength.¹ Radiation-induced grafting of acrylic and vinyl monomers into polymeric films provides a noble way to produce membranes for many practical applications.^{2–9} The presence of carboxylic groups in the grafted layer allows us to obtain metal acrylate by alkali treatment^{6,7} or metal acrylate complexes by treatment with some salts of transition metals.^{10–13} The conductivity of the polymer–metal complexes was studied.^{14–16} Electrical properties constitute one of the most convenient and sensitive methods for studying the polymer structure.^{17,18}

This study was devoted to investigate the role of cobalt and potassium treatment on thermal stability and electrical properties of poly(tetrafluoroethylene ethylene) copolymer, (ET), grafted with polyacrylic acid (PAAc), (ET-g-PAAc), ET-g-PAAc complexed with cobalt, (ET-g-PAAc-Co) and ET-g-PAAc treated with potassium, (ET-g-PAAc-K).

EXPERIMENTAL

Graft polymerization

The poly(tetrafluoroethylene ethylene) copolymer films (ET), of 100 μm thickness (Hoechst, Germany) acrylic acid (AAc), with a purity of 99%, (Merck, Germany) and graft copolymer of ET films with polyacrylic acid, (ET-g-PAAc) were the same as in the previous study.¹⁹ The graft copolymer was prepared by direct radiation grafting of aqueous AAc onto ET films.

Synthesis of graft copolymer–metal films

The different graft copolymers with K⁺ or Co²⁺ ions complexed of ET-g-PAAc films were prepared by refluxing with 1.0 wt % of metal salt solutions (KOH or CoCl₂) for 2 h at 100°C. The treated films were then dried in a vacuum oven at 50°C until constant weight.

Electrical conductivity measurements

Measurements of electrical conductivity of grafted copolymer treated with K⁺ or Co²⁺ ions films were carried out by using a specially designed cell equipped with two probe electrodes whose temperature was controlled by an electronic temperature regulator with an accuracy $\pm 0.5^\circ\text{C}$. The electric resistivity of different investigated films was measured at tem-

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TABLE I
Thermogravimetric Analysis of the ET-g-PAAc, ET-g-PAAc-Co, and ET-g-PAAc-K at 33% Grafting Yield

	Temperature range (K)	Weight loss (%)	Total weight loss (%)
ET-g-PAAc	303–443	2.12	93.81
	443–585.5	7.14	
	585.5–760.5	14.00	
	760.5–873	68.20	
ET-g-PAAc-Co	303–473	2.00	94.65
	473–595	4.50	
	595–758	10.40	
	758–873	77.60	
ET-g-PAAc-K	303–423	8.40	88.91
	423–653	7.50	
	653–873	52.90	

peratures in the range of 303–449 K. These measurements were conducted by measuring the current by using a Keithly 617 programmable digital electrometer at a certain applied voltage. The conductivity (σ) was readily determined from the equation

$$\sigma = \frac{1}{R} \times \frac{d \cdot}{A}$$

where R is the resistivity, d is the film thickness in (cm), and A is the surface area in (cm^2). The data of σ measured at different temperatures allowed a ready determination of ΔE_σ by direct application of the Arrhenius equation

$$\sigma = \sigma_0 \exp -\Delta E_\sigma / kT$$

where σ_0 is a constant and k is Boltzmann constant.

Thermogravimetry (TG)

TG was carried out in a dynamic atmosphere of pure nitrogen gas flowing at a rate of 20 ml/min by means of a Shimadzu DSC 50 analyzer (Japan) at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Thermal stability

The thermal stability of different films was investigated by using TG analysis curves. The obtained curves, not given, showed that four weight loss processes took place in the case of ET-g-PAAc and ET-g-PAAc-Co²⁺. In the case of K⁺-treated films, three weight loss processes were observed. Table I includes the values of weight losses taking place at different temperatures for the investigated films. Inspection of Table I revealed that (1) ET-g-PAAc and ET-g-PAAc-Co films remained thermally stable by heating

at temperatures ≤ 758 K, showing the absence of any significant role of cobalt in modifying the thermal stability of ET-g-PAAc film. (2) Heating ET-g-PAAc and ET-g-PAAc-Co²⁺ films at temperatures above 763 K resulted in their thermal degradation, which continued until 873 K. (3) The weight loss observed in the case of ET-g-PAAc and ET-g-PAAc-Co²⁺ films by heating from room temperature to about 473 K was accompanied by almost the same weight loss value. (4) The observed weight loss by heating these two films from ~ 473 –763 K was smaller for Co²⁺-treated film than those for ET-g-PAAc film. This finding may indicate that Co²⁺ treatment of such film decreased its hydrophilicity (i.e., decreased the amount of removed water). (5) Potassium treatment of ET-g-PAAc much enhanced its thermal degradation, which started 273 K below the temperature observed in the case of the other two films. (6) The values of weight losses accompanying heating of K⁺-treated films at temperatures within 303–653 K are greater than those observed in the case of the other two films. These results clearly reflect the role of potassium in increasing the hydrophilicity of the treated films and it is expected to modify the electrical property of different investigated films.

DC electrical conductivity (σ)

Degree of grafting effect on σ

Figure 1 shows the electrical conductivity (σ) of the untreated grafted ET with AAc and treated ET-g-

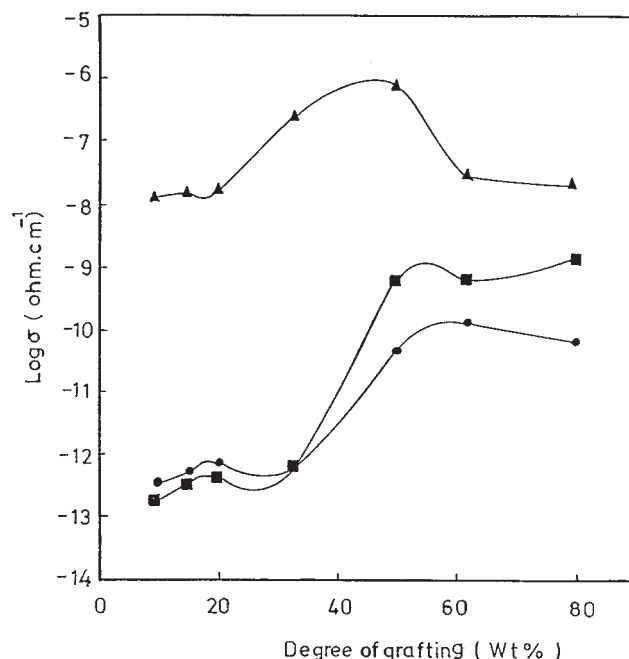


Figure 1 The variation of $\log \sigma$ as a function of degree of grafting for (●) ET-g-PAAc, (■) ET-g-PAAc-Co, and (▲) ET-g-PAAc-K films.

PAAc with K^+ or Co^{2+} ions as a function of the degree of grafting. It can be seen that the σ of all investigated films suffers little change as a function of degree of grafting until about 30% grafting and then increases significantly by increasing the grafting yield above this limit, reaching to a maximum limit at about 50% grafting. Above this limit, σ tends to acquire almost constant values or decreases as in the case of undoped and K^+ -treated films. It can also be seen from Figure 1 that the values of σ were much higher for K^+ -treated films than those of the other films, which showed values near to each other. The effective increase in σ values by increasing the degree of grafting can be attributed to an effective increase of the concentration of the produced carboxylic groups which contribute in the electric conduction of the treated films. The early region of curves relating σ as a function of grafting yield can be ascribed to relatively small concentrations of carboxylic groups. The superiority of σ values of K^+ -treated films over the other films can reflect a relatively high mobility of K^+ -carboxylate ($-COOK$) as compared to that manifested in the case of the other films and also to the contribution of K^+ ions in the electric conduction of the treated films. The relatively small values of σ in the case of Co^{2+} -treated films may reflect an effective decrease in the degree of freedom of free Co^{2+} ions because of their chelation with carboxylic groups. This finding may reflect an effective decrease in the mobility of charge carriers in such film. It seems that the increase in concentration of carboxylic groups via increasing degree of grafting showed a maximum limit in the case of grafted ET and Co^{2+} -treated grafted films. This trend, maximum limit for built-in carboxylic groups; was confirmed in previous investigations via determining FTIR spectra of each poly(tetrafluoroethylene-perfluorovinyl ether) copolymer film (PFA) or poly(tetrafluoroethylene ethylene) copolymer film (ET) with AAc, which showed the formation of carboxylate ion with different metals together with free or unreacted carboxylic groups.^{9,11} The observed decrease in σ values of K^+ -treated film at grafting yield $>50\%$ may reflect a possible decrease in the mobility of charge carriers due to a possible scattering of these charge carriers.

Effect of temperature on σ of grafted and grafted-treated films

The variation of σ as a function of temperature for all investigated films gives useful information about the charge carriers concentration and their mobility. Figure 2 shows the relationship of $\log \sigma$ as a function of $1/T$ for ET-g-PAAc subjected to 20, 33, and 80% degree of grafting. Inspection of this figure reveals that (1) σ of 80% grafted film measured at different temperatures (338–448 K) is much higher than that measured for the other two films. (2) σ showed both an

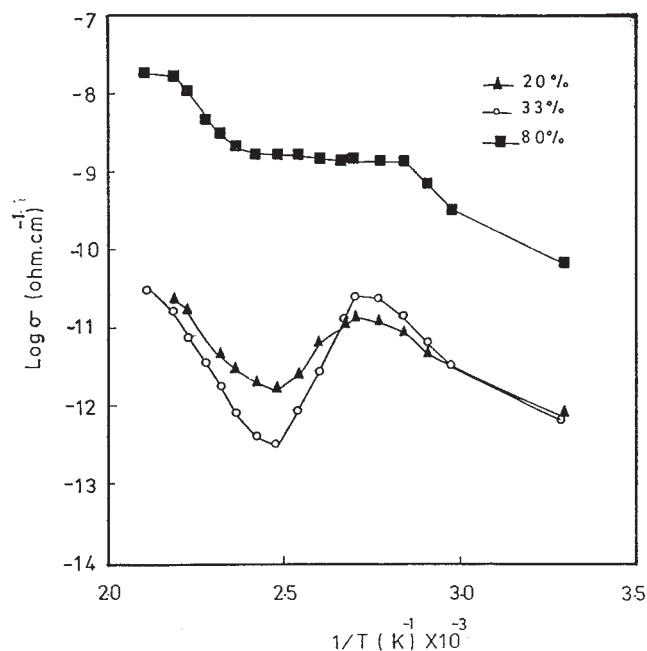


Figure 2 The variation of $\log \sigma$ as a function of $1/T$ for ET-g-PAAc undergoing different degrees of grafting.

increase and a decrease in its values for different investigated films as a function of temperature. The increase in σ value by increasing temperature of measurement is at normally expected trend for semiconducting substrate. The semiconducting substrates might be generally defined as the materials that have relatively small electrical conductivity that increases by increasing the temperature of measurements. On the other hand, the decrease in σ by increasing temperature reflects some kind of scattering of charge carriers. The activation energy of electric conduction of different grafted films was calculated from the data of σ measured at different temperatures through a range of the normal semiconducting behaviors by using the Arrhenius equation. The computed values of ΔE_{σ} are given in Table II. The values of ΔE_{σ} cited in Table II suggested two mechanisms of electrical conductivity; the first dominates at 338–368 K and the second dominates between 398 and 448 K. The speculated conduction mechanisms in the system investigated dominating at two different temperature ranges (338–368 K) and (418–448 K), might be as follows: (1) Diffusion of induced carboxylic groups and dopant K^+ or Co^{2+} ions. (2) The possible hopping process of carboxylic groups and dopant ions. The diffusion mechanism takes place at the lower temperature ranges (338–368 K) and the second mechanism dominates at the higher temperature range (418–448 K). The values of ΔE_{σ} calculated through the first temperature range are smaller than those determined at the second temperature range for different films. The variation of σ as a function of temperature may be attrib-

TABLE II
Effect of Degree of Grafting on the Activation Energy of Electric Conduction (ΔE_σ) for the ET-g-PAAc, ET-g-PAAc-Co and ET-g-PAAc-K films

Degree of grafting (%G)	ET-g-PAAc		ET-g-PAAc-Co		ET-g-PAAc-K	
	ΔE (eV)	Temperature range (K)	ΔE (eV)	Temperature range (K)	ΔE (eV)	Temperature range (K)
20	0.66	398–448	1.30	438–493	0.20	423–493
	0.20	338–368	0.56	333–353	0.33	303–333
33	1.61	418–448	1.06	438–493	0.00	473–493
	0.89	338–368	0.68	333–353	0.32	343–393
80	1.13	418–448	1.36	438–493	0.22	423–493
	0.82	338–368	0.63	333–353	0.31	346–356

uted to a progressive removal of water from the grafted membrane which takes place at about 373 K and enhancement the mobility of charge carriers. The removal of water by heating is expected to decrease the mobility of ionic terminals of carboxylic groups with subsequent decrease of the mobility of charge carriers. This effect brought about a decrease in σ values. So, the relatively small values of ΔE_σ determined at 338–368 K may correspond to the energy needed to expel water from the grafted layers of the treated chains. The fact that the ΔE_σ value calculated at 338–368 K increases significantly by increasing the degree of grafting suggested clearly the difficulty of water removal from the grafted films subjected to a high degree of grafting. This behavior is expected simply because the greater the degree of grafting, the greater the hydrophilicity of the grafted films, and the difficulty will be the removal of water retained.

Figure 3 depicts the variation of $\log \sigma$ as a function of $1/T$ for Co^{2+} -treated films subjected to different degrees of grafting namely 20, 33, and 80%, respectively. The variation of σ as a function of $1/T$ of these grafted treated films with Co^{2+} ions is similar to that obtained in the case of ET-g-PAAc illustrated in Figure 2. The values of ΔE_σ calculated at different temperatures within the range where σ increases by increasing temperature and the data obtained are given in Table II. The data obtained for ΔE_σ showed two mechanisms of electric conduction: the first dominates at 333–353 K and the second dominates at 438–493 K. The values of ΔE_σ at the low temperature range are also smaller than those calculated at the high temperature range. It is worth mentioning that the degree of grafting of Co^{2+} -treated films did not much affect the energy needed for removal of retained water. In other words, the Co^{2+} treatment of such films did not change their hydrophilicity and may play a role in improving σ via increasing the mobility of charge carriers through the amorphous region of the grafted films.

Figure 4 shows the variation of $\log \sigma$ as a function of $1/T$ for K^+ -treated films subjected to different degrees of grafting, namely 20, 33, and 80 wt %, respectively. Again, the variation of σ as a function of temperature

of these grafted treated films is similar to those observed for ET-g-PAAc and ET-g-PAAc- Co^{2+} illustrated in Figures 2 and 3. So, σ increases and decreases by increasing the temperature, depending on the temperature ranges at which σ was measured. The data of σ measured at different temperatures within the range where σ increases by increasing temperature enabled us to calculate ΔE_σ by using the Arrhenius equation. The computed ΔE_σ values are given in Table II. Inspection of this table revealed that (1) two values of ΔE_σ were observed for each film subjected to different degrees of grafting. (2) The values of ΔE_σ calculated at the high-temperature range are always smaller than those calculated at lower temperature range. (3) The degree of grafting of these K^+ -treated films showed no significant influence in the value of ΔE_σ . (4) All computed values of ΔE_σ , especially those measured at the low-temperature range, are smaller than those found in the case of the other films, except that for 20%

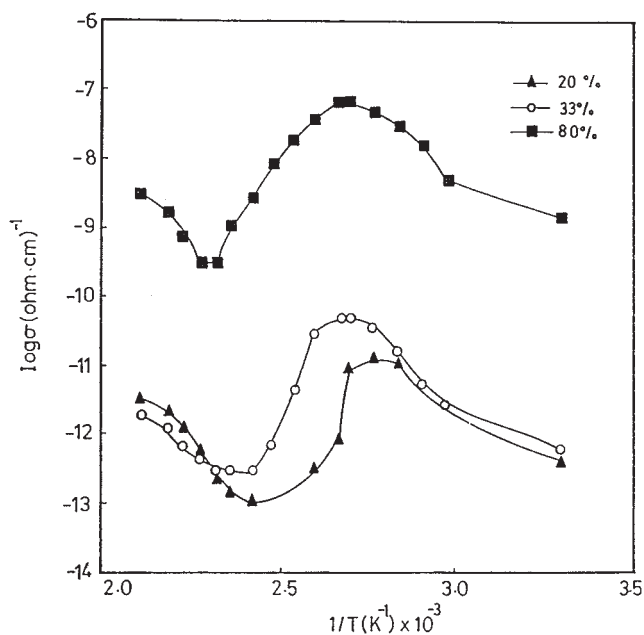


Figure 3 The variation of $\log \sigma$ as a function of $1/T$ for ET-g-PAAc-Co undergoing different degrees of grafting.

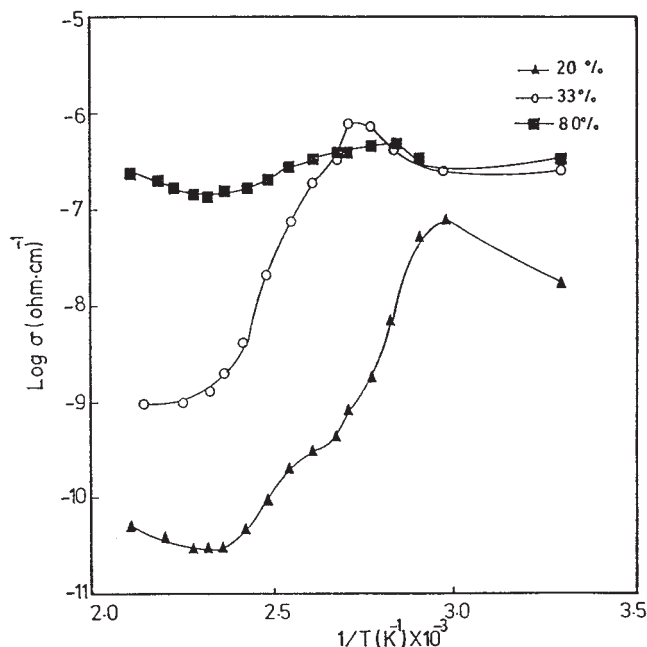


Figure 4 The variation of $\log \sigma$ as a function of $1/T$ for ET-g-PAAc-K undergoing different degrees of grafting.

grafting. These findings clearly indicate the role of K^+ treatment in much increasing the electrical conductivity of the films under investigation. The role of K^+ treated is much more pronounced than those observed in the case of Co^{2+} -treated films. The fact that the degree of grafting between 20 and 80 wt % did not much affect the values of ΔE_σ , suggested the role of K in much increasing the concentration and mobility of charge carriers responsible for electric conduction of the ET-g-PAAc. This result points to the effect of chemical nature of dopant in modifying the electrical conductivity of these films.

The comparison between Co^{2+} and K^+ treatment of the films under investigation shows the superiority of K^+ in much increasing the electrical conductivity of these films. This finding may be discussed in terms of the role of K^+ ions as ionic semiconductor resulting in an effective increase in the charge carriers concentration in K^+ -treated films. On the other hand, cobalt species added may undergo a complexation process with the film constituent without acting as foreign cations. In other words, Co^{2+} ions may not exist in the treated films, opposite of the case of K^+ -treated films.

CONCLUSION

The obtained results permitted us to derive the main following conclusions.

1. The grafting of ET with AAC was carried out by using γ -radiation.
2. The effects of treating the grafted films with a small amount of K^+ or Co^{2+} ions on the thermal stability and electrical properties of the treated films were investigated.
3. K^+ treatment enhanced the thermal degradation of ET-g-PAAc, which starts 273 K lower than that observed in the case of the untreated and Co^{2+} -treated films.
4. Potassium and cobalt treatment of the investigated films increased their electrical conductivity and decreased the activation energy of electrical conductivity (σ). The increase in σ values was, however, greater in the case of K^+ treatment.

References

1. Carlson, D. P.; Schmieget, W. In *Organic Fluoropolymers*; Gerhartz, W., Ed.; Ullman's Encyclopedia of Industrial Chemistry, 5th ed.; VCH: Verlagsgesellschaft; Weinheim, 1988; Vol. AII, p 393.
2. Zouahri, A.; Elmidaoui, A. *J Appl Polym Sci, Part A: Polym. Chem.* 1996, 34, 1793.
3. Hegazy, E. A.; Dessouki, A. M.; El-Sawy, N. M.; Abdel Ghaffar, M. A. *J Polym Sci* 1993, 31, 527.
4. Ruskov, T.; Turmanova, S.; Kostov, G. *Eur Polym J* 1997, 33, 1285.
5. Gupta, B. D.; Chapiro, A. *Eur Polym J* 1989, 25, 1145.
6. Dessouki, A. M.; Taher, N. H.; El-Arnaouty, M.; Khalil, F. M. *J Appl Polym J* 1993, 48, 1249.
7. Hegazy, E. A.; Taher, N. H.; Ebaid, A. R. *J Appl Polym Sci* 1990, 41, 2637.
8. El-Sawy, N. M. *Polym Int* 1996, 40, 193.
9. El-Sawy, N. M.; Alsagheer, F. A. *Polym Int* 1998, 47, 324.
10. Braun, D.; Boudevka, H. *Eur Polym J* 1975, 11, 561.
11. El-Sawy, N. M.; Alsagheer, F. A. *Eur Polym J* 2001, 37, 161.
12. Abdel Ghaffar, M. A.; Hegazy, E. A.; Dessouki, A. M.; El-Assy, N. B.; El-sawy, N. M. *Radiat Phys Chem* 1991, 38, 369.
13. El-Sawy, N. M.; Abdel Ghaffar, M. A.; Hegazy, E. A.; Dessouki, A. M. *Eur Polym J* 1992, 28, 835.
14. Katon, J. E. *Organic Semiconducting Polymers*; Dekker: New York, 1970.
15. Härtel, M.; Kossmehl, G.; Wille, W.; Wöhrel, D.; Zerpner, D. *Angew Makromol Chem* 1973, 12/30, 307.
16. Shehap, A.; Abd Allah, R. A.; Basha, A. F.; Abd El-Kader, F. H. *J Appl Polym Sci* 1998, 68, 687.
17. Garrett, P. D.; Grubb, D. T. *J Polym Sci, Part B: Polym Phys* 1988, 26, 2509.
18. Narula, G. K.; Tripathi, A.; Pillai, P. K. C. *J Mater Sci* 1991, 26, 4130.
19. Hegazy, E. A.; Dessouki, A. M.; El-Assy, N. B.; El-Sawy, N. M.; Abdel Ghaffar, M. A. *J Polym Sci, Part A: Polym Chem* 1992, 30, 1969.