Electrical Properties of Modified-Grafted Polypropylene

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ABSTRACT: The electrical properties of polypropylene (PP), grafted polypropylene (PP-*g*-PVP), and modified-grafted PVP with α-cyano-β-(2-thienyl) crotononitrile were investigated. Also, the electrical characteristic of the modified-grafted PVP subjected to γ-irradiation (60 kGy) was studied. The results show that the σ of trunk polymer undergoing different degree of grafting generally increases as function of the grafting yield. The grafting yield between 64.1 and 149% resulted in a progressive decrease in ΔE_σ value. Inclusion of sulfur-containing substrate in different films, having various grafting yields, leads to both increase and decrease in σ values. A significant increase in σ values is observed upon inclusion of sulfur-containing substrate having maximum grafting yield (149%). These changes are accompanied by fluctuation in σ values. The exposure of sulfur-containing substrate in grafting film to a dose of 60 kGy results in a significant decrease in ΔE_σ values for the films undergoing a grafting yield between 64.1 and 149%. The observed changes in ΔE_σ of different films investigated could be attributed mainly to corresponding changes in σ'_0 values. The observed improvement in electrical properties is mainly because of possible increase in concentration of charge carrier and/or their mobilities. The scanning electron micrographs of some selected films show significant changes in the morphology of the films investigated due to changing the grafting yield, inclusion of sulfur-containing substrate, and exposure to γ-irradiation. J Appl Polym Sci 104: 3797–3803, 2007

Key words: polypropylene; radiation; activation energy

INTRODUCTION

Radiation grafting is a convenient method for the modification of physical and chemical properties of polymeric materials. The modification of grafted of *N*-vinyl-2-pyrrolidone (NVP) onto low density polyethylene (LDPE) or polypropylene (PP) with α, β-unsaturated nitrile[1–3] has already been studied. The electrical property of insulating polymers is very complicated, because many additives and impurities are included in polymer films. In the last few years, a considerable amount of investigations on conduction polyheterocyclic polymers have been carried out because of their good environmental stability.[4] The conduction mechanism is mainly characterized by the transport parameters, such as charge carrier density and charge carrier mobility.[5–9] Much attention has been devoted to understanding the structure, the ion interactions, and the transport mechanism, which govern the conductivity.[10] Electrical properties constitute one of the most convenient and sensitive methods for studying the polymer structure.[11–13] One of the tools, which give information about defects in the gap is the dc electrical conductivity. Disorder cause localization of the electronic wavefunction for electron energies through much of the band of states.[14] Elliotte[14] has reported that a criterion for localization may be chosen to be the behavior of the dc electrical conductivity as $T \to 0$; essentially, this is related to the electron diffusion. States of energy E are deemed to be localized if the ensemble average of the dc conductivity (σ_E) is zero at $T = 0$ whereas extended (metallic-like) states have a finite conductivity at $T = 0$. (In other words, conduction between localized states can only take place by means of thermal assisted ''hopping.'' The minimum metallic conductivity σ_{min} is the minimum conductivity of the mobility edge on the delocalized side before all states become localized and the conductivity (σ) precipitously to zero for three dimension. The significance of the minimum metallic conductivity, σ_{min}, is that it would be the pre-exponential factor σ'_0 for electrons excited from E_f to E_c for conduction in nonmetals, or the limiting value of the metallic conductivity before localization sets in for the case of metals. The effects of γ-irradiation on the electrical properties were investigated for some applications.[15]

In this work, a grafted PP with PP-*g*-PVP copolymer was prepared and reacted with α-cyano-β-(2-thienyl) crotononitrile.[2,3,16] The characterization was carried out by scanning electron microscope (SEM) and electrical conductivity of grafted, modified grafted, and

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TABLE I
The Grafting of PP with NVP (N_{series}) and Its Modified Grafted (S_{series})

PP-*g*-PVP (N_{series})	Grafting yield (*G*, %)	Modified PP-*g*-PVP (S_{series})
N_1	17.5	S_1
N_2	41.3	S_2
N_3	64.1	S_3
N_4	95	S_4
N_5	149	S_5

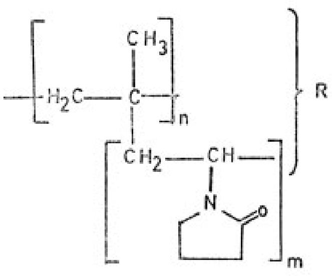
irradiated modified-grafted films, irradiated with γ-irradiation of a dose of 60 kGy. The main objective was to study the change of conductivity with activation energy and γ-irradiation.

EXPERIMENTAL

Materials

Used as a polymer substrate was 35-μm-thick PP film (El-Nasr for medical supplies, Egypt). *N*-vinyl-2-pyrrolidone (NVP) 99% pure (Merck, Germany) was used without further purification. Other chemicals were of reagent grade and were used without further purification.

The radiation graft polymerization process of NVP onto PP, preparation of a-cyano-β-(2-thienyl) crotononitrile (2a) and preparation of the modified-grafted films with (2a) have been given in our previous studies.[1–3,15] The structure of grafted and modified grafted were obtained as follows:



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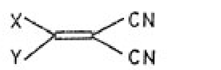
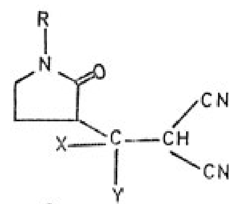


2a: X = -CH3 Y = 2-thienyl



3a

The grafting of PP with NVP (N_{series}) and its modified grafted (S_{series}) is listed in Table I.

Electrical conductivity measurements

The dc conductivity of trunk PP, grafted copolymer, and its modified grafted have been measured by a two-probe technique. Good electrical contact on both faces of the investigated films was ensured by two silver electrodes. The area of the electrode is equal to 0.25 cm^2. The measuring system consisted of copper cell connected to the sample by two copper wires. A programmable digital electrometer (Keithly-617) was used for the current measurements with an accuracy of ±1.6% with reliable fast response, together with a high precision power supply. The current measures at voltage about 100 V. The temperature of the sample was measured using a digital thermometer having chromel–alumel thermocouple in the temperature range of 303–473 K. The temperature range of the conductivity measurements was limited because of the possible thermal degradation of the samples. The dc conductivity (σ) has been calculated from the formula:

$$\sigma = Id/VA \quad (1)$$

where *I* is the measured current, *d* is the film thickness, *V* is the applied voltage, and *A* is the surface area. The data of σ measured at different temperatures allowed a ready determination of ΔE_σ by direct application of the Arrhenius equation:

$$\sigma = \sigma'_0 \exp(-\Delta E_\sigma/KT) \quad (2)$$

where σ'_0 is a pre-exponential factor, which corresponds to a minimum metallic conductivity, and *k* is Boltzmann constant.

Scanning electron microscope examination

Scanning electron microscope (SEM) is utilized to study the surface morphology of some selected polymers to reveal the possible textural transformation by grafting, modified grafting, and its irradiated modified grafting. The samples are gold sputtered for 8 min and then scanned by electron microscope model JSM-5400 from (JEOL Tokyo, Japan).

RESULTS AND DISCUSSION

The modified-grafted copolymer films (3a) exposed to γ-irradiation at a dose 60 kGy to reveal the presence of

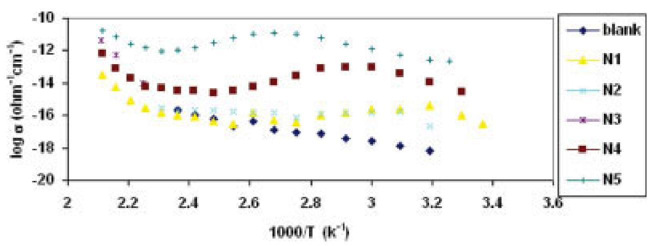


Figure 1 The effect of grafting yield on the temperature dependence of dc conductivity of PP-*g*-PVP films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Activation Energy and Pre-Exponential Factor of PP-*g*-PVP Samples

N_{series}	$\Delta E\sigma$ (eV)	Correlation	Covariance	High temperature range (K)	log σ'_0 (ohm^{-1} cm^{-1})	Correlation
Blank	1.00	0.983	−0.02	393–423	−28.49	0.979
N_1	2.86	0.983	−0.04	443–473	−46.21	0.987
N_2	0.19	0.999	−0.00	383–403	−18.19	0.999
N_3	3.70	0.958	−0.04	444–474	−53.41	0.953
N_4	2.77	0.984	−0.04	443–463	−43.92	0.988
N_5	1.51	0.994	−0.02	443–473	−28.14	0.996

a cyano groups at 2195–2191 cm^{-1}, which were absent in the grafted PP with NVP. The characteristic absorption of a carbonyl group appeared at 1659 cm^{-1}. The effect of γ-rays on the modified-grafted copolymer films exhibits the decrease in the intensity of the nitrile groups.[16]

Effect of grafting yield on σ and ΔE_σ

Figure 1 shows the values of log σ as a function of $1/T$ measured at temperatures within the range 303–473 K for different films undergoing various grafting yields varying between 17.5–149%. It is clearly seen from this figure that σ, generally, increases as a function of the grafting yield. The increase was, however, more pronounced for the films having a maximum grafting yield.

ΔE_σ values of different films were determined from the slope of the linear regression line of log σ versus $1000/T$ Arrhenius plots. The computed values of ΔE_σ, the correlation and covariance are given in Table II.

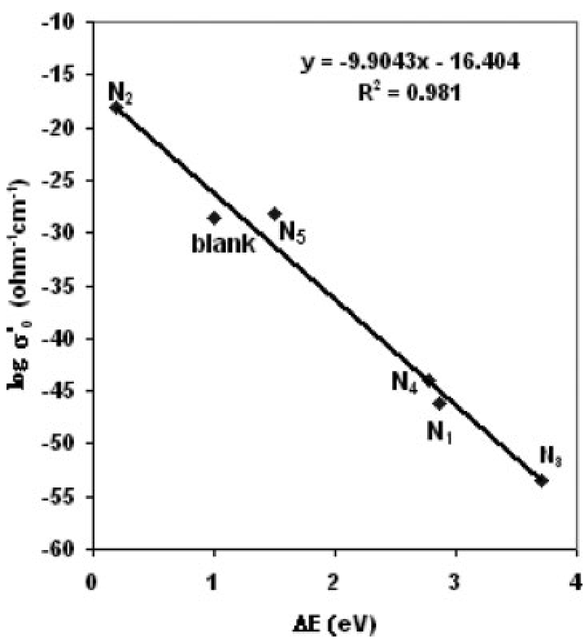


Figure 2 Relation between activation energy and log σ'_0 of PP-*g*-PVP films.

This table also includes the temperature range and log σ'_0 of various films. Examination of Table I shows that the change in grafting yield resulted in fluctuation in ΔE_σ values, i.e., the change of the grafting yield exerted both increase and decrease in ΔE_σ values depending on the extent of grafting yield. In other words, the observed change in ΔE_σ values due to increasing the grafting yield resulted mainly from a corresponding change in log σ'_0 values. In fact, by plotting log σ'_0 versus ΔE_σ, a straight line was obtained with correlation $R^2 = 0.98$. The observed increase in σ values due to increasing the grafting yield of various films could be attributed to an increase in charge carrier's concentration via an enhanced crosslinking of PVP chains through polymeric substrate, i.e., the possible increase in electron pair concentration and their mobilities can account for the significant improvement in the electrical conductivity of the films investigated.

Electrical properties of modified-grafted films (3a) by inclusion of sulfur-containing copolymer

Figure 3 depicts the variation of log σ as a function of $1/T$ for different sulfur-containing substrate films measured at temperatures of 300–473 K. It is seen from Figure 3 that inclusion of sulfur-containing substrate in different films undergoing various grafting yields (S_1–S_5) resulted in a significant increase in σ values measured at 403–443 K. The increase was, however, more pronounced for the film having maximum grafting yield (149%). This treatment resulted in

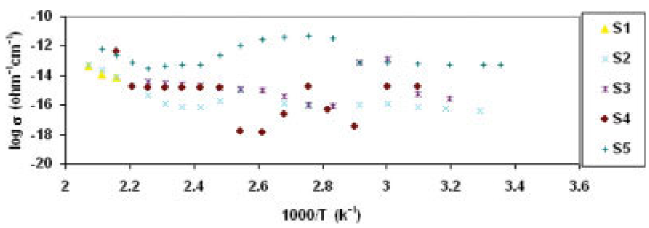


Figure 3 Temperature dependence of dc conductivity of modified-grafted PP films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Activation Energy and Pre-Exponential Factor of Modified-Grafted Samples

S_{series}	$\Delta E\sigma$ (eV)	Correlation	Covariance	High temperature range (K)	log σ'_0 ($ohm^{-1}\ cm^{-1}$)	Correlation
S_1	2.10	0.986	−0.01	468–483	−35.98	0.988
S_2	2.25	0.997	−0.08	433–483	−39.24	0.993
S_3	0.55	0.935	−0.09	353–443	−22.00	0.904
S_4	0.18	0.943	−0.00	423–453	−16.94	0.952
S_5	1.79	0.997	−0.03	443–473	−32.61	0.997

fluctuation in σ values depending on the extent of grafting yield.

The computed ΔE_σ values of S_1–S_5 given in Table III showed both increase and decrease by increasing the grafting yield. The decrease was, however, more pronounced for the sample having a grafting yield of 95%. The increase in grafting to 149% resulted in significant increase in ΔE_σ values, which are still smaller than those measured for S_1 film.

The observed increase in σ due to increasing the amount of sulfur-containing substrate in different films, via increasing the grafting yield reflected an effective increase in charge carrier's concentration. This effect might result from a possible increase in lone pairs concentration localized on sulfur and the two-cyano group (present in the compound 2a). In fact, the plotting of log σ'_0 versus ΔE_σ for different films give a straight line with correlation $R^2 = 0.99$ (cf. Fig. 4). These findings show clearly that the observed change in ΔE_σ values because of the sulfur inclusion in different films investigated might result mainly from corresponding change in σ'_0 value.

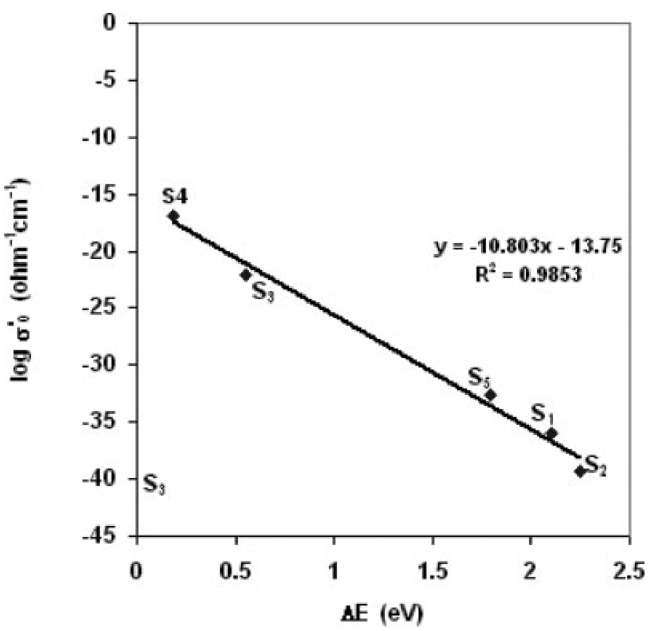


Figure 4 Relation between activation energy and log σ'_0 of modified-grafted PP films.

Electrical properties of modified-grafted films subjected to γ-radiation

The electrical conductivity σ and activation energy ΔE_σ of sulfur-containing substrate films exposed to dose 60 kGy γ radiation were determined. Figure 5 shows that the variation of log σ versus $1/T$ measured at 300–374 K of different investigated films. It is clearly shown in this figure that σ generally increases by increasing the extent of sulfur-containing substrate included in different films. The increase was, however, more pronounced for the irradiated films undergoing a maximum grafting yield.

The ΔE_σ values were determined for different films via considering the linear portion of curves relating log σ versus $1/T$ by direct application of Arrhenius equation. The temperature range and the determination of ΔE_σ with the correlation R^2 and covariance were given in Table IV.

Inspection of Table IV clearly shows that γ radiation of sulfur-treated polymeric films resulted in decrease in ΔE_σ values for the films undergoing a grafting yield between 64.1 and 149%. In fact, by plotting log σ'_0 versus ΔE_σ for different films, a straight line with correlation $R^2 = 0.96$ was obtained as seen in Figure 6. These results indicate clearly that the observed change in ΔE_σ values resulted mainly from corresponding change in log σ'_0. The observed decrease in ΔE_σ because of γ-irradiation could be attributed to an effective increase in charge carrier's concentration. This increase might result from a possible degradation leading thus to the creation of active sites involved

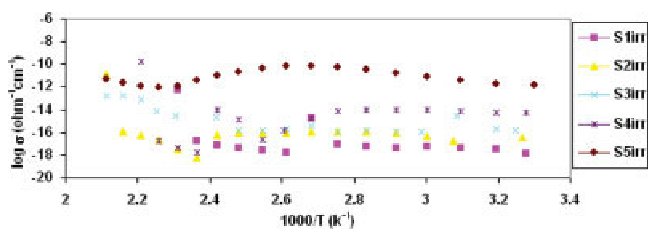


Figure 5 Temperature dependence of dc conductivity of irradiated modified-grafted PP films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
Activation Energy and Pre-Exponential Factor of Irradiated Modified-Grafted Samples

$S_{irr\ series}$	$\Delta E\sigma$ (eV)	Correlation	Covariance	High temperature range (K)	log σ'_0 ($ohm^{-1}\ cm^{-1}$)	Correlation
S_{1irr}	0.64	0.986	−0.02	383–423	−25.64	0.991
S_{2irr}	2.30	0.997	−0.06	423–463	−43.04	0.955
S_{3irr}	2.65	0.935	−0.04	434–463	−43.40	0.931
S_{4irr}	2.08	0.943	−0.02	423–443	−41.57	0.992
S_{5irr}	1.06	0.997	−0.01	443–473	−27.35	0.999

in the electrical conduction. These active sites might consist of free radicals throughout at the polymeric materials.

Some thoughts about activation energy and pre-exponential factor

Concerning the results relating log σ versus $1/T$, more than one straight lines portion can be observed depending, mainly, on the temperatures at which σ was measured. Each portion has its own slope and consequently having more than ΔE_σ values. Therefore, there is more than one conduction mechanism present in the material. In general, the high temperatures ranges were considered in calculations of both ΔE_σ and σ'_0. The pre-exponential factor varies slightly with temperature, although not much. It is often taken as constant across small temperature ranges. The fluctuation of computed activation energy of investigated films may be because of density variations, which shift the valance and conduction band states in opposite directions.

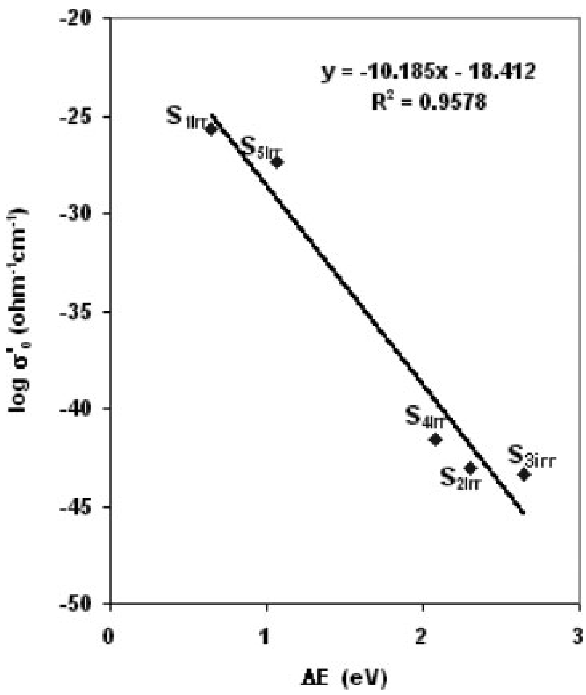


Figure 6 Relation between activation energy and log σ'_0 of irradiated modified-grafted PP films.

The measured values in the mentioned temperature ranges cited in Tables II–IV follow the linear model and the superposition rules. To elaborate the best fitting to the linear form, we applied the cross correlation and the covariance to estimate the degree of precision of measurements. The use of the correlation coefficient can be readily considered to determine the relationship between two properties, covariance is the average of the products of deviations for each data point pair. And the use of covariance is to determine the relationship between two data sets.

The inclusion of the temperature-dependent effects has an important ramification for the interpretation of measured values of both the activation energy and the pre-exponential factor of the dc conductivity. In fact, an exponential relation (Meyer–Neldel rule) between them of the form: $\sigma'_0 = \sigma_0 \exp(G\Delta E_\sigma)$ is rather widespread, and is observed in time-independent transport behavior as well as in steady-state properties such as σ_{dc}. The slope parameter (G) in the equation sets on the trend line as shown in Figures 2, 4, and 5 has the values of 9.9, 10.8, and 10.19 eV – 1, respectively, and the log of exponential factor σ_0 has the values of −16.04, −13.75, and −8.96, respectively, in the interesting correlation observed between the measured values of log the conductivity pre-exponential factor σ'_0 and the activation energy ΔE_σ.

The Meyer–Neldel correlations between σ'_0 and ΔE_σ can occur for a variety of reasons: for example, a collection of differently prepared samples can contain different concentrations of dopant impurities, thereby shifting E_F, or of defects, thereby changing the gap-state; alternatively, the effect may be observed in a single sample in which the danging-bond) defect density can be changed in some way, e.g., by irradiation, either by light effect or by electrons.[15]

Philibert[17] reported that the relation between σ'_0 and ΔE_σ has often been considered as physically meaningless, because any error on the slope of the straight line in an Arrhenius plot involves a corresponding error on the value of σ'_0. The Meyer–Neldel rule seems to be obeyed in most of cases, for experimental results as well as computed ones. Nevertheless, its physical

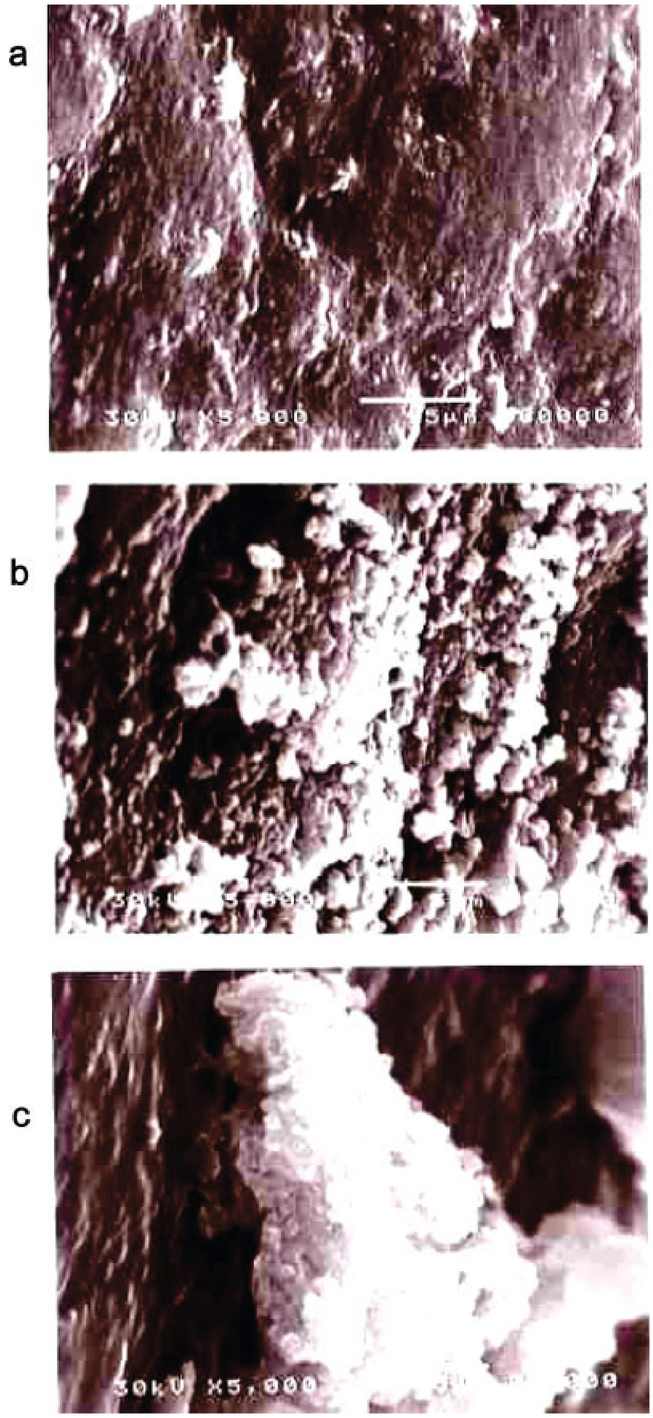


Figure 7 Scanning electron micrographs of investigated films having the same grafting yield (149%): (a) showing the grafted film, (b) showing the effect of sulfur inclusion on grafted film, (c) showing the effect of irradiation on modified-grafted film. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

meaning remains questionable, especially when the isokinetic temperature lies in the temperature range of the measurements. Moreover, predictions based on this rule are not accurate enough to derive reliable value of the pre-exponential factor from the activation energy.

Morphological investigation of some selected films

The scanning electron micrographs of some selected films were determined. These films include the film undergoing the maximum grafting yield (149%) [Fig. 7(a)], the same film with inclusion of sulfur-containing substrate, [cf. Fig. 7(b)] and the same film subjected to a dose of 60 kGy [cf. Fig. 7(c)]. The surface morphology of PP-*g*-PVP [Fig. 7(a)] at room temperature has a distinct shape as a mountain due to embedding of PVP chains in the matrix of PP. The micrograph depicted in Figure 7(b) shows the modified-grafted PP with α-cyano-β-(2-thienyl) crotononitrile (2a). It can be seen that the modified-grafted PP [Fig. 7(b)] appears to have a spherical shape because of the inclusion of the compound 2a to the grafted film. However, the irradiated modified film at 60 kGy led to the formation of aggregates of these spheres ring of sulfur inclusion to the grafted film. The formation of these sphere ring aggregates could be attributed to the rearrangement of the structure after degradation due to exposure to γ-irradiation.

CONCLUSIONS

The main conclusion derived from the results obtained can be summarized as follows:

1. The increase of grafting yield PP-*g*-PVP resulted in corresponding increase in σ values. The increase was, however, more pronounced in the case of the film undergoing maximum grafting yield.
2. Inclusion of sulfur-containing substrate in different films undergoing various degree of grafting brought about a considerable increase in σ values.
3. γ-Irradiation at 60 kGy of sulfur-containing substrate films also effect a measurable increase in the values of electrical conductivity.
4. The different treatments of the investigated films did not affect the ΔE_σ values much but rather increase the charge carrier's concentration. The observed change in the apparent activation energy of electrical conductivity of different films resulted mainly from corresponding change in σ'_0 values (pre-exponential factor of Arrhenius equation).
5. The scanning electron micrographs of some selected films showed significant change in the morphology of these films. This modification includes a creation of sphere ring as a result of inclusion sulfur-containing substrate and aggregation of these spheres via γ-irradiation.

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