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Electrical Conductivity Effect for Grafted Polystyrene at Different Grafting and Gamma Dose

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Abstract: Grafted polystyrene with acrylonitrile using gamma-irradiation was studied the electrical current (I)**,** electric field strength (E), at different ionic jump distance (a) and room temperature (T). The gamma-irradiation dose, acrylonitrile percentage (as a monomer), ferrous ammonium sulphate (FAS) percentage (as a catalyst) and grafting percentage on the electrical conductivity were studied. It was found that the electric current increases upon increasing both gamma-irradiation dose and grafting percentage. The ionic jump distances values were calculated and the variation of ionic jump distance with both gamma-irradiation doses and grafting percentage were reported. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) of polystyrene with out grafting and with grafting were studied**.** Effect of temperature on the redox process of $K_3Fe(CN)_6$ was studied on grafted polymer by cyclic voltammetry using Arrhenious equations. The new grafted polymer has high redox stability and is considered to belong to the most useful conductive grafted polymer for practical application. *Copyright © 2012 IFSA.*

Keywords: Grafted polymer, Electric current, Ionic jump distance, Conductivity, Gamma-irradiation.

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1. Introduction

Most of conductive polymers had been synthesized and characterized at recent times, that polymers were reported largely focused on polyacetylene, polyaniline, polyfuran, polythiophene, polypyrrole and their functional derivatives, whilst relatively lesser work was conducted on polyselenophene [1-3].

Effective side wall functionalization of single-walled carbon nanotube (SWCNT) with 4-vinylaniline was carried out through solvent free functionalization. The functionalized SWCNT was characterized through FT-IR and NMR. Typical peaks to identify the functionalization were observed. Thermal analysis shows around 48 % weight loss in functionalized SWCNT in comparison to the pure SWCNT. The ratio of disordered to order transition (I_D/I_G) in FT-Raman, indicated the generation of some surface defects due to functionalization. Near infrared spectrum of functionalized SWCNT also confirmed the functionalization of SWCNT. The polystyrene nanocomposite materials were prepared with functionalized SWCNT as fillers by solution casting from tetrahydrofuran. The functionalized SWCNT nanocomposite showed significant improvement in mechanical properties and electrical properties. The dispersibility of the carbon nanotube in the composite was investigated by using scanning electron microscopy [4].

Radiation-induced graft copolymerization of N-isopropylacrylamide (NIPAAm) and acrylic acid (AA) mixture was investigated on polypropylene nonwoven fabric to develop a thermosensitive material [5].

Electrical conductivity of the copolymer was studied using the four-probe method, which gave a conductivity of 4.5×10^{-3} S cm^{-1} of polyacrylonitrile-*graft*-polyaniline [6].

Thermoelectric properties of new poly(2,7-carbazole) derivatives are made to carbon nanotube/polymer composites and their improved electrical and thermalelectric performance. Studies on polymer/inorganic materials composites have also taken a step forward and have shown very promising thermalelecrtic properties [7].

Conductive nano filler, expanded graphite was introduced into polyvinylidene fluoride (PVDF) by direct melt blending process [8].

It has been synthesized pyrrole in the presence of poly(*para*-chloromethylstyrene-*co*-styrene-*co*-pyrrolemethylstyrene) by chemical and electrochemical polymerization, it would that seem this conducting co-polymer using as chemical sensors [9].

In the present work polystyrene was grafted by acrylonitrile, irradiation procedure was carried out by introducing the polystyrene with acrylonitrile as monomer and ferrous ammonium sulfate (FAS) as a catalyst. Polystyrene molecule was successfully grafted by acrylonitrile and 0.25-2 % of FAS as a catalyst [10].

2. Experimental

A new grafted polymer (GP), acrylonitrile grafted on polystyrene at different grafting percentage was obtained using different gamma-irradiation [10]. The solution was prepared by dissolving 0.1 gm of different grafting ratio in 50 ml of dimethyl formamide (DMF) (from BDH Limited Poole England). Thin films were chemically deposited on a glass substrate using spray pyrolysis technique [11]. The substrate temperature was kept at 80 ^{o}C. For electrical measurement a coplanar aluminum electrodes with gap of 2 mm and length of 10 mm was thermally evaporated on the samples in vacuum system. All current potential (I-V) measurements were carried out in a dark screened enclosure.

Electrochemical workstations from Bioanalytical System Inc. USA: Models BAS CV 50W with potentiostates driven by electroanalytical measuring software was connected to a PC computer to perform cyclic voltammetry (CV) [12].

The surfaces of the polymer and grafted polymer were studied using a JEOL. The scanning electron microscopy (SEM) operated at 20 - 30 kV. SEM was recorded at a magnification of 1000 - 6000X depending on the nature of the sample. SEM analysis was carried out to investigate microcrystals. Samples were dehydrated for 45 min before being coated with gold particles using SEM coating unit baltec SC030 sputter coater. SEM was used to examine the morphology of polymer and grafted polymer by solvent evaporation method on a graphite electrode surface.

3. Results and Discussion

3.1. Dose and Grafting Dependence of Irradiated Samples

Fig. 1 shows that the increasing in the dose of gamma-irradiation from the range 0.4-1.5 Mrad produced a sharp increasing in grafting percentage, with keeping the concentration of the catalyst Ferrous ammonium sulfate (FAS) and the monomer acrylonitrile at 0.25 % (w/w) and 90 % (w/w), respectively [10].

The temporary and the permanent changes in polystyrene conductivity resulting from exposure to different sources and intensities of radiation been reported by several workers [13-15]. The permanent changes where only observed on this study after different ranges of gamma-irradiation.

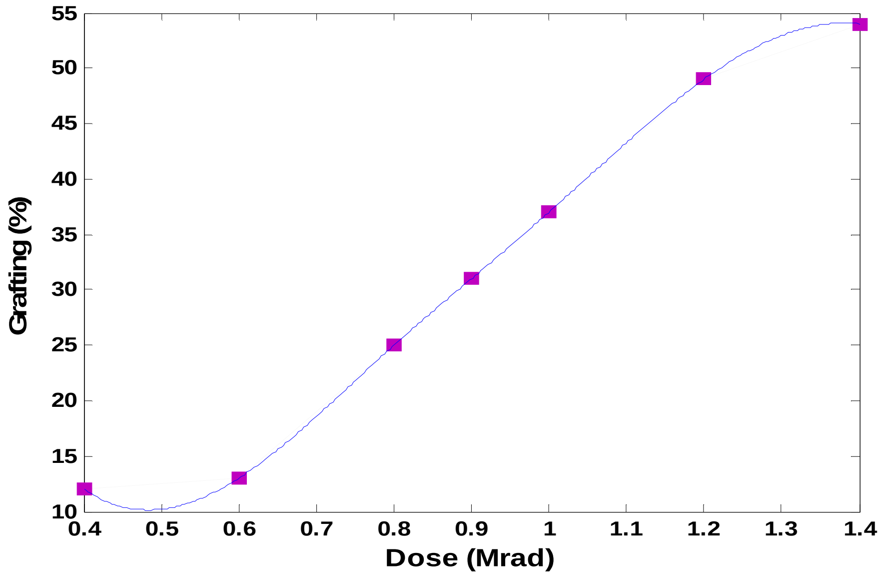


Fig. 1. Variation of grafting% (w/w%) as a function of gamma dose at constant catalyst and monomer (w/w%).

3.2. Dose Dependence of the Electrical Current

Fig. 2 shows the electric current plotted versus the dose of gamma irradiation. Where the circles indicate the experiments and the solid line indicates the theoretical equation (1) for ionic conduction at constant temperature [16, 17].

$$J = G \sinh (q\, a\, E / 2\, K\, T), \tag{1}$$

where E is the electrical field values, q is the ionic charges, a is the ionic jump distance, K is the Boltzmann constant, and T is the absolute temperature.

Fig. 2 and 3 show the effect of radiation dose and the grafting percentage on the current passing through the thin film of grafted polystyrene with acrylonitrile molecule. The current was increased with increased in both gamma dose and grafting percentage. The grafted polymer (GP) at high doses of gamma-irradiation produces high grafting percentage of GP with higher current. The conductivity of GP is more than pure polystyrene conductivity value is ~ $10^{-18}\ \Omega^{-1}cm^{-1}$ [18].

Increasing in the current means increasing in conductivity could be scission predominates at high irradiation doses in an irradiated grafted polymer. It was found that the acrylonitrile at high radiation dose to produce high quality of free radical and the pair of electrons which were the main reason for increasing the conductivity.

However, the further of increasing the gamma-irradiation doses which produced increasing in the grafting percentage of grafted polymer. The explanation for this behavior appears to be that during irradiation radicals are formed in the polystyrene, these react with the polystyrene molecules, forming radicals the concentration of molecules the greater the share each with have from these aqueous fragments.

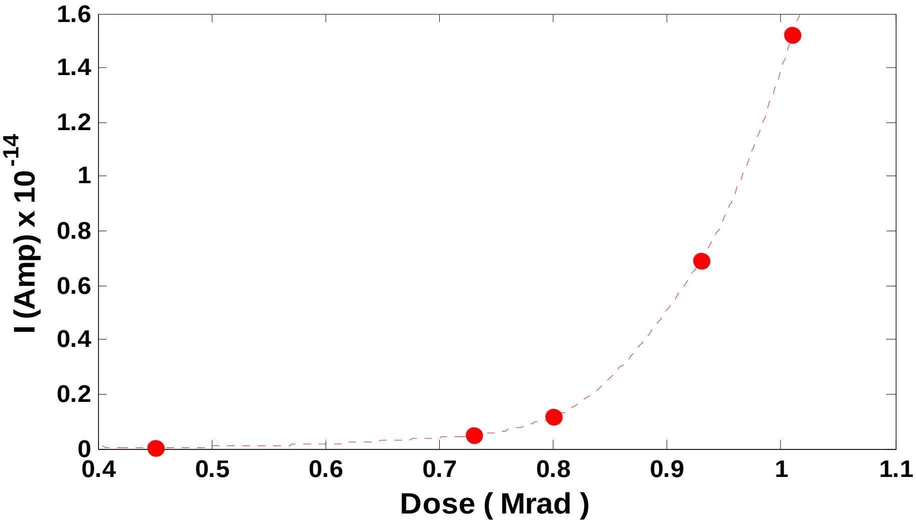


Fig. 2. The effect of dose of gamma irradiation on the current at the grafted polymer.

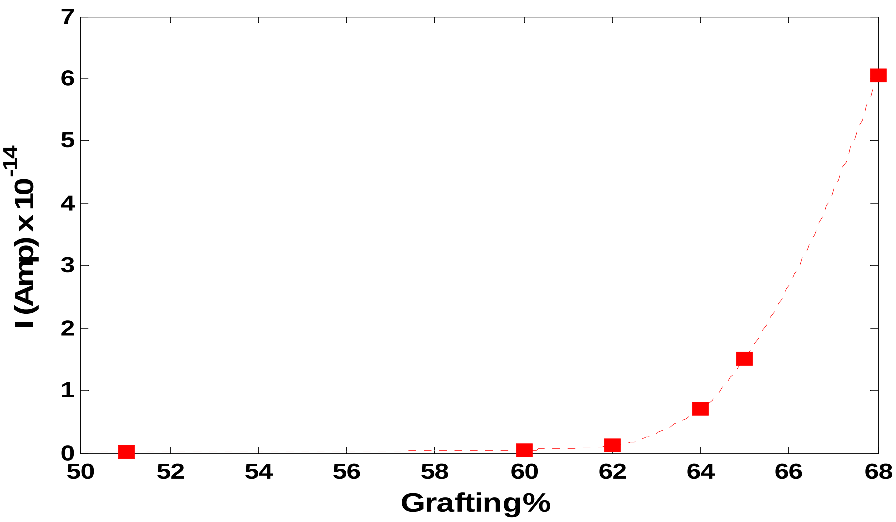


Fig. 3 The effect of dose of grafting (%) on the current at the grafted polymer.

3.3. Grafting Dependence of the Electric Current Versus Electrical Field Strength

Fig. 4 represented the current effect (I) relation for thin film of grafting polymer versus electric field strength (E) at different ionic jump distance (a) and constant temperature (T) from equation 1. The curves behavior is obvious that the current response against the ionic jump distance is proportionally increased at the different electric field strength.

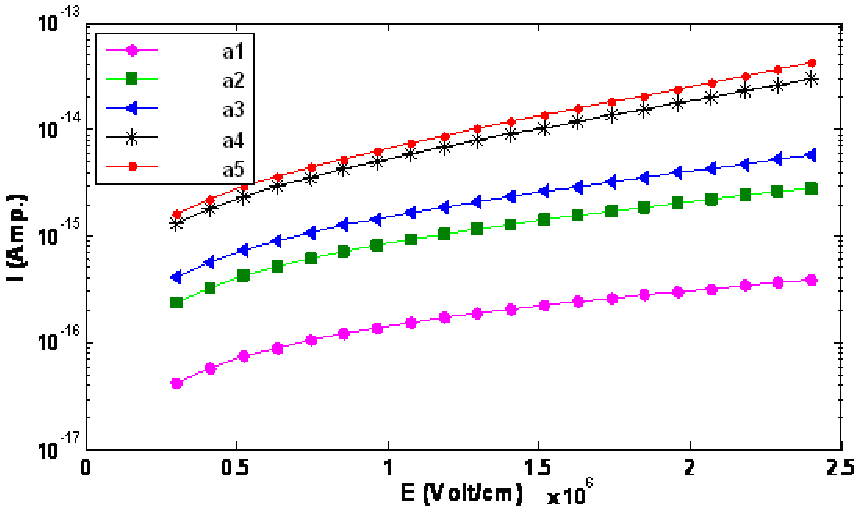
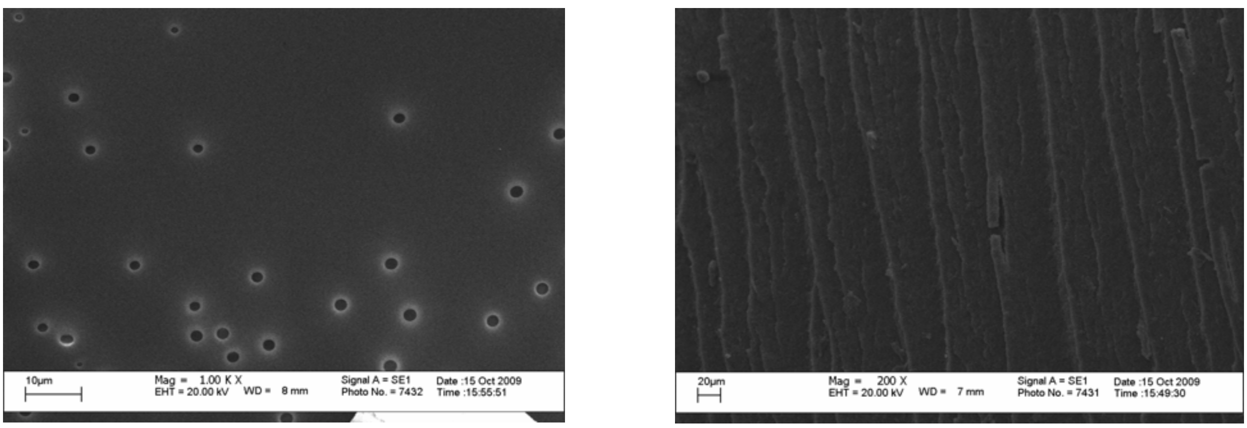


Fig. 4. The current effect (I) for thin film of grafting polymer versus electric field strength (E) at different ionic jump distance (a).

3.4. Scanning Electron Microscopy (SEM) of Grafted Polymer

SEM of polymer sample (polystyrene) and grafted polymer (polystyrene grafted with acrylonitrile) were studied. Fig. 5a shows the polymer surface which appears porous and homogenous uniformity film. While grafted polymer appears compact, nonporous and the uniformity surface as shown in Fig. 5b, it seems that monomer molecules at serious of polystyrene polymer matrix was grafted with symmetrical system lines.



(a) (b)

Fig. 5. Scanning electron micrographs (SEM) of grafted polymer:
(a) before irradiated, (b) after irradiated.

3.5. Atomic Force Microscopy (AFM) of Grafted Polymer

The surface image of AFM in an area of 20 µm x 20 µm of the grafted polymer (polystyrene-acrylonitrile) is shown in Fig. 6. The surface of grafted polymer appeared to be compact and rougher surface in nature. According to AFM image, the average grain size of the film was estimated to be 11.23 µm.

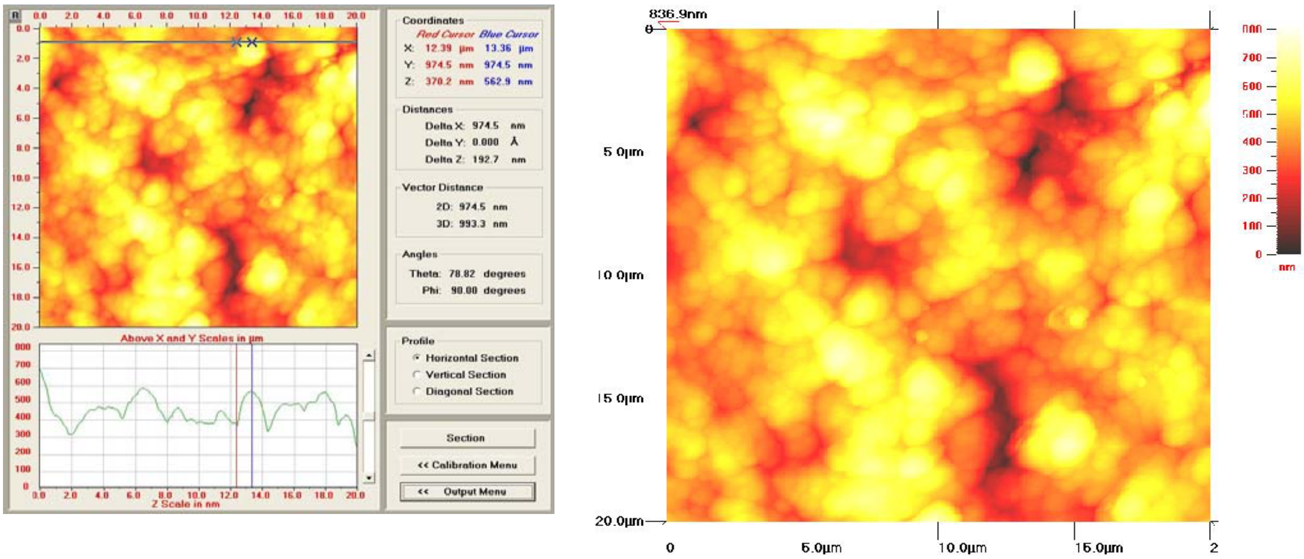


Fig. 6. AFM image of grafted polymer.

3.6. Effect of Varying Temperature

Effect of temperature on the redox process of $K_3Fe(CN)_6$ was studied on grafted polymer using cyclic voltammetry technique. The current increases gradually at the temperature of 10 to 90^{o}C. Fig. 7 and 8 is plot of log Ipa (oxidation current) and Log Ipc (reduction current) of $K_3Fe(CN)_6$ versus reciprocal of temperature respectively, which is found to be fairly linear in agreement with thermodynamic expectation of Arrhenious equations [19]:

$$\sigma = \sigma o \text{ Exp } (- Ea/ RT) \tag{2}$$

$$D = Do \text{ Exp } (-Ea/ RT), \tag{3}$$

where σ/D is conductivity/diffusibility and σo/Do are standard conductivity / the initial diffusibility.

From slope of linear relationship the value of activated energy of grafted polymer is Ea =4.03 kJ/mol (for oxidation process of FeII/FeIII). While the value of activation energy is more high at other technique (Ea=57.89 kJ/mol) [20]. For reduction process of $K_3Fe(CN)_6$ the activation energy value is 23.3 KJ/mol. comparing with other technique is Ea=33.59 kJ/mol [21] as shown in Fig. 8. The conductivity of GP with increasing temperature also plays a significant influence on the activation energy for diffusion of the substrate of interest, Ea.

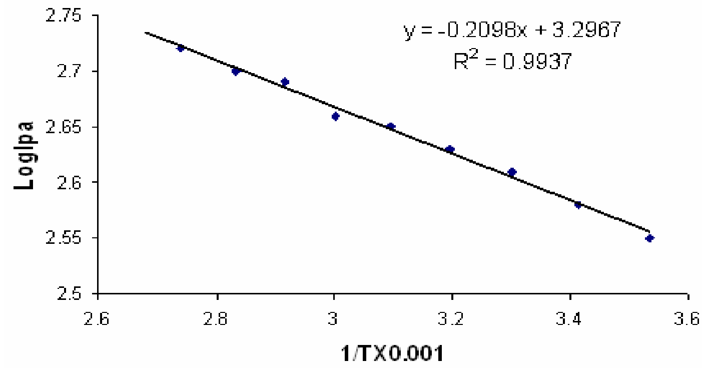


Fig. 7. Plot of Log (Ipa) versus 1/Tx10^{-3} of 1mM $K_3Fe(CN)_6$ in 0.1M KCl at different temperature (10-90 ^oC) using GP versus Ag/AgCl and 100 mV/sec.

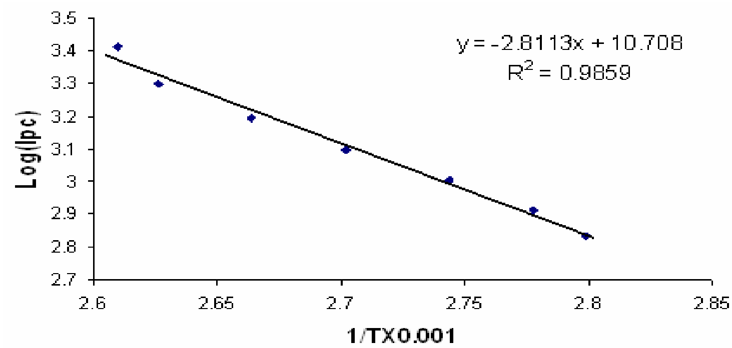


Fig. 8. Plot of Log(Ipc) versus 1/Tx10^{-3} of 1mM $K_3Fe(CN)_6$ in 0.1M KCl at different temperature (10-90 ^oC) using GP versus Ag/AgCl and 100 mV/sec.

4. Conclusion

The electric current and electric potential distance of new grafted polystyrene-acrylonitrile was increased with increasing the gamma-irradiation dose and grafting percentage. The activation energy of the grafted polymer was studied by cyclic voltammetry technique with low values for both redox processes. AFM and SEM of the polystyrene and grafted polymer were studied to proving the complication of the grafting on polystyrene in homogenous uniformity film.

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