MODIFICATION OF LOW DENSITY POLYETHYLENE BY RADIATION-INDUCED GRAFTING

I. GRAFTING PROCEDURE, CHEMICAL MODIFICATION OF GRAFTED FILMS AND ELECTRICAL PROPERTIES

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ABSTRACT

Radiation grafting of monomers onto suitable trunk polymers is a useful tool for tailoring new polymers for special purposes. The introduction of new characteristics to some synthetic polymers was achieved through the γ-radiation-induced graft copolymerization of methyl methacrylate onto low density polyethylene films (in the presence of aniline as inhibitor) for the preparation of grafted films. The influence of the reaction conditions on the grafting yield, such as the irradiation dose and the inhibitor was investigated. An alkaline treatment was carried out for the prepared graft copolymer to improve its ion-exchange property. The grafted and treated membranes were characterized to determine the structural changes with Fourier transform infrared spectroscopy. The electrical properties of the graft copolymer were studied. Improvements in the electrical conductivity with grafting were observed. The KOH treated films possessed higher electrical conductivity than the untreated ones.

1-INTRODUCTION

Polymer grafting is a process where monomer molecules are covalently bonded to polymer chains through chemical reactions between there active species and the substrate during matrix modify-cation [1]. This process differs from curing where the polymerization process occurs for an oligomer mixture and the coating formed adheres physically to the polymer substrate. Grafting is a process that allows for the development of new materials that feature unique properties. The introduction of new functional groups on a substrate surface improves properties such as hydrophilicity, adhesion, bio-compatibility, conductivity and antifogging, among others.

Radiation crosslinking and radiation grafting are widely used in industrial applications of radiation processing of polymeric materials. In collaboration with the local polymer industry an effort has been made to demonstrate the advantage of the radiation processing as compared with the conventional chemical process. Radiation grafting of polar monomers on low density polyethylene were performed to improve the electrical conductivity of polyethylene. The improvement of the polymer stability continues to be an area of active industrial concern and intensive research effort [2-6]. Poly-ethylene's, as well as most organic polymers require protection against the effects of heat, oxygen, light, high energy radiation and so on. In the radiation grafting process, the high energy level is responsible for hemolytic bond scission of mole-cules and release of free radicals [7]. Compared to chemical and photochemical grafting, radiation grafting is fast, occurs in the absence of an initiator and produces low byproduct levels, costs and hazards.

Mutual irradiation takes just one step to perform the grafting process, since the polymer and monomer are irradiated simultaneously with the subsequent formation of free radicals, which result in the formation of chemical bonds at the

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polymer substrate [8]. Although homo polymer is a byproduct of this process, and this phenomenon has not been observed in the previous techniques discussed, this one-step process has advantages: it is faster than the pre-irradiation methods and, most importantly, also leads to low chain scission levels a clear advantage when the final product requires adequate mechanical properties [9].

In this work, mutual radiation grafting of methyl methacrylate (MMA) in the presence of aniline (Ani) was performed and the effect of irradiation dose were studied to verify their influence on grafting of low density polyethylene (LDPE). The grafting yield was measured by gravimetric determination and qualitative MMA analysis was made by infrared spectrometry. The effects of the chemical treatment as well as the electrical properties of the prepared films were studied.

2- EXPERIMENTAL

2-1- MATERIALS

Low density polyethylene (LDPE) films used throughout this work (thickness ~50 μm) were provided by El-Nasr Co. for Medical Supplies, Cairo, Egypt. Methyl methacrylate monomer (MMA, $C_5H_2O_2$ =100.12) and aniline (Ani, $C_6H_5.NH_2$ = 93.13), were obtained from BDH, Chemical Ltd., England and used as received. Solvents and chemical reagents were of laboratory grade and were used without further purification.

2-2-GRAFT COPOLYMERIZATION ONTO LDPE

The graft copolymers were prepared through the radiation grafting of an MMA/Ani binary monomer system onto LDPE films with ^{60}Co-γ-rays to different irradiation doses (5- 50 kGy) at a dose rate 9.23 kGy/h. Strips of LDPE were washed with methanol, dried at 50°C in a vacuum oven, weighed, and then immersed in a 30 wt % 80/20 MMA/Ani comonomer solution. The direct radiation grafting method was used in an air atmosphere. The glass ampules containing the LDPE films and comonomer solution were then subjected to ^{60}Co-γ-rays. The grafted films were removed and washed thoroughly with hot distilled water and then acetone to extract the residual monomers and the homopolymer, which may have accumulated in the films. The films were then dried in a vacuum oven at 50°C for 24 h and weighed. The degree of grafting was calculated by the percentage increase in the weight of the LDPE films after the grafting process as follows:

Degree of grating (%) = $[(W_g - W_o)/ W_o] \times 100$...(1)

Where

W_o and W_g represents the weight of the ungrafted and grafted films, respectively.

2- 3 - ALKALINE TREATMENT

The grafted films were alkali-treated with a 3% KOH solution at 80^0C for 24 h. The films thus obtained were washed with distilled water several times.

2- 4 - IR SPECTROSCOPIC ANALYSIS

Absorption infrared Fourier transform spectroscopy characterization was obtained from films using a holder designed for samples of 2 x 2 cm. The spectra were obtained by FTIR spectrometer (6300, JASCO Japan) in the range from 400-4000 cm^{-1}.

2-5- ELECTRICAL CONDUCTIVITY MEASUREMENTS

The electrical measurements were carried out using a programmable DC voltage/ current generator, along with a precision digital electrometer (Keighley 6514) to determine the current generated on application of a known voltage to grafted films. The said measurements were made at room temperature (25^0C) for each grafted film. Thus, through the determination of the resistance (R) of the sample, the electrical conductivity could be calculated:

$$\sigma = \left(\frac{1}{R}\right)\left(\frac{L}{A}\right), \Omega^{-1} m^{-1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where

Ω is the electrical conductivity,

L is the thickness of the specimen (m),

A is the cross-sectional area the disc (m^2), and

R is the ohmic resistance of the specimen (Ω).

3 - RESULTS AND DISCUSSION

Radiation grafting is a technique that can be used for surface modification of polymeric materials. It allows introducing active functional groups to the surface of plastic films, which after modification can be used as selective membranes, sorbents as well as for preparation of catalysts and metallized materials, etc. [10, 11].

In this work, the radiation-induced graft copolymerization of a methyl methacrylate (MMA)/ Aniline (Ani) (80/20) comonomer mixture onto low density polyethylene LDPE films was investigated for the preparation of grafted copolymer systems.

In this study, the radiation-induced graft copolymerization of MMA onto LDPE film was investtigated at a single irradiation dose (10 kGY) for comparison (Table (1)).

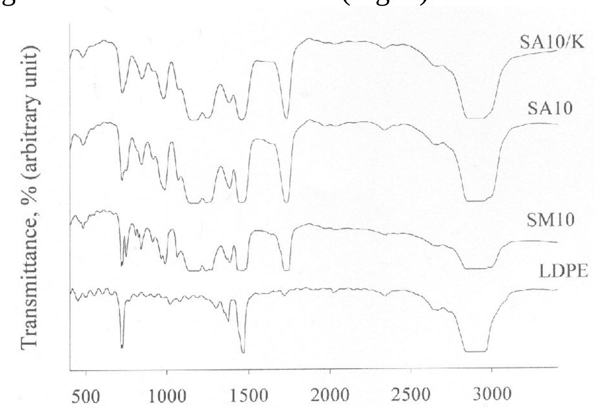
Table 1- Effect of irradiation dose on the Graft Copolymerization of a 80/20 (V/V) MMA/Ani Mixture onto LDPE Films

Sample name	Monomer	Irradiation Dose (kGy)	Degree of Grafting (%)	Sample name (after KOH treatment)
SM10	**MMA**	10	61.5	SM10/K
SA5	**MMA/Ani (80/20)**	5	37.0	SA5/K
SA10	**MMA/Ani (80/20)**	10	89.0	SA10/K
SA15	**MMA/Ani (80/20)**	15	120.5	SA15/K
SA20	**MMA/Ani (80/20)**	20	127.0	SA20/K
SA30	**MMA/Ani (80/20)**	30	143.0	SA30/K
SA40	**MMA/Ani (80/20)**	40	154.0	SA40/K
SA50	**MMA/Ani (80/20)**	50	211.0	SA50/K

Monomer concentration = 30 wt % in methanol

3-1- FTIR

The FTIR plots of untreated and KOH treated PE grafted with polymethyl methacrylate are shown in Fig. (1), the frequencies 1466 and 1379 cm^{-1} are assigned to CH_3 asymmetric bending and C-CH_3 stretching vibrations of PMMA. The frequencies 1450, 1266, 962 and 755 cm^{-1} are assigned to CH_2 scissoring, twisting, wagging and rocking modes of PMMA. The C-H stretching frequency of the PMMA at 2992 cm^{-1} and Clear characteristic band for C=O of PMMA ester groups at 1730 cm^{-1} are also shown. The PE films grafted with methylmethacrylate in the presence of aniline shows the same characteristic FTIR bands of the PE films grafted in absence of aniline (Fig. 1).



Wave number (cm^{-1})

Fig. 1- IR spectra of pure LDPE and grafted copolymer films

3-2- EFFECT OF IRRADIATION DOSE ON THE GRAFTING YIELD

If the kinetics of heterogeneous radiation grafting is considered, the following assumptions can be generally made for polyethylene (PE):

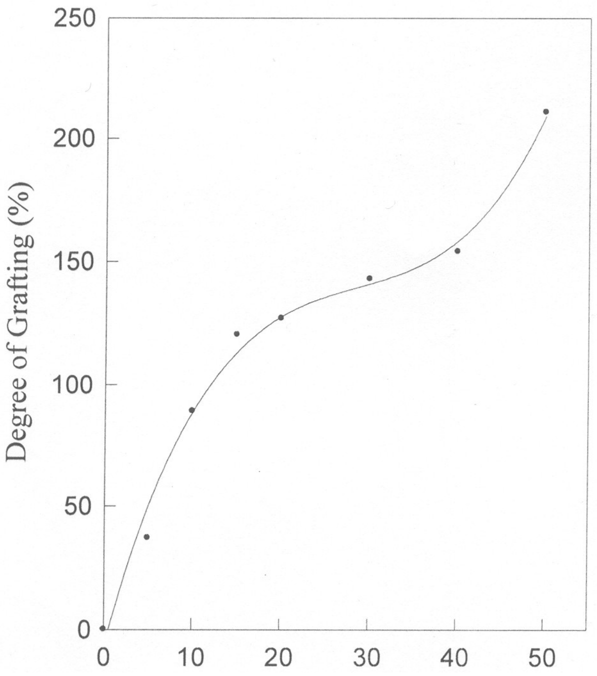
(i) The radical yield of PE is higher than most of the monomers.

(ii) The chain transfer coefficient for a growing chain radical to PE is high.

(iii) Any chain transfer coefficient of a PE radical species to a growing graft chain is low.

These result in the formation of many radical sites on PE, but only a few on growing graft chains. Hence, once the entire PE surface is grafted, the rate of grafting drops such as occurs for MAA on PE [10]. If these assumptions were not correct and a significant amount of chain transfer to growing graft chain were to have taken place, the resulting graft would be highly branched and of uniform density. But, it seems that real situation probably lies between two extremes.

The influence of irradiation on the extent of the grafting process is shown in Fig. (2). It is clear that under the chosen reaction conditions, the grafting yield within the studied range of irradiation dose ranging from 5 to 50 kGY increases with increaseing irradiation dose. This trend can be explained to the fact that the increase in the irradiation dose leads to more free radical formation in the grafting site which leads to an increase in the grafting yield.



Irradiation Dose (kGy)

Fig. 2- Effect of irradiation dose on the degree of grafting of MMA onto LDPE in the presence of aniline.

At irradiation doses above 50 kGY, a very rigid homopolymer was formed and was difficult to extract.

The total degree of grafting of MMA onto LDPE at 10 kGY irradiation dose was 61.5%. It can be noted that the addition of Ani increases the total degree of grafting *DG* at the similar irradiat-ion dose. Madani studied the radiation-induced graft copolymerization of methyl methacrylate (M MA) monomer onto LDPE films in the presence of different organic solvents [10]. Optimum graft-ing is achieved at a dose of 10 kGY for all sol-vents. The decrease in grafting yield above 10 kGY may be due to the graft chain degradation.

Here, the increase of the total degree of grafting with irradiation dose above 10 kGY in the presence of aniline may be attributed to the effective protection of aniline which can act as an effective protection agent against structural damage caused by gamma radiation in the copolymer matrix [12].

The introduction of new characteristics to some synthetic polymers was achieved through the γ-radiation-induced graft copolymerization of an acrylamide/vinyl acetate comonomer onto polypropylene films for the preparation of synthetic membranes [13].

The influence of the reaction conditions on the grafting yield, such as the solvent and its composition and the inhibitor and its concentration, was investigated [13].

In this study, the addition of Aniline to the reaction mixture was investigated in an attempt to minimize the homopolymerization and to optimize the grafting conditions. A possible explanation is that when the dose rate is high the concentration of free radicals is increased. Accordingly recombinetion of primary radicals into inert species in the bulk medium is significant and therefore there are only a few radicals available to start copolymerization. Most radicals undergo recombination or initiate homopolymerization.

The lower dose rate due to the presence of inhibitor (aniline) initiates mainly graft copolymerization due to lesser termination of free radicals with the polymer growing radicals and recombination of primary radicals resulting a longer chain length of the grafted copolymer and elimination of homopolymer [14].

3-3- ELECTRICAL PROPERTIES

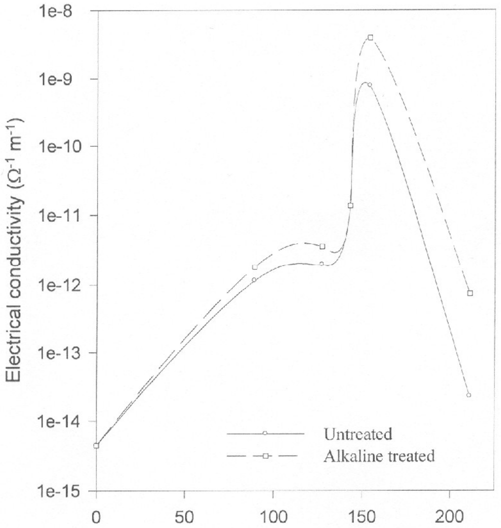
Radiation-induced grafting is a beneficial method for introduction of functional groups into different polymer materials using specially selected monomers. There have been several reports on radiation graft copolymerization of polar monomers onto polymer film to obtain hydrophilic property for versatile application [15-19].

Radiation grafting technique does also impart the conductivity to the matrix. This is the unique method of combining of conducting matrix on to the insulating one. This technique involves deactivation of backbone polymer with a suitable monomer by grafting and subsequent deposition of the conducting polymer over the active surface of the backbone. Apart from the insulating behavior, in this case polymer can behave as conducting one.

Most of the studies on characterization of radiation graft copolymer membranes show that the degree of grafting plays a key role in affecting the membranes most important properties, i.e. swelling behavior, ion exchange capacity, ionic conductivity, mechanical strength, crystallinity and thermal stability. The effect of the degree of grafting is so pronounced that it dictates all the membrane properties particularly when: (1) polar monomers such as MMA are grafted and (2) non-polar monomers such as styrene are grafted and the subsequent post-grafting reaction to introduce ionic characters achieved 100% functionalization (e.g. 100% sulfonation of polystyrene grafted into polymer film). However, other factors including the procedures (number of steps) by which the membrane is prepared and the degree of functionalization upon using post-grafting reaction are also affecting the properties but to lesser extent.

Grafted LDPE (non polar) films were prepared by the direct radiation graft copolymerization of MMA onto LDPE films. Grafted LDPE films, having different degrees of grafting were obtained and used for this study. Meanwhile, the grafted films were alkaline treated using KOH solution.

The data given in Fig. (3) show the change in the electrical properties of LDPE caused by the grafting process. Also Table (2) presents the electrical conductivity of the original LDPE and grafted films as a function of irradiation dose (degree of grafting). In fact, the polymer substrate and graft chains of PMMA were nonconductive materials. Meanwhile, the grafted copolymers, which prepared in the presence of aniline, possess electrical conductivity (σ) of approximately one million (10^6) times higher than that of LDPE original material.



Degree of Grafting (%)

Fig. 3: Electrical conductivity of MMA-g-LDPE (in the presence of aniline) as a function of the degree of grafting and its KOH-treated form.

Table 2- Electrical conductivity of untreated and alkaline treated grafted films.

Dose (kGy)	DG (%)	Untreated		Treated	
		Sample	Electrical conductivity (Ω^{-1} m^{-1})	Sample	Electrical conductivity (Ω^{-1} m^{-1})
0	0	LDPE	4.5 E-15		
10	61.5	SM10	6.8 E-15	SM10/K	9.0 E-13
10	89	SA10	1.1 E-12	SA10/K	1.8 E-12
20	127	SA20	2.0 E-12	SA20/K	3.6 E-12
30	143	SA30	1.4 E-11	SA30/K	1.4 E-11
40	154	SA40	7.9 E-10	SA40/K	4.0 E-9
50	211	SA50	2.3 E-14	SA50/K	7.3 E-13

The addition of aniline (inhibitor) to the reaction mixture leads to minimize the homopolymerization and optimize the grafting conditions. The grafting process did not proceed successfully in the absence of an inhibitor because of the fast homopolymerization of MMA, which prevented the diffusion of more monomer molecules into the polymer matrix during radiation grafting and consequently reduces the conductivity.

The value of σ increases with the degree of grafting up to a certain *DG* for both untreated and treated films. The increase of σ for LDPE grafted with MMA (in the presence of aniline) may be due to the free mobility of carboxylic groups (COOH) of the graft chains. The effect of ionizing radiation on the polymer substrate during grafting process must also be taken into consideration and its influence on electrical properties is included [20].

The electrical conductivity of the grafted films increases with increasing gamma dose up to 40 kGY and then decreases. The decreasing behavior in σ, for both untreated and treated grafted films above certain irradiation dose can be reasonably explained by the formation of new phase transition in the copolymer structure above such irradiation dose. The similar maximum conductivity value indicates that there are no fundamental changes in the conduction mechanism caused by alkaline treatment.

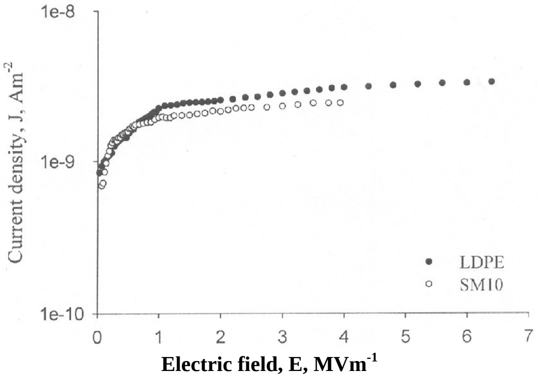
At a given degree of grafting, the KOH-treated films possessed a higher σ than the untreated ones. The alkaline treatment resulted in the hydrolysis of the grafted chains, and the carboxylic groups (COOH) of the graft chains were converted into highly solvated ionic units of the type -COOK [13]. Adding electrolytic groups to the grafted side chains resulted in improved electrical behavior.

3-4- CURRENT-VOLTAGE (I-V) CHARACTERISTICS

The current-voltage I-V characteristics of pure LDPE, MMA-g-LDPE (SM10 only for comparison), untreated grafted films and treated grafted films were studied at 25^0C. I-V characteristics of all samples are shown in Figs. (4-7) in the form of plots of log current density and electric field. The current density J flowing through a specimen across which an electric field E is applied at certain temperature is given by [21]

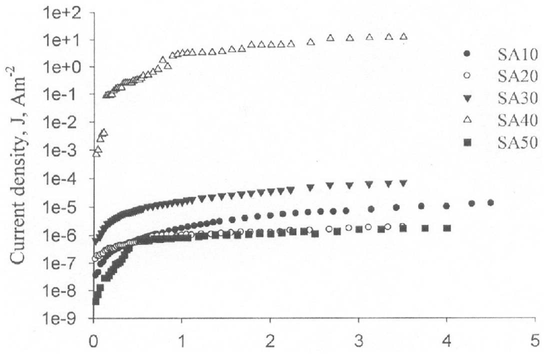
$$J = J_0 \sinh\left(\frac{aeE}{2KT}\right) \quad \ldots\ldots(3)$$

Where*a* is the jump distance of charge carrier, *T* is the temperature in Kelvin, *e* is the electron charge, *k* s Boltzmann's constant, and J_o is a fitting parameter that depends on the operating condition of the polymer.



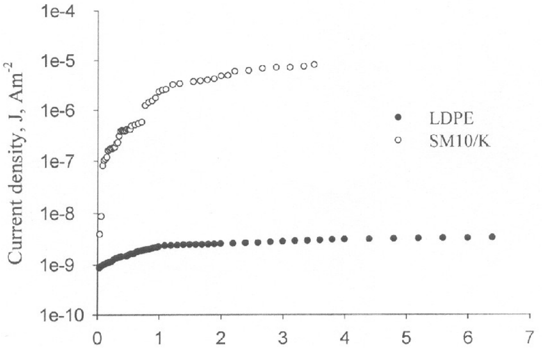
Electric field, E, MVm^{-1}

Fig. 4: Plot of log (current density) vs. electric field at room temperature for LDPE and MMA-g-LDPE



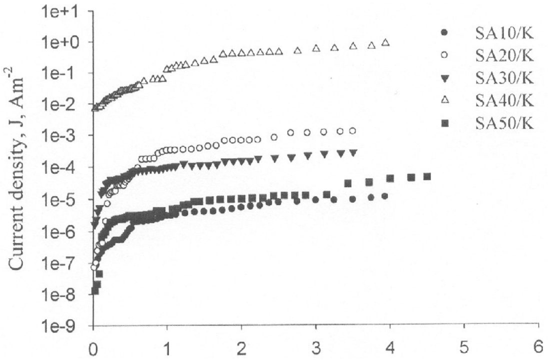
Electric field, E, MVm^{-1}

Fig. 5: Plot of log (current density) vs. electric field at room temperature for all grafted samples



Electric field, E, MVm^{-1}

Fig. 6: Plot of log (current density) vs. electric field at room temperature for LDPE and alkaline treated MMA-g-LDPE.



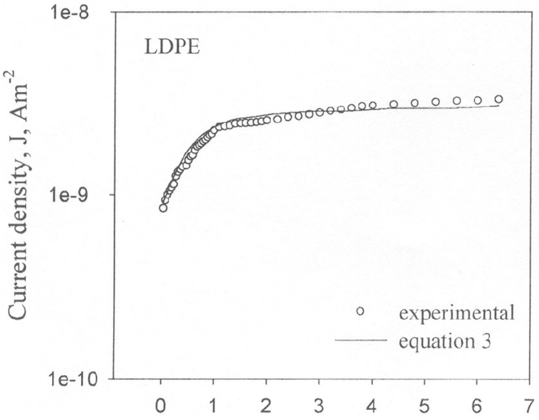
Electric field, E, MVm^{-1}

Fig. 7: Plot of log (current density) vs. electric field at room temperature for alkaline treated grafted LDPE.

Figs. 8 and 9 show how well the results, for LDPE and the sample namely SA10, respectively, as examples, fit this formula over a wide range of the field. The parameters *a* and J_o were detected for all studied compositions and presented in Table (3). The parameters *a* and J_o were found to be strongly dependent upon the changes in the chain structure of the grafted films that induced by gamma irradiation. The jumping distance in grafted polymer depends on the irradiation dose and *DG*. Higher DG showed a lower *a* value (higher conductivity).

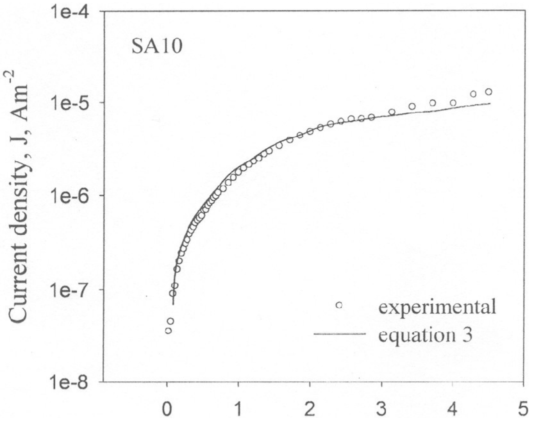
Table 3- The parameters *a* and J_o of the untreated and treated grafted films

Untreated			Treated		
Sample	*a* (µm)	J_0 ($\Omega^{-1}m^{-1}$)	Sample	*a* (µm)	J_0 ($\Omega^{-1}m^{-1}$)
LDPE	0.08	2.0e-7			
SM10	0.05	0.1e-5	SM10/K	0.05	0.1e-5
SA10	0.6	0.5e-5	SA10/K	0.006	0.2e-5
SA20	0.05	0.4e-5	SA20/K	0.005	0.3e-5
SA30	0.02	0.2e-5	SA30/K	0.004	0.5e-5
SA40	0.01	0.3e-5	SA40/K	0.0025	0.7e-5



Electric field, E, MVm^{-1}

Fig. 8: log current density for LDPE versus electric field at room temperature: experimental data and fitting using Eq. (3).



Electric field, E, MVm^{-1}

Fig. 9: log current density for sample namely SA10 versus electric field at room temperature: experimental data and fitting using Eq. (3).

CONCLUSION

The introduction of new characteristics to some synthetic polymers was achieved through the γ-radiation-induced graft copolymerization of methyl methacrylate onto low density polyethylene films (in the presence of aniline as inhibitor) for the preparation of grafted films. The lower dose rate due to the presence of inhibitor (aniline) initiates mainly graft copolymerization due to lesser termination of free radicals with the polymer growing radicals and recombination of primary radicals resulting a longer chain length of the grafted copolymer and elimination of homo-polymer**.**

From the obtained results the following conclusion can be derived:

1- Irradiation dose plays an important role in the grafting process.

2- Improvements in the electrical conductivity with grafting were observed.

3- The KOH treated samples possessed higher conductivity values than the untreated ones.

4- The alkaline treatment resulted in the hydrolysis of the grafted chains, and the carboxylic groups (COOH) of the graft chains were converted into highly solvated ionic units of the type –COOK

5- Higher degree of grafting showed a lower jumbling distance value (higher conductivity).

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