Radiation-Induced Graft Copolymerization of Acrylic Acid/Acrylonitrile onto LDPE and PET Films and Its Biodegradability

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ABSTRACT: Graft copolymerization of acrylic acid/acrylonitrile (AAc/AN) comonomer onto low-density poly(ethylene) (LDPE) and poly(ethylene terephthalate) (PET) films using direct radiation grafting technique has been investigated. The effect of different reaction conditions on the grafting yield was studied. The structure of the grafted films at different compositions was characterized by FTIR, TGA, SEM, and XRD. Biodegradation of grafted LDPE and PET was investigated by burial method in two types of Egyptian soils (agricultural and desert soils). The bacteria responsible for biodegradation were isolated and characterized, and the capacities for the growth on these polymers as substrates were compared. The isolates from agricultural soil were characterized as *Pseudomonas*, *Alcaligenes*, *Bacillus*, *Proteus*, and *Enterobacter*, whereas the isolates from desert soil were characterized as *Alcaligenes*, *Bacillus*, and *Pseudomonas*. The highest degradation rate was found to be achieved using agricultural soil. It is found that the isolated strains belonging to the genus *Pseudomonas* were mainly responsible for the degradation of both polymers. It has also been found that the increase of AAc ratio in the composition increases the hydrophilicity of the films and the degradation rate. PET polymer is generally found to be more resistant to the biodegradation than LDPE in the two types of soils tested. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 744–754, 2008

Key words: radiation; grafted films; comonomer composition; biodegradation; graft copolymers; biodegradable

INTRODUCTION

Plastics derived from petrochemical processes cause environmental problems mainly because of their accumulation in ecosystems. This accumulation is mainly due to their macromolecular structure. Hydrophobicity, in particular, makes these molecules difficult targets for naturally occurring decomposers such as soil fungi and bacteria. At present, polymers are being designed to overcome these problems.[1]

The grafted polymers prepared by radiation-induced grafting methods are applicable to any shape of the base polymer, and have sufficient mechanical and chemical stabilities because the initial strength of the base polymer hardly changes in the process of synthesis.

The evolution of the biodegradability of the novel graft copolymers is of practical and fundamental interest, since their overall biodegradability will depend on the behavior of the monomer used and, in particular, the composition and properties of the interacting surfaces of the polymer and microorganisms that characterized adhesion—the initial stage of the complex biodegradation.

The reliability and character of the adhesion bond is defined by the nature of the chemical substances, separated by microorganism cells, which finally convert biodegradation to chemical degradation.[2]

Also, the combination of different environmental factors such as oxygen, temperature, sunlight, water, stress, and living organisms that is responsible for degradation of the polymer may result in synergistic effects on the polymer degradation rate.[3–6]

Low-density poly(ethylene) (LDPE) and poly(ethylene terephthalate) (PET) are thermoplastics, with excellent general properties, and are widely used as they are or as grafted polymers in multiple applications such as food packaging, beverage containers, mineral water bottles, fiber, and films.

The presence of LDPE and PET residues in the waste stream is substantial because of their extremely high resistance to atmospheric and biological agents. Several million tonnes of LDPE and PET postconsumer plastic waste reach the environment, and this only 7% is recycled to produce low-grade plastic product.[7,8] Therefore, the search for modified LDPE and PET polymers that are most susceptible to either biological or chemical degradation is currently receiving considerable attention.[9–11]

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The present work has focused on the possibility of replacing nondegradable LDPE and PET with biodegradable ones for controlling lifetime of their plastic waste. Therefore, our approach to degradability design is to introduce functional group (AAc/AN) onto LDPE and PET by radiation grafting technique with different compositions for improving susceptibility of the grafted films to microbial attack.

EXPERIMENTAL

Materials

- Low density poly(ethylene) (LDPE) and poly (ethylene terephthalate) (PET) films of thickness 35 and 70 μm, respectively, were supplied by El-Nasr Company, Egypt, for medical supplies.
- Reagent grade acrylic acid (AAc) of purity 99.9% (Merck, Germany) and acrylonitrile (AN) of purity 98.9% were supplied from Laboratory Rasayan, SD Fine Chem, India. Other chemicals such as solvents, inhibitor (Mohr's Salt), etc, were of reagent grade.

Grafting method

The direct radiation grafting method was used as a technique in which the polymer and monomer solution mixture was subjected to radiation. The irradiation was carried out in the presence of nitrogen gas, where the glass ampoules containing the comonomer solution at concentration of 60 wt % and different compositions, cosolvent (DMF/H_2O) at 40% concentration and composition ratio (50/50 wt %), inhibitor (Mohr's salt) at 2.5 wt % concentration, and films were deaerated by bubbling nitrogen gas for 5 min, and then sealed. The glass ampoules were then subjected to ^{60}Co-γ-rays at a dose rate of 1.19 Gy/s. After irradiation, the grafted films were washed thoroughly with hot distilled water and soaked overnight in water to extract the residual monomer and the homopolymer. The films were then dried in vacuum oven at 60°C for 24 h and weighed. The degree of grafting was determined by the percentage increase in weight as follows:[12]

$$\text{Degree of grafting } (\%) = \frac{W_g - W_o}{W_o} \times 100,$$

where W_g and W_o represent the weights of grafted and original films, respectively.

Swelling measurement

The water uptake of the known weight of original and grafted films was measured by immersing the samples in distilled water for 24 h. After whipping with filter paper, the samples were weighed as quickly as possible. The water uptake percent was calculated from the following equation:[13]

$$\text{Water uptake } (\%) = \frac{W_s - W_g}{W_g} \times 100,$$

where W_g and W_s are the weights of dry and wet grafted films, respectively.

Spectrophotometric analysis

Fourier transform infrared

The functional groups of both original and grafted films were studied using Mattson 1000 Fourier Transform Infrared (FTIR) spectrophotometer product of Unicam, England.

X-ray diffraction

X-ray diffraction (XRD) measurements were conducted for blanks and grafted samples at room temperature. XRD pattern was recorded in the range of diffraction angle 2θ on Phillips PW 1730 and X-ray generator was equipped with scintillation counter .The diffraction patterns were run with nickel filter (cuka), λ = 1.45 Å. The X-ray diffractograms were obtained using the following experimental condition: filament current = 28 mA, voltage = 40 kV, and scanning speed = 20 mm/min.

Scanning electron microscopy

The surface topography of the original and grafted films was studied using JEOL SEM-25; before the examination, the films were dried and coated with gold under sputter.

Thermal analysis

Shimadzu thermogravimetric analysis (TGA) system of type TGA-50. The TGA flow rate of pure nitrogen gas is 50 mL/min and heating rate was 10°C/min, from the ambient temperature up to 600°C.

Degradation by burial test

Degradation studies of the grafted LDPE and PET films were conducted under agricultural and desert soils.[14] Samples were periodically removed, washed with distilled water, and dried to constant weight.

Screening grafted LDPE and PET-degrading microorganisms

The screening for LDPE and PET-degrading microorganisms was done by the *in vitro* rapid plate test method.[15,16] Samples were taken from agricultural

and desert soils of burial test, in addition to washing water of burial polymers. For each agricultural and desert soils sample, 1 g of agricultural and desert soils was resuspended in 25 mL of phosphate-buffered saline. It was agitated with a magnetic stirrer for 20 min and then allowed to sediment. The supernatant was used as inoculum.

The minimum mineral peptone yeast extract medium is the rich medium used for the first preculture in the enrichment procedures. It contained minimum mineral culture medium (MM) 1×; bactopeptone, 0.01%; and yeast extract, 0.01%. Trypticase soy agar was used to isolate pure strains.

The microorganisms showing degradation capabilities were isolated from suspended agar growth media with LDPE and PET. The MM used contained the following (per liter): KH_2PO_4, 0.7 g; K_2HPO_4, 0.7 g; $MgSO_4{\cdot}7\ H_2O$, 0.7 g; NH_4NO_3, 1.0 g; NaCl, 0.005 g; $FeSO_4{\cdot}7H_2O$, 0.002 g; $ZnSO_4{\cdot}7H_2O$, 0.002 g; and $MnSO_4{\cdot}1H_2O$, 0.001 g. The pH was adjusted to 7.0. Agar (1.5%, w/v) was added to the solid media.

The polymer substrates were grounded and added to suspended agar growth media and finely dispersed into the medium with maximum homogeneity and appropriate turbidity. The substrate was the only carbon source for the microorganisms. After inoculation with the strains, the plates were incubated at 30°C for up to 60 days, and formation of the clear zone was monitored. On cultivation, microorganisms showing a clear zone around their colonies were further isolated. These microorganisms were then purified and characterized microscopically and macroscopically.[17]

The decreasing percentage, the biodegradation rate/week percentage (Br/w%), the half-life in weeks, and the time for 100% degradation in weeks were calculated for each polymer and each grafting percentage as following:

$$\text{Decreasing percentage of the weight } (-\%) = Y = 100 - (\text{the weight loss of the sample after the period of burying}).$$

$$(-\%) = 100 - \frac{W_o - W_t}{W_o} \times 100 = Y,$$

where W_o is the original weight of the sample and W_t is the decrease in weight after the period of burying.

$$\text{Biodegradation rate/week percentage (Br/w\%)} = \frac{(-\%)}{\text{number of weeks } (X)}$$

Half-life in weeks $T(1/2) = \frac{50X}{Y}$, and $T \sim 100\%$: Time for 100% degradation in weeks = Half life in weeks (T(1/2) × 2).

Characterization of microorganisms with grafted LDPE and PET-degrading capacities

Identification of the isolated microorganisms was done by biochemical tests, which included a number of biochemical reactions with the various enzymes within the cells. A positive result would indicate that the strain under investigation exhibited these enzymes within their metabolic system. Otherwise, a negative reaction indicates the absence of such enzymes. In addition, the growth of the bacterium on some common carbon sources such as glucose, mannitol, and sucrose was also tested. For this purpose, the identification of the microorganisms was done at the genus level only.

RESULTS AND DISCUSSION

Preparation of grafted membranes

A set of preliminary experiments were carried out for the objective of obtaining reasonable percentage grafting by changing the solvent type, inhibitor concentration, comonomer composition, and irradiation dose. The presence of DMF/H_2O as a cosolvent with composition 50/50 wt % and concentration 40 wt %, and using ammonium ferrous sulfate (Mohr's salt) as inhibitor with concentration of 2.5 wt % resulted in obtaining graft copolymer with reasonable graft yield and retarded the homopolymerization process.

Effect of solvent

The effect of different solvents on the graft copolymerization process of AAc/AN binary monomers onto LDPE and PET was investigated and shown in Figure 1. It can be seen that for both polymers the presence of solvents such as benzene, butanone, methanol, or dioxane, and the graft copolymer yield slightly decreases. Meanwhile, the use of acetone or DMF/H_2O greatly increases the AAc/AN graft copolymer yield. This is may be because acetone or DMF/H_2O with composition 50/50 wt % influence the AAc/AN graft copolymerization process by enhancing the accessibility and diffusion of the comonomer to the active sites in polymer substrate generated by gamma radiation.

Effect of comonomer concentration and composition

Radiation grafting of binary monomer mixtures can introduce different types of functional groups with dual properties. Besides, in most cases the synergistic effects were observed upon grafting from monomer mixtures.[18,19] Figure 2 shows the effect of comonomer composition (AAc/AN) on the grafting yield onto LDPE and PET films. It was found that, the

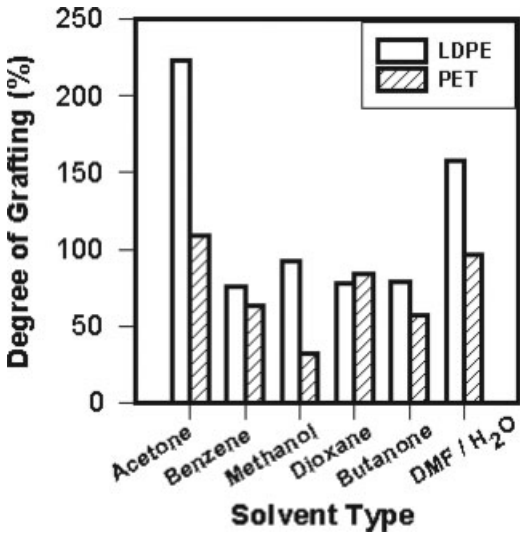


Figure 1 Effect of different solvent types on the grafting yield of (AAc/AN) grafted onto LDPE and PET at an irradiation dose of 20 kGy, comonomer concentration of 50 wt %, and monomer composition (AAc/AN) of 50/50 wt %.

comonomer composition (AAc/AN), 60/40 wt %, gives the maximum and homogenous grafting yield for both LDPE and PET films, whereas after or before this ratio, the degree of grafting for both polymers was decreased and high homopolymer obtained. This may be due to the fact that after or before these ratios the rate of diffusion of the comonomer through the polymer matrix decreased and hence homopolymer formed and the comonomer solution became viscous; thus, the degree of grafting decreased.[19–23] Also, it is observed that the degree of grafting onto LDPE films is higher than that for PET

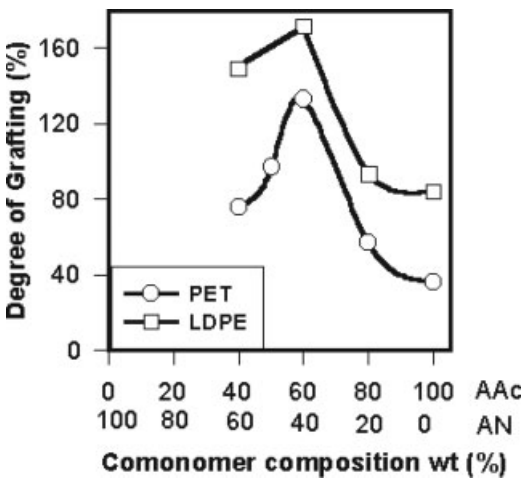


Figure 2 Effect of comonomer composition (AAc/AN) onto the grafting yield for LDPE and PET at an irradiation dose of 20 kGy, comonomer concentration of 50 wt % at various comonomer compositions, cosolvent (DMF/H_2O) (50/50 wt %), and inhibitor Mohr's salt (2.5 wt %).

TABLE I
Water Uptake Percent of Grafted LDPE and PET as a Function of AAc/AN Composition Ratio

Polymer type	AAc/AN composition ratio	Water uptake
LDPE	Blank	0.024
	20/80	63.2
	40/60	68
	50/50	77
PET	Blank	1.0
	20/80	28.9
	40/60	38.9
	50/50	45.6

films. This is due to the aromatic structure in which PET is generally found to be more resistant to radiation effect and production of free radicals that decreases the grafting percent. In addition, its bulky structure decreases the diffusion of the comonomer because of steric hindrance.

Characterization of grafted films

Swelling behavior

Table I shows the water uptake percent as a function of AAc/AN composition ratio for LDPE and PET films. It can be seen that the grafted films with higher AAc content have the better hydrophilic character than do the grafted films with higher AN content. This can be attributed to the hydrophilic character of the carboxylic acid of AAc. In addition, it is reasonable to conclude that the swelling behavior of the grafted films is dependent mainly on the amount of hydrophilic group added, i.e., on the amount of hydrophilic groups introduced in the graft copolymer. Thus, graft copolymer with higher AAc ratio has the better hydrophilic character than that having higher AN content. Therefore, the swelling percent increases as the concentration of AAc increases.

FTIR spectroscopy

Figures 3 and 4 show the infrared spectroscopic analysis of the original, grafted LDPE, and PET films respectively. In Figure 3(a), the characteristic band of LDPE appeared around 2900, 1496, and 730 cm^{-1} correspond to C—H_2 stretching and bending of normal alkane, respectively. The last strong peak at 730 cm^{-1} is assigned to CH_2 rocking. The characteristic bands of PET in Figure 4(a) are similar to those obtained in case of LDPE with addition to the absorption at the peak 1724 cm^{-1} assigned to C=O, and the two peaks at 728 and 1458 cm^{-1} corresponding to presence of phenyl group in its chemical structure. The two peaks at 1290 and 1120 cm^{-1} are caused by the CH_2—O—C=O stretching.

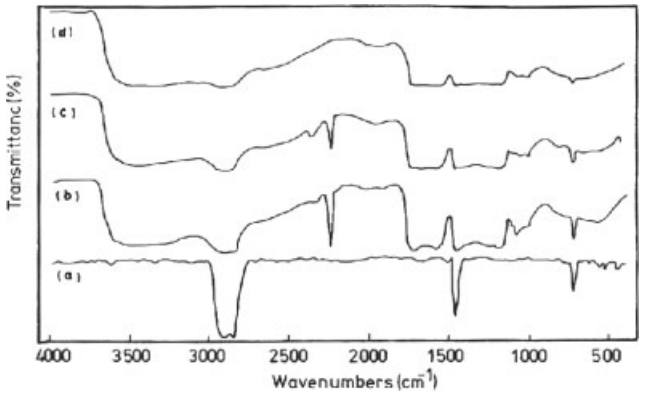


Figure 3 FTIR spectra for (a) original LDPE, (b) LDPE-*g*-AAc/AN (60/40 wt %), (c) LDPE-*g*-AAc/AN (80/20 wt %), and (d) LDPE-*g*-AAc/AN (100/0 wt %).

The comparison between the FTIR spectra of grafted LDPE and PET films with the original one shows a broad peak, as the characteristic peaks of grafted chains appear clearly between 3217 and 3447 cm^{-1}, coming from the merge of the OH of AAc. The previous peak becomes broad with increasing ratio of AAc in the comonomer composition.

Also, a sharp peak appeared at 2250 cm^{-1}, coming from the merge of the cyano group of AN, and previous data were not observed for the ungrafted LDPE and PET.

The intensity of the previous absorption bands increases with the increasing graft percentage as shown in Figures 3(b,c) and 4(b,c). The previous data indicate that AAc and AN molecules are grafted onto both LDPE and PET films.

Scanning electron microscopy

Scanning electron microscopy (SEM) analyses were performed for the original and grafted LDPE and PET films with different (AAc/AN) comonomer compositions as represented in Figures 5 and 6. It

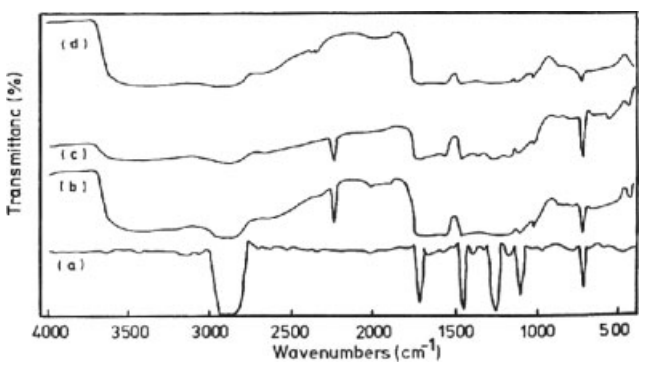


Figure 4 FTIR spectra for (a) original PET, (b) PET-*g*-AAc/AN (60/40 wt %), (c) PET-*g*-AAc/AN (80/20 wt %), and (d) PET-*g*-AAc/AN (100/0 wt %).

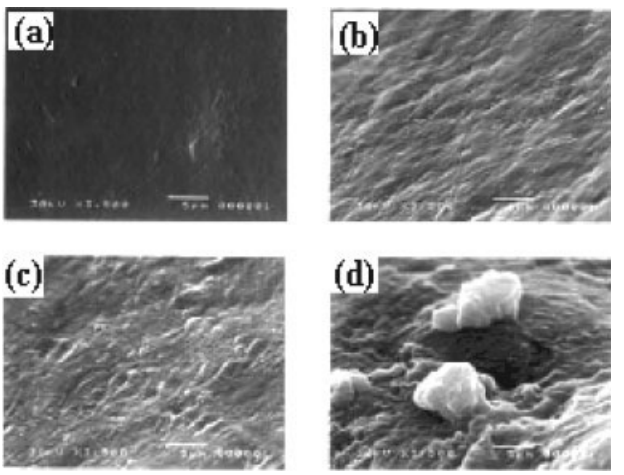


Figure 5 SEM for (a) original LDPE, (b) 171% grafted LDPE (60/40 AAc/AN wt %, (c) 93.5% grafted LDPE (80/20 AAc/AN wt %), and (d) 83.9% grafted LDPE (100/0 AAc/AN wt %).

was observed that the surface of the original (ungrafted) LDPE and PET films was smooth and there were no pores with large diameter. In case of grafted LDPE and PET, the surface is not smooth and many wrinkles are observed; the structure is totally different from the smooth surface of the original ones. The observed pores and wrinkles increased with the increasing AAc-ratio in the component, although the degree of graft decrease confirms the structure change (topography) by the grafting process.

X-ray diffraction measurement

The XRD technique was performed for the original and grafted LDPE and PET to measure the crystallinity and the changes caused by the grafting process

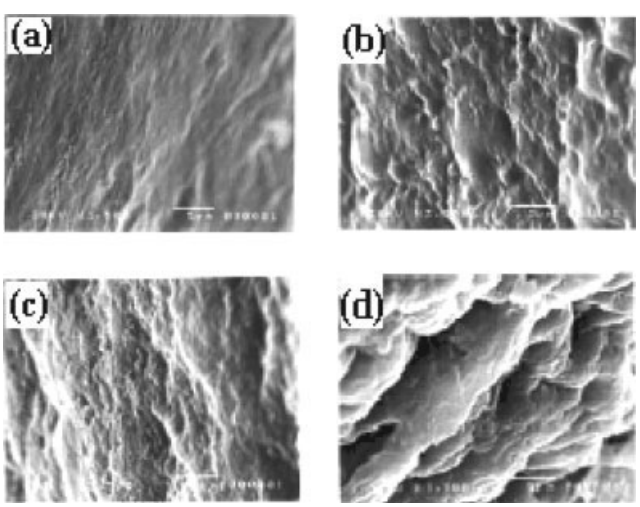


Figure 6 SEM for (a) original PET, (b) 133% grafted PET (60/40 AAc/AN wt %, (c) 56% grafted PET (80/20 AAc/AN wt %), and (d) 36% grafted PET (100/0 AAc/AN wt %).

TABLE II
Effect of Composition and Degree of Grafting on the Intensity and Particle Size of LDPE and PET Films

Polymer type	AAc/AN composition ratio	Degree of grafting (%)	2θ (°)	Particle size, *d* (Å)	Intensity
LDPE-*g*-(AAc/AN)	0	0	21.41	183.05	0.433
	50/50	76	21.24	185.53	0.108
	20/80	162	21.08	190.95	0.093
PET-*g*-(AAc/AN)	0	0	21.41	186.02	0.56
	50/50	63.2	21.07	186.0	0.125
	40/60	75	21.07	189.9	0.128

with different compositions of monomers as shown in Table II. For both polymers, a big drop in the relative intensity was found with increasing grafting percent. This clearly indicates that the grafting of AAc and AN onto LDPE and PET resulted in disordering of the graft chains, and consequently, the crystallinity content decreases in both polymers. Also, the result shows an effective increase in particle size on the polymeric grafted films and a decrease of 2θ with the increase in grafting (%) and AN ratio. These findings were evidences of the observed huge drop in the relative intensity of the main diffraction value and to its broadening.

Thermal properties

Thermogravimetric analysis

The weight loss percent of the original and grafted LDPE and PET films with various degrees of grafting is shown in Figures 7 and 8, respectively. Un-

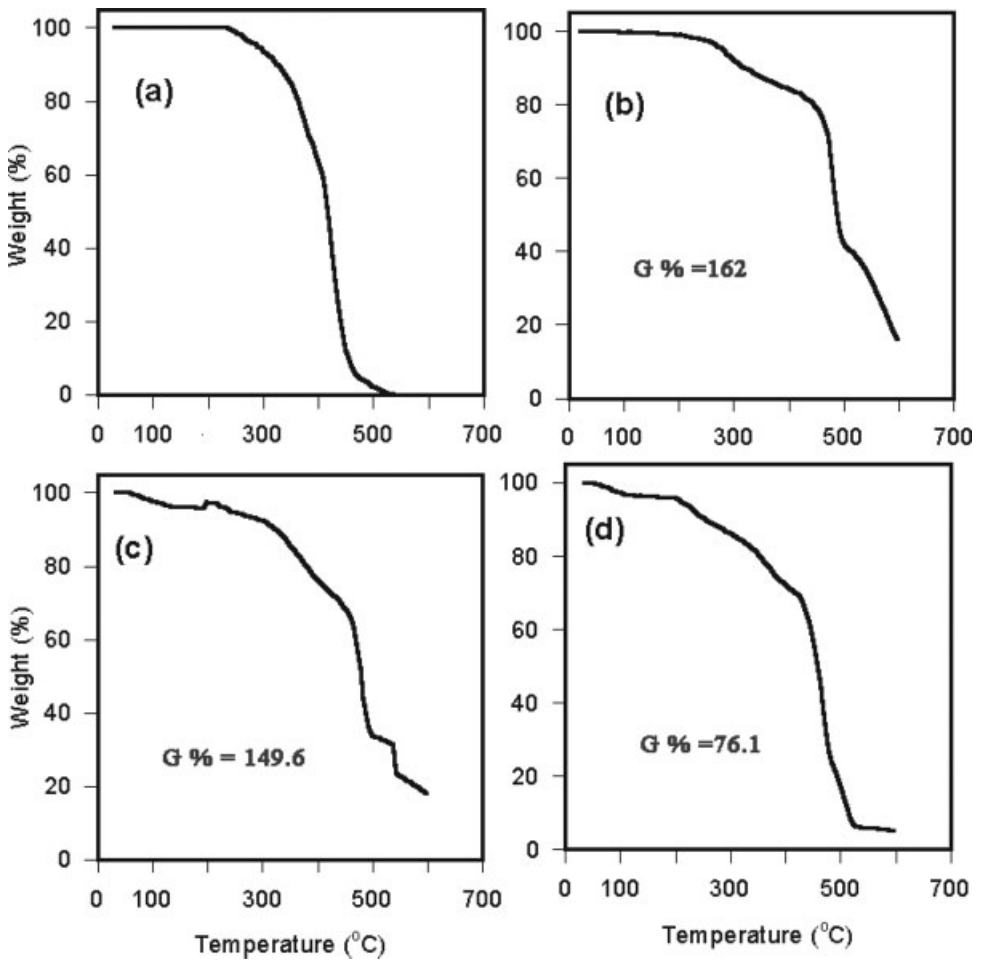


Figure 7 TGA of LDPE films, (a) blank, (b) LDPE-*g*-(AAc/AN) (20/80) wt %, (c) LDPE-*g*-(AAc/AN) (40/60) wt %, and (d) LDPE-*g*-(AAc/AN) (50/50) wt %.

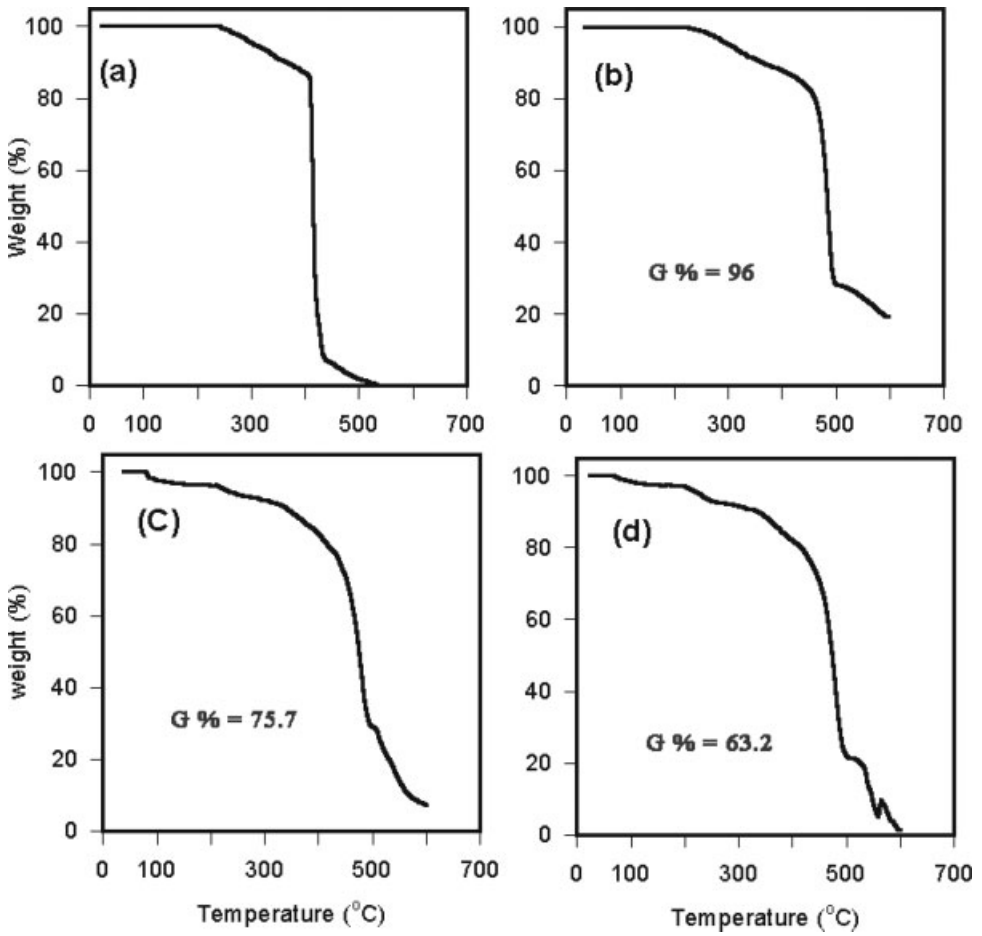


Figure 8 TGA of PET films, (a) blank, (b) PET-*g*-(AAc/AN) (20/80) wt %, (c) PET-*g*-(AAc/AN) (40/60) wt %, and (d) PET-*g*-(AAc/AN) (50/50) wt %.

grafted LDPE and PET films showed stable thermal properties and significant change up to a temperature of 230 and 250°C for LDPE and PET, respectively, beyond which a deep decrease in weight and complete depolymerization of the LDPE films at about 480°C are observed. But for PET films there are another two steps of weight loss. The first step of weight loss in the temperature range from 250 to 420°C followed by sharp decrease and complete depolymerization of the sample.

In case of grafted LDPE and PET, three distinct steps of weight loss were observed. The first step of weight loss in the range of 100–200°C may be attributed to the elimination of adsorbed moisture. There are differences in the weight loss behavior in the range of 100–200°C, which is probably due to the difference in AAc ratio where with the increase of AAc content in the composition the hydrophilicity increase and thus increase in weight loss occur because of elimination of adsorbed moisture. The second step of weight loss observed by smooth decrease in weight occurred up to 450°C, which is due to the elimination of graft side-chains.[24] The latter decomposition step (third step) observed in temperature above 500°C corresponds to the region of major weight loss occurring because of the extensive degradation of the polymer backbone chain leaving a residue. The increment in temperature weight loss may be due to the sequence distribution of the comonomer AAc/AN in the graft copolymer, which affects the thermal behavior beside the nature of the comonomer at the decomposition temperature of 450°C, at which the degradation reaction of the grafted side-chains is completed.

These are the regions of major weight loss because of the extensive degradation of the polymer backbone chain leaving a residue (char) behind the final decomposition temperature (FDT). It was found that the residue (char yield) and the FDT values for both grafted LDPE and PET increase with increasing grafting degree. This is due to the increase in the amount of grafted P(AAc/AN) chains. This refers to the increase of the thermal stability upon grafting and the thermally stabilized CN group than COOH group.

Thus, the analysis of TGA curves of the original and grafted investigated polymers showed that the

TABLE III
LDPE and PET-Degrading Microorganisms Isolated at Various Places

Type of soil	Code isolate	Species	Clear zone formation on plate containing	
			LDPE	PET
Agricultural	As1	*Pseudomonas*	++++	++
	As2	*Pseudomonas*	++++	++
	As3	*Pseudomonas*	++++	++
	As4	*Pseudomonas*	+++	++
	As5	*Alcaligenes*	++	+
	As6	*Bacillus*	+	+
	As7	*Bacillus*	++	+
	As8	*Bacillus*	++	+
	As9	*Proteus*	++	+
	As10	*Enterobacter*	+	+
Desert	S1	*Alcaligenes*	+	+
	S2	*Alcaligenes*	+	+
	S3	*Bacillus*	++	+
	S4	*Bacillus*	+	+
	S5	*Bacillus*	+	+
	S6	*Pseudomonas*	++++	++
	S7	*Pseudomonas*	+++	++
	S8	*Pseudomonas*	+++	++

As, agricultural soil; S, desert soil.

thermal stability of the grafted films increases by two ways: as the degree of grafting increases and by increasing the content of AN in the sample.

Isolation and characterization of bacteria in agricultural and desert soils

This part of the biological studies was performed to characterize the responsible bacteria in agricultural and desert soils for the biodegradation of LDPE and PET polymers and to compare their capacities for growth on these polymers as substrates.

It is shown in Table III that 10 isolates were isolated from agricultural soil. Four isolates are characterized as *Pseudomonas*, one as *Alcaligenes*, three as *Bacillus*, one as *Proteus*, and one as *Enterobacter*. Eight isolates were isolated from desert soil. Two isolates were characterized as *Alcaligenes*, three as *Bacillus*, and three as *Pseudomonas*.

The clear-zone method is a simple tool for investigating the microbial degradation of substrates. The formation of a clear zone around the colony indicates the solubilization of the substrate as a result of the degradation caused by the secreted enzyme(s). In this study, the clear-zone method was used for evaluating microbial degradation.

Using the plate-screening method described in ''Experimental'' section, it is found that isolated strains belonging to the genus *Pseudomonas* were found to have the larger clearing zones, indicating the highest capacities of degrading both LDPE and PET polymers. It was shown that genus *Pseudomonas* shows a remarkable capacity to degrade a wide range of substrates, including aromatic compounds, halogenated derivatives, and recalcitrant organic residue.[25]

Biodegradation of grafted LDPE and PET

This part is concerned with the biodegradation of the original and grafted LDPE and PET by burial method in two types of Egyptian soils (agricultural and desert soils). The bacterial population in the burial environment used was determined by using an agar-plate counter. Bacteria were found in a concen-

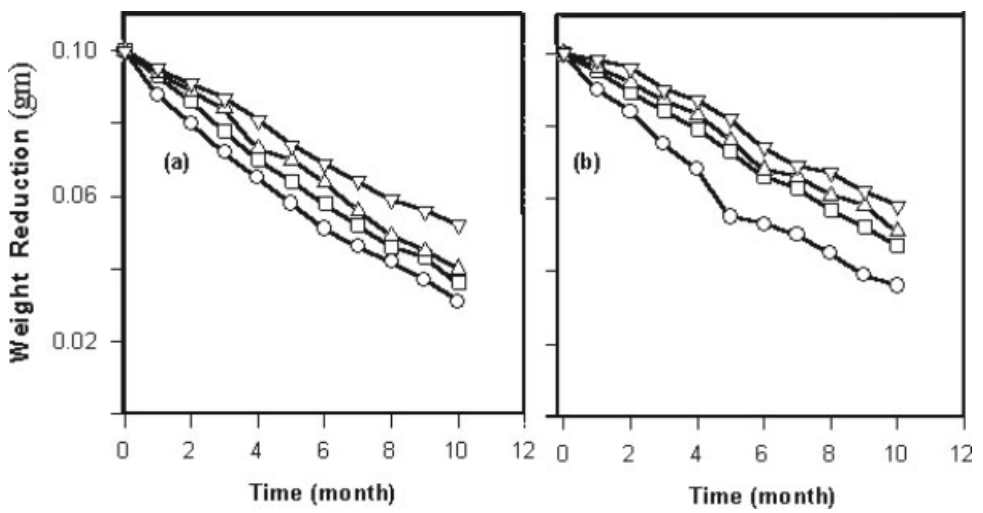


Figure 9 Weight reduction of blank and grafted LDPE (in gram) upon burying in (a) agricultural soil and (b) desert soil. ○, LDPE blank; □, G% = 83.9% (AAc/AN: 100/0 wt %); △, G% = 93.5% (AAc/AN: 80/20 wt %); and ▽, G% = 171.4% (AAc/AN: 60/40 wt %).

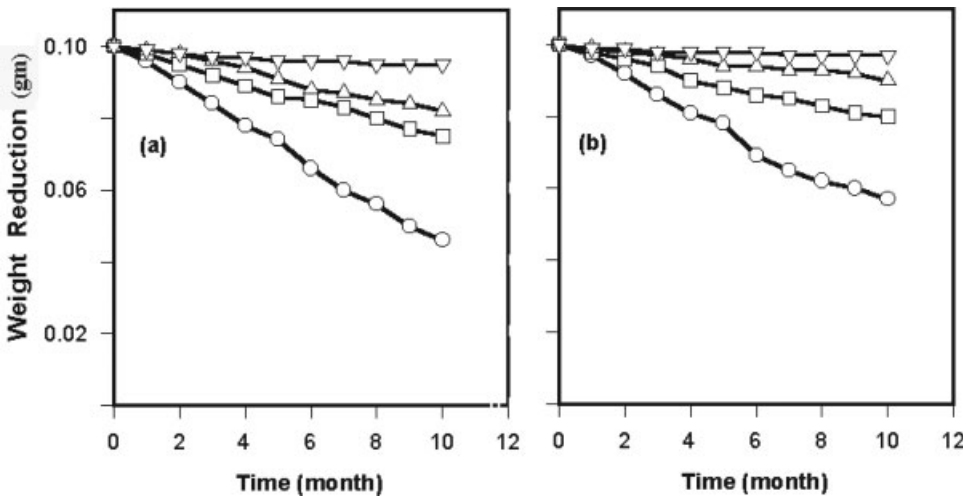


Figure 10 Weight reduction of blank and grafted PET (in gram) upon burying in (a) agricultural soil and (b) desert soil. ○, PET blank; □, G% = 36.9% (AAc/AN: 100/0 wt %); △, G% = 56% (AAc/AN: 80/20 wt %); and ▽, G% = 133% (AAc/AN: 60/40 wt %).

tration of 174×10^{-6} and 106×10^{-6} in agricultural and desert soils, respectively.

The weight reductions of the polymers buried as a function of time in the two types of soils are shown in Figures 9 and 10. The decreasing percentage, the biodegradation rate /week percentage, the half-life in weeks, and the time for 100% degradation in weeks were calculated for each grafted polymer and represented in Table IV. The highest degradation rate using agricultural soil could be explained on the basis of the bacterial population found in the agricultural soil, in addition to many factors including the humidity and the availability of more nutrients in this environment having enhancement effect on the growth and metabolism of microorganisms.

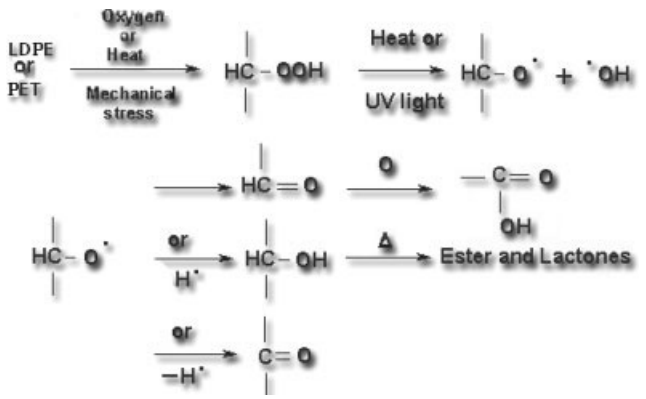
The original LDPE and the PET were found to be more susceptible to the biodegradation than the grafted ones, and it is found that increasing grafting percentage of LDPE and PET make the polymers more resistant microorganisms and hence more resistant to biodegradation. This could be explained on the basis of the effect of gamma radiation and grafting process, where as the AN content increases, the grafting percent increases, and the resulting graft copolymer possesses higher chemical and thermal stability against biodegradation. As the grafting percent decreases, the biodegradation increases because of increase in the AAc content, this increases the hydrophilicity and susceptibility to microbial attack.

The PET polymer is generally found to be more resistant to the biodegradation in the two types of soil tried (Figs. 9 and 10). This could be due to its 20% aromatic building blocks. The LDPE polymer of the aliphatic origin is found to be more susceptible to biodegradability.

TABLE IV
Decreasing Percentage of the Weight (%), Biodegradation Rate/Week (Br/w%), Half-Life in Weeks *T*(1/2), and Time for 100% Degradation in Weeks (*T* ~ 100%) upon Burying for 10 Months

	Agricultural soil				Desert soil			
Polymer	−%	Br/w (%)	*T*(1/2) week	*T* ~ 100% week	−%	Br/w (%)	*T*(1/2) week	*T* ~ 100% week
LDPE	69	1.7	28.9	57.8	64	1.6	31.2	62.5
LDPE1	64	1.6	31.2	62.5	53	1.3	37.7	75.4
LDPE2	60	1.5	33.3	66.6	49	1.2	40.8	81.6
LDPE3	48	1.2	41.6	83.3	42	1	47.6	95.2
PET	54	1.3	37	74	43	1.1	46.5	93
PET1	25	0.6	80	160	20	0.5	100	200
PET2	18	0.4	111.1	222.2	10	0.3	200	400
PET3	5	0.1	400	800	3	0.1	666.6	1333.3

LDPE, blank; LDPE1, [LDPE-*g*-(AAc/AN) (100/0 wt %), G% = 83.9]; LDPE2, [LDPE-*g*-(AAc/AN) (80/20 wt %), G%=93.5]; LDPE3, [LDPE-*g*-(AAc/AN) (60/40 wt %), G% = 171.4]; PET, blank; PET1, [PET-*g*-(AAc/AN) (100/0 wt %), G% = 36]; PET2, [PET-*g*-(AAc/AN) (80/20 wt %), G% = 56]; PET3, [PET-*g*-(AAc/AN) (60/40 wt %), G% = 133].



Scheme 1 The degradation of blank and grafted LDPE and PET by peroxidation.

Mechanism of biodegradation of blank and grafted LDPE and PET

There are common mechanisms of biodegradation that involve bioassimilation from the ''ends'' of substrate molecules. Since commercial polyolefins have relatively high molar mass values, there are very few ends of molecules accessible to oxidation. It has been observed, however, that the oxidation products of polyolefins are biodegradable.[26–31]

Research stretching back several decades[32] has established the sequence of reactions that are regarded as the essence of polyolefin peroxidation. Although the products of the oxidation initiated by heat are similar to those resulting from photooxidation, it was investigations of the latter that confirmed that it was the presence of sensitizing impurities, generated during the fabrication of polyolefin products, that caused the instability of these plastics in the environment.[33] The most significant of these impurities are carbonyl[33,34] and hydroperoxide[33,35,36] groups, with the latter of particular importance as a consequence of thermo-oxidation during processing.

The addition of functionalized group such as AAc, which contains carboxylic group, increases the hydrophilicity and therefore increases the accessibility to microbial attack.

Scheme 1 illustrates[37] one way of describing the formation of some of the products generated as a result of the peroxidation of the original and grafted LDPE and PET. The starting point is shown as hydroperoxide, the formation of which resulted from shear stresses during extrusion, for example, that caused homolytic bond cleavage.

The resultant carbon-centered radical reacted with the oxygen that is never removed completely from the system to form a peroxyl radical which, by hydrogen abstraction, is converted to a hydroperoxide group. This group is unstable to both heat and UV light, and its destruction will lead to the formation of several types of oxygen-containing products. One of the few differences between peroxidation initiated by heat and by light is that ketone products are stable to heat but not to UV light. In either case, one is dealing with a branching chain reaction sequence in which the reaction of the hydroperoxide group is the rate-determining step in peroxidation leading to molar mass reduction.

CONCLUSION

The use of DMF/H_2O as a solvent in the grafting process of AAc/AN comonomer onto LDPE and PET enhances the diffusion and accessibility of the comonomer to the active sites in polymer substrate generated by gamma radiation. The original and grafted PET was generally found to be more resistant to the biodegradation than LDPE in the two types of soil tried. It is found that as the AN content increased the grafting percent increased and the resulting graft copolymer possessed higher chemical and thermal stability against biodegradation. On the other hand, as the AAc content increased, the hydrophilicity and susceptibility to microbial attack increased. Therefore, we can impart the biodegradability property to LDPE and PET by grafting process of comonomer (AAc/AN) with higher AAc content. It is also found that isolated strains belonging to the genus *Pseudomonas* were found to have the larger clearing zones indicating the highest capacities of degrading of both LDPE and PET polymers. The highest degradation rate was found to be achieved using agricultural soil.

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