

Radiation-Initiated Graft Copolymerization of Individual Monomer and Comonomer onto Polyethylene and Polytetrafluoroethylene Films

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Synopsis

Preparation and some properties of the graft copolymers obtained by radiation-induced graft polymerization of methacrylic acid (MAA) and (acrylonitrile/MAA) comonomer onto polyethylene and polytetrafluoroethylene films, were investigated. The effect of reaction conditions, solvent, monomer, and inhibitor concentration, comonomer composition, and comonomer concentration, on the graft copolymerization process was studied. The grafting process was enhanced in the presence of comonomer (AN/MAA) as compared with individual grafting of MAA or acrylonitrile (AN). The optimum comonomer composition, at which the highest grafting yield was obtained, was found to be (80/20) wt % of (AN/MAA) comonomer. The graft copolymerization of (AN/MAA) comonomer was enhanced in presence of AN due to its higher polarity strength. The electrical and swelling properties of the graft copolymers were greatly affected by the contents of PAN and PMAA graft chains. Mechanical properties of the graft copolymers were significantly changed with the grafting yield.

INTRODUCTION

The search for new and improved membrane compositions using almost every available polymeric materials,¹⁻¹⁰ has been the subject of very considerable and extensive research because of the great practical importance of such compositions.

Graft polymerization is a well-known method for modification of the chemical and physical properties of polymeric materials, and is of particular interest for achieving specifically desired properties as well as excellent membrane quality, since various commercial polymers can be used as the grafting substrate. Graft polymerization can be achieved by ionizing radiations, UV, or chemical initiators. Of these, radiation grafting is one of the most promising methods because of its large penetration in polymer matrix and rapid and uniform formation of active sites for initiating grafting throughout the matrix.

In a previous study,¹¹ the direct radiation grafting of methacrylic acid (MAA) onto PTFE films was successfully proceeded in presence of methanol/water mixture (30/70 wt %). The complete inhibition of homopoly-

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merization of MAA solution by the addition of Mohr's salt failed. However, the addition of 0.5 wt % FeCl_3 to MAA solution effectively inhibited the homopolymer formation and higher grafting yield was obtained.

In the present study, the radiation-induced grafting of MAA onto LDPE films was studied. A study has been made also on the radiation-induced graft copolymerization of comonomer (AN/MAA) onto PTFE films. The effect of reaction conditions on the grafting yield was determined. Mechanical properties, swelling behavior, and electrical conductivity of the graft copolymers were investigated. The effect of hydrophilic and much less hydrophilic groups (carboxylic acid and nitrile groups, respectively) on the electrical and swelling properties of the graft copolymers was studied.

EXPERIMENTAL

Materials

Polytetrafluoroethylene (Teflon) (PTFE) films, specific gravity 2.2 g/cm^2 (Nitto Co., Japan) and low density polyethylene (LDPE) films of thicknesses 25, 75, and $190 \mu\text{m}$ (El-Nasr Co. for Medical Supplies, Egypt) were washed with methanol and dried in vacuum oven at 50°C .

Acrylonitrile (AN) (Prolabo) stabilized with 0.005% hydroquinone was used as received. Reagent-grade methacrylic acid (MAA) of purity 99% (Merck), stabilized with 200 ppm hydroquinone, was used after purification by distillation in the presence of N_2 gas atmosphere. The other chemicals were reagent grade and were used without further purification.

Graft Polymerization

The direct radiation grafting method was used as a technique in which the polymer and monomer solution were subjected simultaneously to ionizing radiation at different atmospheres (in air, in nitrogen, and under vacuum).

The inhibitor was added to minimize the homopolymerization of monomers during irradiation. In the case of irradiation in nitrogen gas, the glass ampule containing the monomer solution and films was deaerated by bubbling nitrogen (nitrogen gas contains oxygen impurities about 1.5% was used in this study) for 5–7 min and then sealed, while, for irradiation under vacuum, the glass ampule containing the reactants was frozen, degassed under reduced pressure less than 10^{-3} torr, and thawed. This process was repeated three times; then the glass ampule was sealed. The glass ampules were then subjected to Co-60 γ -rays at a dose rate that ranged from 0.22 to 0.31 Gy/s. The grafted films were washed thoroughly with hot distilled water or toluene in case of AN, and soaked overnight in water to extract the residual monomer and the homopolymer occluded in the films. 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:

$$\text{degree of grafting (\%)} = \frac{W_g - W_0}{W_0} \times 100$$

where W_0 and W_g represent the weights of initial and grafted films, respectively.

Swelling Measurements

The clean dried grafted films of known weight (W_g) were immersed in distilled water for 24 h at constant temperature (30°C). Then, the films were removed, blotted quickly with absorbent paper to remove the liquid attached on the surface, and weighed quickly (W_s). Water uptake percent was determined as follows:

$$\text{water uptake (\%)} = \frac{W_s - W_g}{W_g} 100$$

Electrical Conductivity Measurements

Conductivity measurements were carried out using Mega Ohm Meter-MoM II (WTW Instruments, W. Germany). The electrical resistance of the sample was measured and the electrical conductivity (σ) was calculated as follows:

$$\sigma = \frac{1}{R} \cdot \frac{L}{a} \Omega^{-1} \text{ cm}^{-1}$$

where L = thickness of the specimen (cm), a = the area of the sample surface (cm²), and R = Ohmic resistance (Ω).

Mechanical Properties Measurements

Dumbbell-shaped samples of 50 mm long, with a neck of 28 mm and 4 mm wide were used. Tensile strength and elongation percent at break were measured using an Instron (Model 1195, U.K.) at crosshead speed of 50 mm/min.

RESULTS AND DISCUSSION

Radiation Grafting of MAA onto LDPE Films

Effect of Inhibitor and Monomer Concentration

Table I shows the effect of FeCl_3 concentration on the degree of grafting of MAA solution, methanol/water mixture (30/70 wt %) was used as a diluent, onto LDPE films. The addition of 0.5 wt % FeCl_3 to the monomer solution was found to inhibit effectively the homopolymer formation and reasonable grafting yield was obtained. Under such reaction conditions, the grafting proceeds homogeneously and the grafted films were smooth and flat.

The grafting of MAA solution onto LDPE films proceeds more easily and much higher degrees of grafting were obtained as compared with its grafting onto PTFE films.¹¹ Figure 1 shows the degree of grafting-irradiation time curves for the grafting of various MAA concentrations onto LDPE films under

TABLE I
Effect of FeCl_3 Concentration on the Grafting of MAA Solution in the Presence of $\text{MeOH}/\text{H}_2\text{O}$ mixture (30/70 wt %) onto 75 μm Thick LDPE film^a

FeCl_3 concentration (wt %)	Degree of grafting (%)	Remarks
0.1	60	Homopolymer formation
0.2	65.4	Little homopolymer
0.3	73.9	Little homopolymer
0.4	87.5	No homopolymer
0.5	95.0	No homopolymer
0.6	98.3	No homopolymer
0.7	100.0	No homopolymer

^a Irradiation dose, 20 kGy in nitrogen gas.

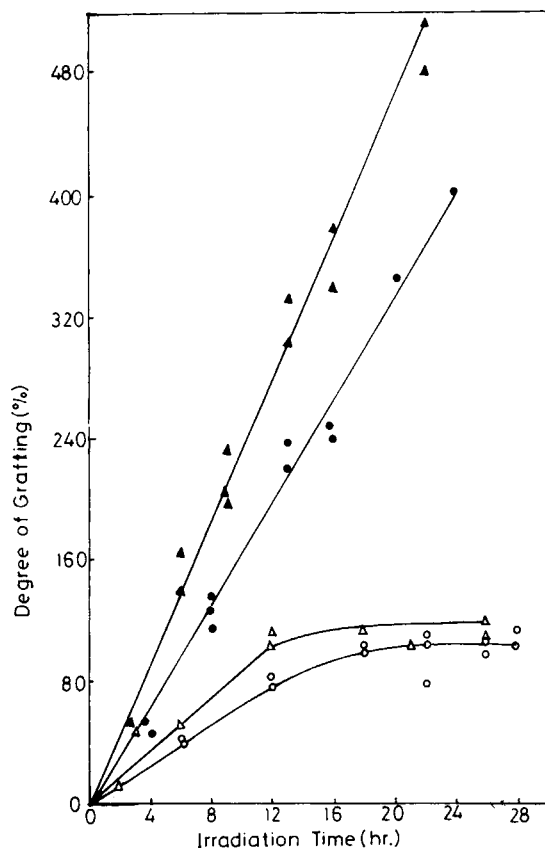


Fig. 1. Degree of grafting vs. irradiation time under vacuum for various MAA concentrations (wt %) [(○) 15; (△) 30; (●) 50; (▲) 70] onto 75 μm thick LDPE films. Diluent, ($\text{MeOH}/\text{H}_2\text{O}$) (30/70 wt %). FeCl_3 concn, 0.5 wt %.

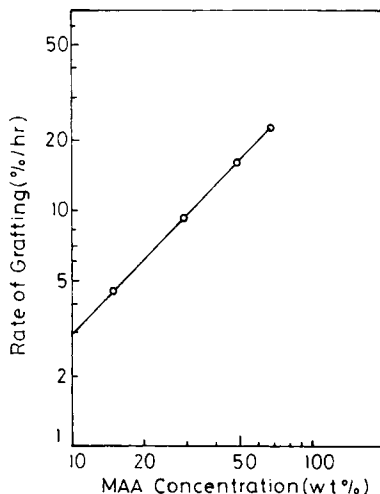


Fig. 2. Logarithmic plots of grafting rate of MAA onto LDPE films vs. MAA concentration.

vacuum irradiation. FeCl_3 (0.5 wt %) was added to all monomer concentrations. It can be seen that the degree of grafting increases linearly with irradiation time for higher MAA concentrations (50–70 wt %). However, at lower concentrations, below 50 wt %, the degree of grafting increases with irradiation time and it tends to level off above 12 h irradiation.

Figure 2 shows the logarithmic relationship between the initial rate of grafting and MAA concentration. The dependence of the grafting rate on monomer concentration was calculated to be 1.05 order. This first-order dependence indicated that this grafting system proceeds with bimolecular termination reaction.

Polymer morphology plays a great role in the diffusibility of monomer solution into the polymer matrix. The diffusion of MAA solution into the already grafted structure of LDPE is enhanced and pronounced high degrees of grafting were achieved. However, in the case of highly crystalline polymers such as PTFE, much lower degrees of grafting were obtained under the same experimental conditions.¹¹

Effect of Film Thickness

Figure 3 shows the effect of LDPE film thickness on the grafting of MAA solution under vacuum irradiation. It is obvious that the thinner the film, the higher the grafting yield and the higher the initial rate of grafting. Meanwhile, the degree of grafting on thin films tends to be S-shaped relationship at higher irradiation time. However, the degree of grafting on thick films apparently increases linearly with irradiation time (in this range of dose).

Figure 4 shows the logarithmic plots of the initial rate of grafting and film thickness to give a linear relationship with a slope of -0.95 . This negative first-order dependence on the film thickness is a good evidence that this grafting system is a diffusion controlled process.

Hoffman et al.¹² carried out the radiolytic grafting of styrene on PE film and postulated that monomer concentration within the film may decrease

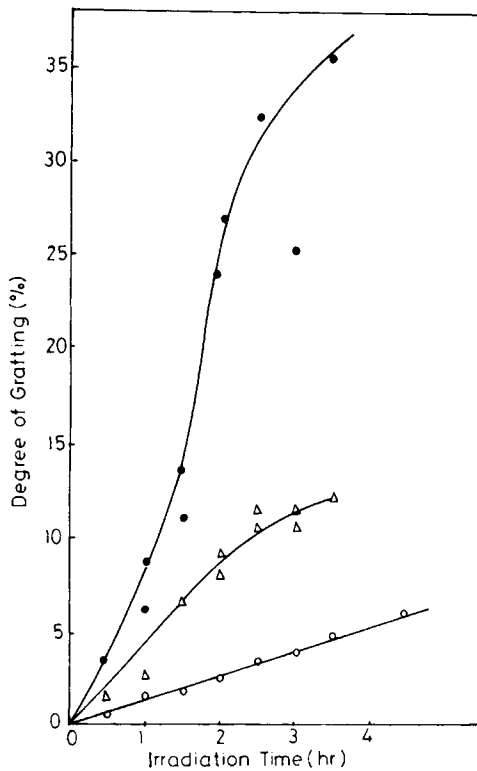


Fig. 3. Degree of grafting vs. irradiation time under vacuum for different LDPE film thicknesses (μm); (●) 25; (Δ) 75; (○) 190 (the observed value $\times 10$). MAA concn, 10 wt %; diluent, MeOH/H₂O (30/70 wt %); FeCl₃ concn, 0.5 wt %.

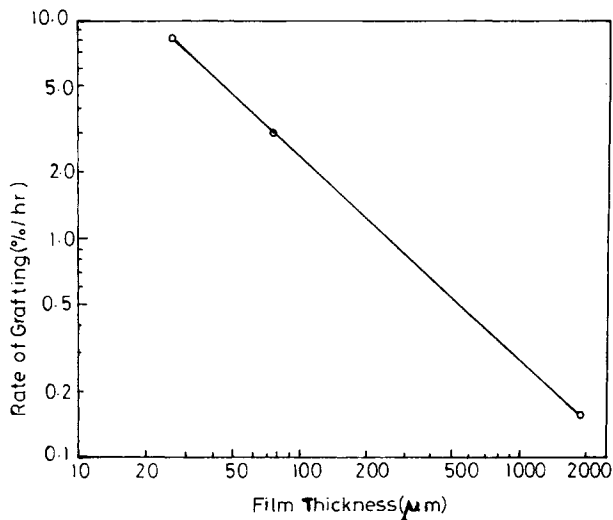


Fig. 4. Logarithmic plots of grafting rate of MAA onto LDPE films vs. film thickness.

during grafting owing to the inability of the diffusion of monomer into the film to keep pace with its rate of reaction in the film. In line with this postulate, he observed that grafting was faster for thin films than for thick films on the basis of percentage of total film weight. He introduces the idea of a critical film thickness, above which the rate of grafting on a weight percentage basis should fall off rapidly.

Radiation-Induced Graft Copolymerization of Comonomer (AN / MAA) onto PTFE Films

Direct radiation grafting of comonomer (AN/MAA) onto PTFE films was carried out. The grafted films, thus obtained, contain both nitrile and carboxylic acid groups. The nitrile groups have a good affinity toward the separation process of heavy elements and salts from industrial wastes and sea water, and it is well known that the acrylic residues possess hydrophilic properties and swell in aqueous medium. Such grafted films may be of interest in some practical uses, e.g., in the field of separation processes and in the treatment of low level nuclear waste.

Effect of Solvent and Irradiation Atmosphere on the Graft Copolymerization of (AN / MAA) Comonomer

Table II shows the effect of solvent and irradiation atmosphere on the individual grafting of AN and MAA, and also on the grafting of comonomer (AN/MAA) onto PTFE films. It can be seen that, in all solvents used, the degrees of grafting onto PTFE films are much higher for AN than those of MAA in air or nitrogen gas irradiation. It was found that the suitable solvent for the grafting process of AN and (AN/MAA) comonomer is the mixture of water and DMF (50/50 wt %), at which a reasonable yield of grafting was obtained. The addition of 0.25 wt % Mohr's salt to the reaction medium results in reducing the homopolymerization process and the grafting yield was increased.

It is interesting that the degrees of grafting of the comonomer, at a given reaction condition, are much higher than those of AN or MAA grafted individually. It can be assumed that one of the two monomers promotes the

TABLE II
Effect of Solvent on the Graft Polymerization of AN, MAA,
and (AN/MAA) Comonomer at Different Irradiation Atmospheres^a

Solvent	Solvent concn (wt %)	Mohr's salt concn (wt %)	Degree of grafting (%)					
			AN		MAA		AN/MAA (50/50 wt %)	
			Air	N ₂ gas	Air	N ₂ gas	Air	N ₂ gas
Methanol	50	—	9.3	10.0	8.1	7.9	31.6	19.3
DMF	50	—	16.2	14.1	0.6	0.5	—	—
H ₂ O/DMF (50/50)	50	—	—	—	1.2	0.9	14.9	12.8
H ₂ O/DMF (50/50)	50	0.25	14.2	11.7	7.5	6.1	43.1	26.5

^a Irradiation dose, 20 kGy; PTFE film thickness, 80 μm.

grafting process of the comonomer. Therefore, it is a matter of increasing the diffusion coefficient of one of them or maybe both through the already grafted layer initially formed.

Effect of Comonomer Composition and Concentration

Figure 5 shows the effect of comonomer composition on the grafting process onto PTFE films in the presence of water/DMF mixture (50/50 wt %). It is obvious that the degree of grafting increases as the content of AN in the comonomer increases to reach the maximum at composition of (80/20) wt % of (AN/MAA) comonomer. Thereafter, at higher contents of AN, the degree of grafting falls down to reach a lower value at 100% AN. Meanwhile, little higher degree of grafting were obtained in air irradiation than those in nitrogen gas one.

Results suggest that the presence of AN enhances the graft copolymerization of (AN/MAA) comonomer. Increasing the content of MAA may result in more steric hindrance of the grafting process due to the increase in methyl side groups. On the other hand, the grafting process of (AN/MAA) comonomer may be enhanced in the presence of AN due to its higher polarity strength.

Odian et al.¹³ found that, in the copolymerization of styrene-acrylonitrile and styrene-methyl acrylate onto Teflon, the composition of the various grafted copolymers are richer in the more polar monomer. This is attributed to the preferential solvation of the relatively immobile growing graft polymer free radicals by the polar monomers.

The effect of comonomer (80/20 wt % AN/MAA) concentration in the water/DMF mixture on the graft copolymerization onto PTFE films was

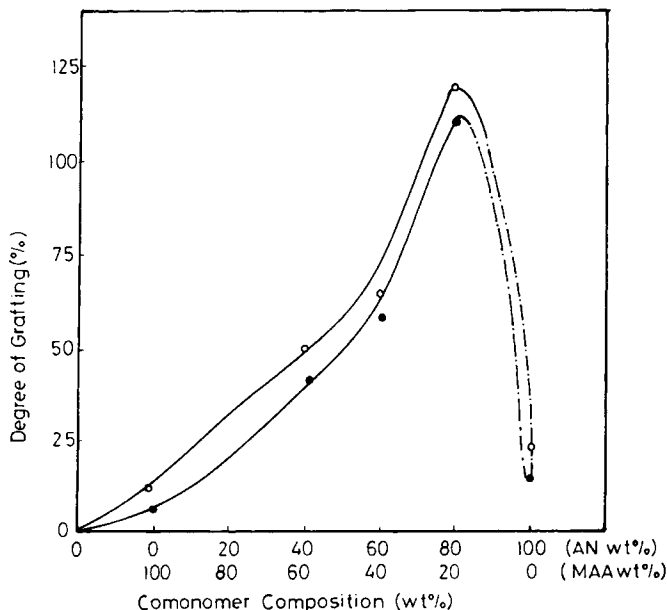


Fig. 5. Degree of grafting of comonomer (AN/MAA) onto 50 μ m thick PTFE films vs. comonomer composition: (O) irradiation in air; (●) irradiation in N₂ gas. Diluent, H₂O/DMF (50/50 wt %); irradiation dose, 20 kGy; Mohr's salt concn, 0.25 wt %.

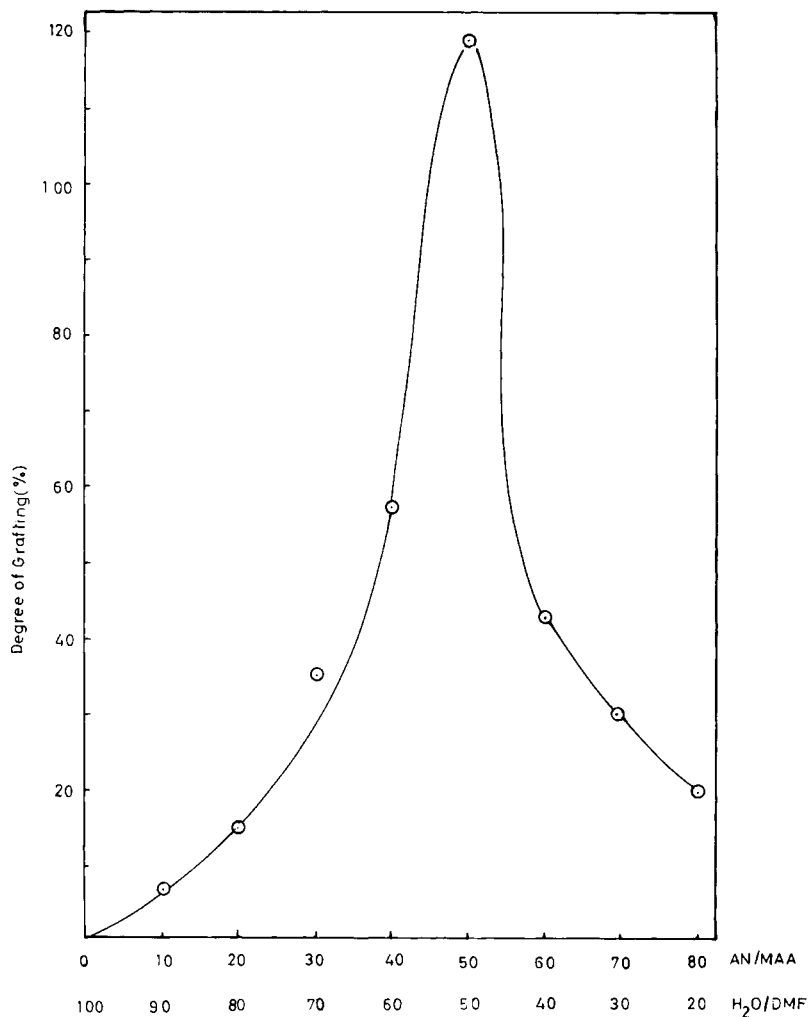


Fig. 6. Degree of grafting of comonomer (AN/MAA) (80/20 wt %) onto PTFE films vs. comonomer concentration. Grafting conditions are the same as in Figure 5.

investigated and shown in Figure 6. It can be seen that the degree of grafting increases with comonomer concentration to reach the optimum at 50 wt % in the solvent mixture. Thereafter, it decreases as the comonomer concentration increases.

Results suggest that the diluent (water/DMF) has a great effect on the graft copolymerization of the comonomer. The grafting yield reached its maximum at 50 wt % comonomer concentration presumably due to the fact that the gel effect and diffusion of the comonomer in the already grafted structure may be enhanced at such concentration. The gel effect enhances the propagation process and retards the termination reactions because of the low mobility of the growing chain radicals.

It must be recalled that the graft polymerization of 4-vinylpyridine onto polyethylene films was studied,¹⁴ and it was found that the dilution of the

monomer with methyl ethyl ketone or cyclohexanone causes a decrease in the grafting yield. It was assumed that the gel effect may be reached if the graft polymerization was carried out in a highly viscous medium at a relatively high monomer concentration.

Some Properties of the LDPE-*g*-PMAA Graft Copolymers

Mechanical properties, electrical conductivity, and swelling behavior of the graft copolymers obtained by radiation grafting of MAA were investigated.

Mechanical Properties

Figure 7 shows the change in tensile strength (T_b) and elongation percent (E_b) at break with the degree of grafting for the LDPE-*g*-PMAA films. E_b gradually decreases with increasing the degree of grafting. However, T_b tends to increase with degree of grafting to reach its maximum value at 50% grafting. Thereafter, it decreases as the degree of grafting increases because of the brittleness of the film.

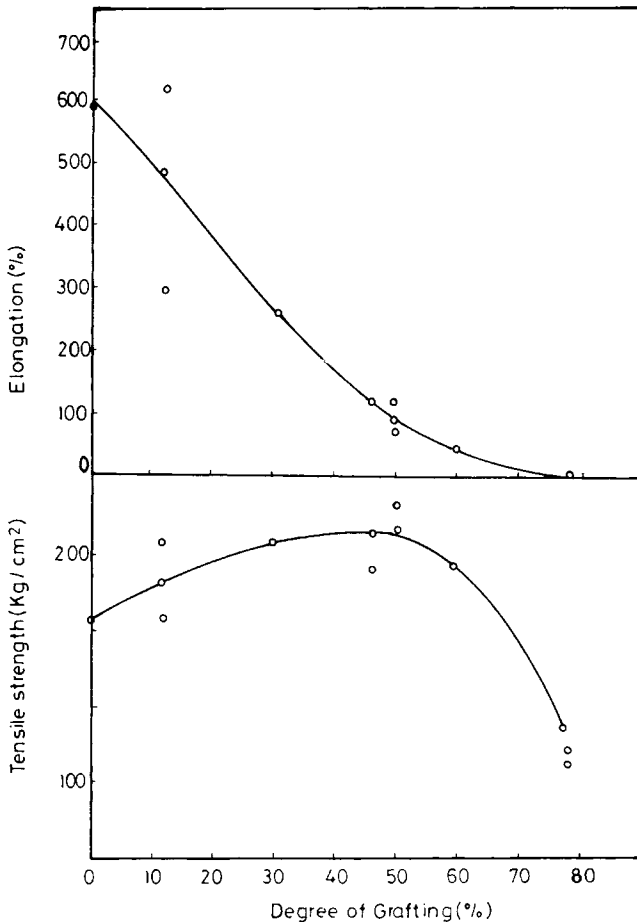


Fig. 7. Change in tensile strength and elongation percent with degree of grafting for LDPE-*g*-PMAA films.

Generally, at high degrees of grafting, the rigidity of some graft copolymers increases, especially if the grafted chains possess higher T_g . Consequently, a decrease in E_b and an increase in T_b is expected for such graft copolymers.

Electrical Conductivity

Figure 8 and Table III show the electrical conductivity of the alkali-untreated and alkali-treated LDPE-*g*-PMAA films. The electrical conductivity of the alkali-untreated grafted LDPE films increases linearly with degree of grafting (Fig. 8). The KOH-treated LDPE-*g*-PMAA films possess much higher electrical conductivity than those of the KOH-untreated ones, at a given degree of grafting (Table III).

Results indicate that the electrical properties of the LDPE-*g*-PMAA copolymer mainly depend on the amount and form of the grafted side chains. Converting the carboxylic acid groups into easily ionizable groups by the KOH treatment results in increasing the electrical conductivity of the graft copolymer.

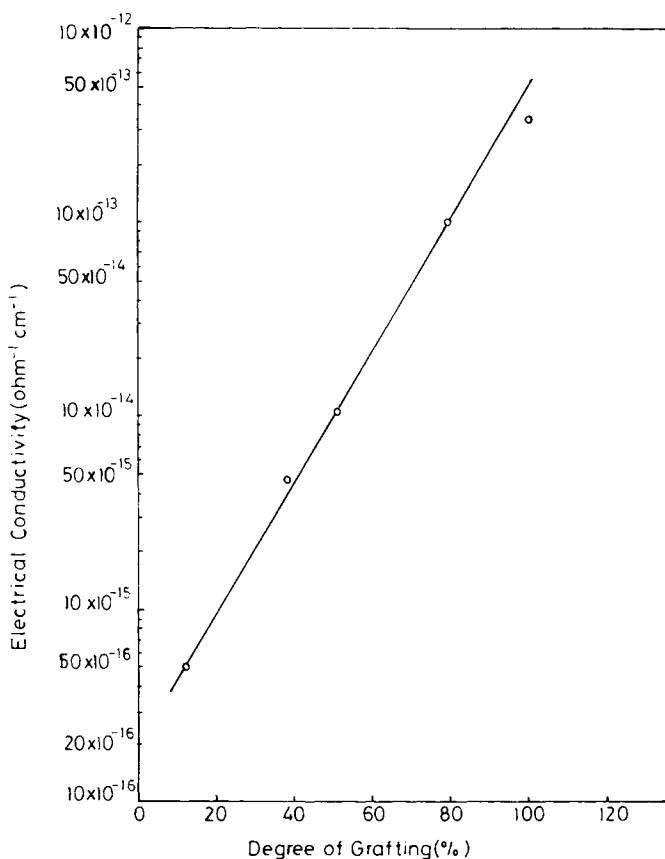


Fig. 8. Electrical conductivity for alkali-untreated LDPE-*g*-PMAA films as a function of degree of grafting.

TABLE III
Electrical Conductivity of KOH-Treated LDPE-*g*-PMAA films

Degree of grafting (%)	Electrical conductivity ($\Omega^{-1} \text{ cm}^{-1}$)
0	0.26×10^{-15}
38.8	2.0×10^{-9}
50.8	3.5×10^{-9}
79.7	12.0×10^{-9}
101.4	18.0×10^{-9}
114.0	32.0×10^{-9}

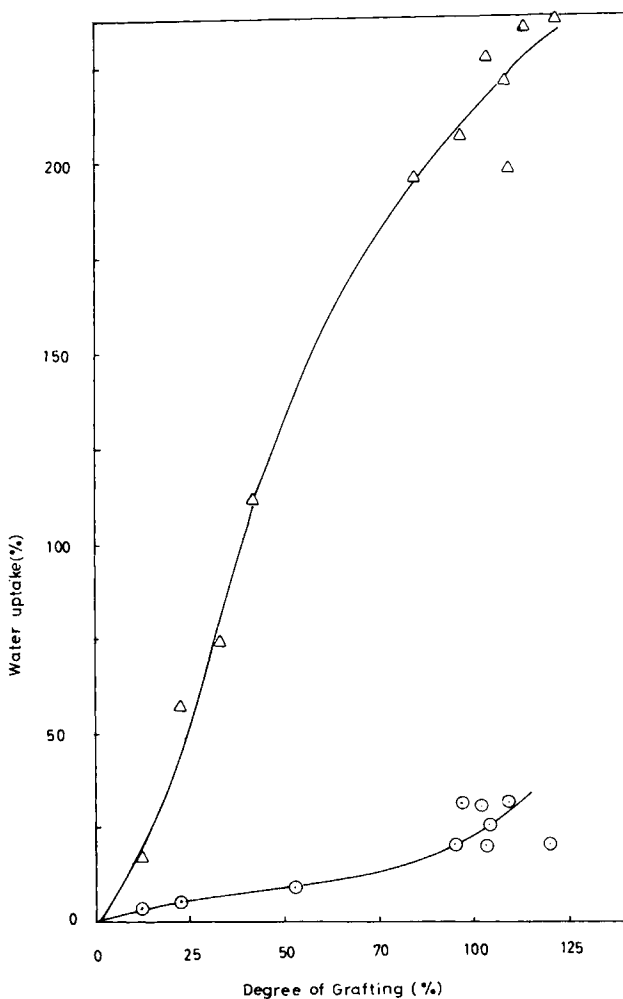


Fig. 9. Water uptake percent vs. degree of grafting for the KOH-untreated (O) and -treated (Δ) LDPE-*g*-PMAA films.

Swelling Properties

Figure 9 shows the water uptake percent as a function of degree of grafting for the KOH-treated and -untreated LDPE-*g*-PMAA films. It is obvious that the alkaline treatment of graft copolymer results in improving its hydrophilic properties and much higher water uptake was obtained as compared with that of KOH-untreated grafted films.

Some Properties of the PTFE-*g*-P(AN / MAA) Copolymer

PTFE-*g*-P(AN/MAA) copolymer contains both cation exchanging (carboxylic acid groups) and nonionic (nitrile groups) graft chains may be of interest in some practical use. The contents of PAN and PMAA side chains will greatly affect the properties of the graft copolymer.

Electrical Conductivity

Table IV shows the electrical conductivity of the KOH-treated and -untreated PTFE-*g*-P(AN/MAA) copolymer. As mentioned before, the increase in AN content in the comonomer mixture, during the radiation grafting process, enhanced the grafting yield. Therefore, it can be assumed that, at high contents of AN in the reaction medium, the graft copolymer may contain higher contents of PAN side chains. From Table IV it can be seen that as the AN content in the reaction medium increases, the electrical conductivity of the graft copolymer decreases. On the other hand, the electrical conductivity of the grafted films increases as the content of MAA increases. Table IV shows also that the alkaline treatment improves the electrical conductivity of the grafted films due to the introduction of easily ionizable groups.

Swelling Behavior

The swelling behavior of the graft copolymers that contain both PAN and PMAA side chains is shown in Figure 10. It can be seen that the water uptake

TABLE IV
Electrical Conductivity for KOH-Treated and untreated PTFE-*g*-P(AN/MAA)
Copolymer

Comonomer composition (wt %)		Degree of grafting (%)	Electrical conductivity ($\Omega^{-1} \text{ cm}^{-1}$)	
AN	MAA		KOH-untreated films	KOH-treated films
0	100	4.8	9.0×10^{-13}	6.0×10^{-12}
0	100	10.8	2.5×10^{-12}	9.0×10^{-10}
20	80	50.1	7.3×10^{-12}	2.5×10^{-8}
40	60	42.9	11.4×10^{-12}	9.2×10^{-9}
40	60	50.9	3.6×10^{-14}	1.3×10^{-9}
60	40	58.0	1.1×10^{-13}	4.5×10^{-9}
60	40	64.4	1.4×10^{-13}	7.2×10^{-9}
80	20	109.2	1.3×10^{-13}	2.3×10^{-10}
100	0	14.9	6.0×10^{-15}	
100	0	22.6	8.0×10^{-14}	

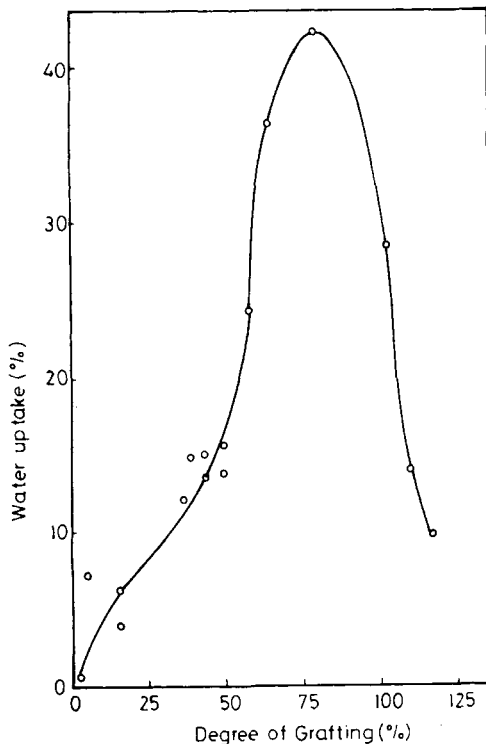


Fig. 10. Water uptake percent vs. degree of grafting for LDPE-*g*-P(AN/MAA) graft copolymer films at room temperature (30°C).

percent increases with degree of grafting to reach its maximum value at about 80%. Thereafter, it decreases as the degree of grafting increases.

These results may be presumably understood by assuming that at degrees of grafting higher than 80%, the graft copolymer contains much fewer hydrophilic groups of PAN than those of PMAA side chains. Such graft copolymers may be of great interest in some practical uses such as in separation processes and reverse osmosis desalination of sea water.

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