Modification of Adhesive Properties of a Polyethylene Film by Photografting

O. El Kholdi,[1] L. Lecamp,[1] P. Lebaudy,[1] C. Bunel,[1] S. Alexandre[2]

[1]*Laboratoire de Matériaux Macromoléculaires, Institut National des Sciences Appliquées de Rouen, Place E. Blondel, BP 08, 76131 Mont Saint Aignan Cédex, France*
[2]*Equipe des Systèmes Biomoléculaires Organisés, UFR des Sciences, Université de Rouen, 76821 Mont Saint Aignan Cédex, France*

ABSTRACT: Graft polymerization of acrylic acid from monomer solutions in water or in bulk onto low-density polyethylene film substrate was carried out by the method of continuous process under UV radiation. Effects of the nature of photoinitiator on acrylic acid grafting was first studied. One PI_2 and two PI_1 photoinitiators were used. Benzophenone was then retained for the following study. The influence of photoinitiator and monomer concentration was investigated by determining polymerization kinetics and grafted polymer amount. A study of surface wetting and morphological structure was then carried out on a bulk system and as a function of the photoinitiator concentration. Finally, such surface modification was studied with respect to its effect on the adhesion of an acrylic stick on its surface. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2803–2811, 2004

Key words: photografting; acrylic acid; polyethylene (PE); adhesion; kinetics (polym.)

INTRODUCTION

Modification of polymer surface is nowadays a quite common process to enhance polymer properties. Indeed, according to the nature of the grafted functional groups, properties such as biocompatibility, wetting with water, printability, and adhesion, for example, can be changed in a revolutionary way. Several methods of chemical modification already exist and are largely developed in the literature.[1] The polymer surface can be oxidized by acid or base such as chromic acid, nitric acid, and so forth.[2] The oxidation surface can also be achieved by flame treatment, corona discharge, plasma treatment, gamma rays,[3] accelerated electron beam radiation, and finally ultraviolet radiation.[4] This latter method remains one of the fastest and most efficient methods for permanently modifying the surface properties of organic substrates and has been successfully applied to various polymers, particularly to polyolefins.

In the case of photoinitiated graft polymerization, two operating processes are essentially used: (1) the vapor phase or batch process and consists in irradiating the substrate with UV light in an atmosphere of initiator and monomer vapor[5]; and (2) the liquid phase or continuous process, in which polymer films are covered by a solution of initiator and monomer,

which gives a thin liquid layer on the surface of the substrate.[6–8] A variant to this latter method consists in laminating the solution of initiator and monomer between two polymer films.[9–11] Moreover, the continuous process can be carried out in one or two steps. When a solution of initiator and monomer is irradiated on the substrate that must be modified, only one step is necessary. In a two-step setup, a solution of photoinitiator is first irradiated on the film surface to create initiating sites on this film. Then, a solution of monomer is added to this pretreated film and also irradiated. The monomer is thus grafted onto the film.

Many experiments using different monomers (acrylamide,[12] maleic anhydride,[4,13] vinyl acetate,[14–16] acrylic acid,[7,17,18] etc.) and different substrates (polypropylene,[7] polycarbonate,[19] polyethylene,[17,18] etc.) were previously reported in the literature. In this work, we were interested in the photoinduced graft polymerization of acrylic acid on polyethylene film by a one-step continuous process. Many works treated this subject by studying the consequences of photografting on the ultimate properties of the film.[5–7] The originality of this work was to use several analysis techniques to investigate the consequences of the treatment during and after the UV curing. Thus, realtime infrared (RTIR) spectroscopy, contact angle, and atomic force microscopy (AFM) were used to carry out this study. The effect of both the nature and the concentration of photoinitiator and the influence of monomer concentration on the photografting were characterized. Finally, the adhesive properties of the modi-

Correspondence to: L. Lecamp (Laurence.Lecamp@ insa-rouen.fr).
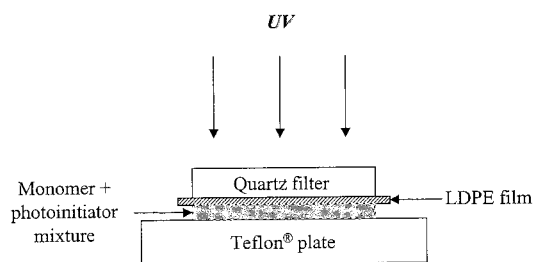
Scheme 1 Setup for the film interlayer photopolymerization technique.

fied film toward a photopolymerizable reference acrylic stick were tested.

EXPERIMENTAL

Materials

The polymer substrate is a low-density polyethylene (LDPE) film of 45 μm thickness (DSM, France), without additive, and whose transmittance for 200- to 400-nm UV radiation is nearly 100%. This film was used either in pristine form or after a corona treatment (γ_t = 42 mJ m^{-2}).

Acrylic acid (AA) was purchased from Aldrich (Milwaukee, WI). Three radical photoinitiators were used. 2,2-Dimethyl-2-hydroxyacetophenone (Darocur 1173) and benzophenone (BP) were purchased from Ciba Geigy (Summit, NJ). 2,4,6-Trimethylbenzoyldiphenylphosphine oxide (Lucirin TPO) was purchased from BASF (Ludwigshafen, Germany). All chemical products were used without further purification.

A commercial photocrosslinking acrylic stick was purchased from BASF.
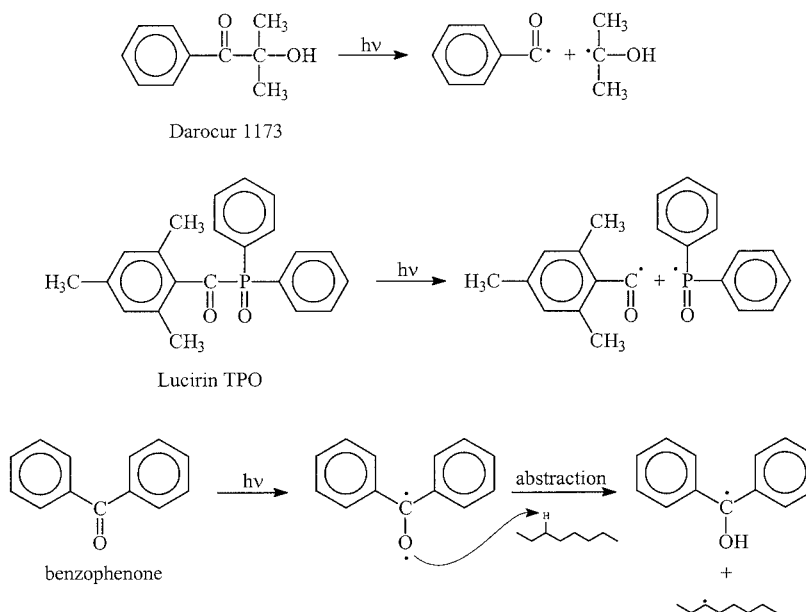
Setup of photografting

The setup for the photopolymerization experiments is schematically shown in Scheme 1. A mixture of monomer and photoinitiator, with or without solvent, was laminated between the LDPE film and a Teflon plate. A quartz plate was applied to the LDPE top film to spread the solution into an even and very thin liquid layer. The assembled unit was irradiated at room temperature by monochromatic UV radiation from the top side, which was constituted by the LDPE film. UV radiation was generated from a 30-W mercury vapor lamp whose intensity was 6 mW/cm^2 at the sample level at 254 nm.

After irradiation, the film was separated from the Teflon plate, thoroughly washed with acetone for 24 h at room temperature, rubbed with Joseph paper, and again washed with water to remove unreacted monomer, residual photoinitiator, and homopolymer. Before analysis, the film was finally dried at 80°C for 15 min.

Analysis and evaluation techniques

Real-time infrared spectroscopy

Photocrosslinking reactions were followed by real-time infrared (RTIR) spectroscopy (PE FTIR 2000 spectrometer; Perkin Elmer Cetus Instruments, Norwalk, CT) in attenuated total reflection (ATR) mode. A sample drop was deposited and spread out over the ATR diamond crystal by means of a quartz plate. A polyethylene film was introduced between this filter and the solution drop. UV radiation, from a 350-W Oriel mercury vapor lamp, was introduced into the FTIR spectrometer sample

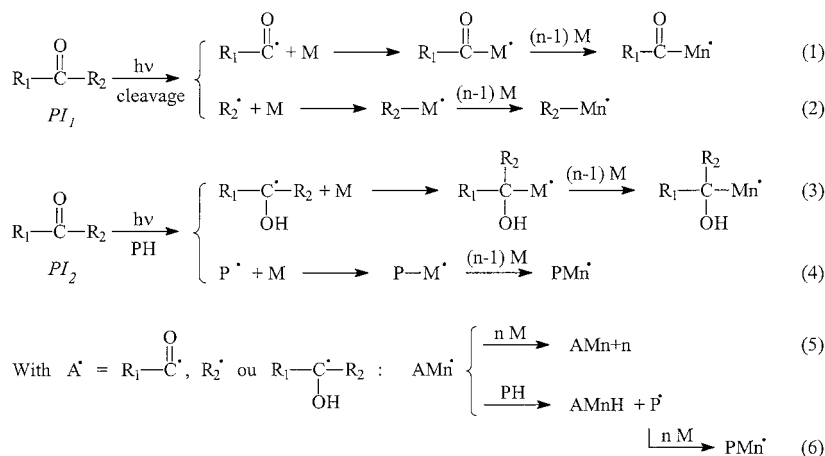**Figure 1** Mechanism of photochemical decomposition of the used photoinitiators.

Figure 2 Mechanism of photografting as a function of the photoinitiator nature.

chamber by a flexible light guide so that it did not interfere with the IR beam. The polychromatic UV radiation was filtered by means of an interferential filter, centered on 254 nm, and its intensity was then 3 mW/cm^2 at the sample level at 254 nm.

The C=C stretching vibrations of the acrylic functional groups at 980 cm^{-1} were used to calculate the conversions. After correction of the baseline, conversion of acrylic functional groups can be calculated by measuring the absorbance at each time of the reaction and determined according to the following expression:

$$\chi_{C=C_{(t)}} = \frac{A_0^{980} - A_t^{980}}{A_0^{980}} \times 100 \quad (1)$$

where $\chi_{C=C_{(t)}}$ is the conversion of acrylic double bonds at time t, A_0 is the initial absorbance (before UV irradiation), and A_t is the absorbance of these double bonds at time t.

Contact angle

Modifications of the polymer surface energy γ upon grafting were quantified by measuring the static contact angle of water and diiodomethane (Digidrop from GBX Instruments). The image of the droplet deposited on the sample, which appeared on the screen, allowed an accurate evaluation of the contact angle. The dispersive (γ_{LD}) and polar (γ_{LP}) components of the surface energy were determined from the linear plot of $\gamma_L(1 + \cos \theta)/2\gamma_{LD}^{0.5}$ versus $(\gamma_{LD}/\gamma_{LP})^{0.5}$ by using the Owens–Wendt equation.[20] Surface polarity was determined by the ratio γ_{LP}/γ.

Grafted polymer amount

Weights of the original film and of the photografted film after washing and drying at 80°C were measured.

The amount of grafted polymer was obtained as the difference between these two weights.

Atomic force microscopy

The surface morphology of the films was investigated by using a Digital Instruments Nanoscope II (Santa Barbara, CA) in contact mode with a 100-μm scanner. The cantilever used was characterized by a low spring constant of about 0.06 N/m. A standard tip of silicon nitride was used.

The images were top-view images, presented in height mode (palette of color for height: dark colors
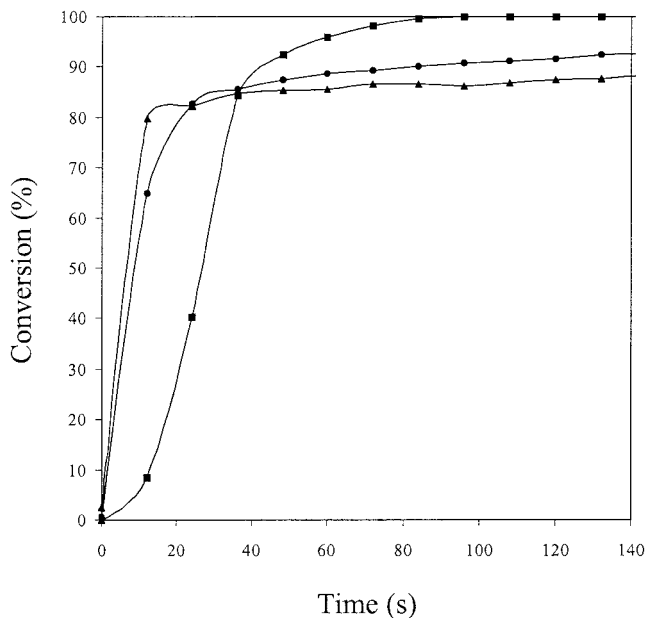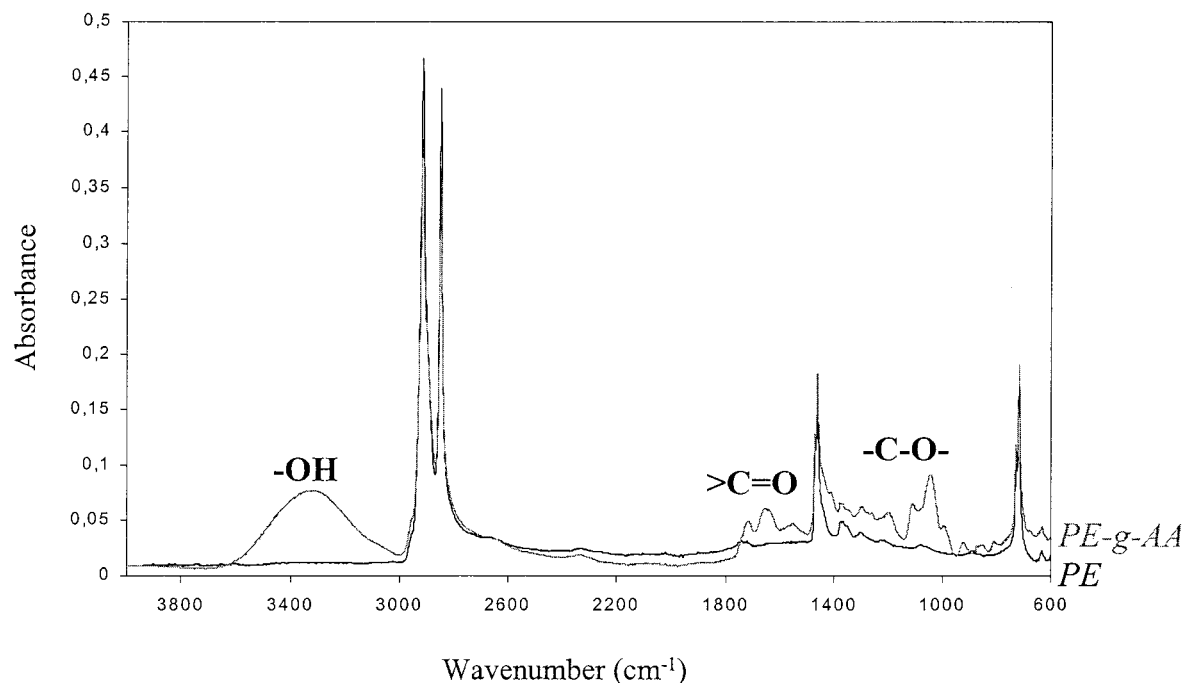

Figure 3 RTIR conversion curves as a function of irradiation time for different acrylic acid + 3% (w/w) photoinitiator mixtures. $I_0 = 3$ mW/cm^2 at 254 nm. (●) Darocur 1173; (▲) Lucirin-TPO; (■) benzophenone.

Figure 4   IR spectrum of the original polyethylene film and the grafted film in the presence of 3% benzophenone.

for low zones, light colors for high zones). All images were presented without processing, except a baseline correction (the flatten operation in the Nanoscope II software).
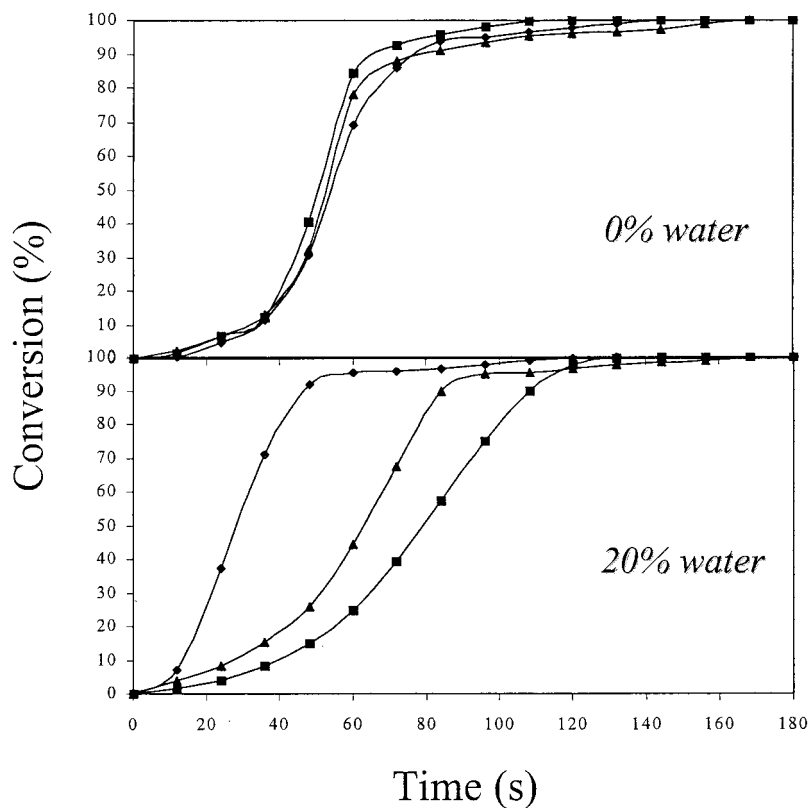
Peeling test

Samples submitted to the peeling test were prepared as follows. A non-pretreated LDPE film or a metallic plate (aluminum or inox; 3×10 cm) was first covered by the photocrosslinking acrylic stick and then by the photografted polyethylene film or by a corona-pretreated polyethylene film (γ_t = 42 mJ m^{-2}). The unit was pressed for 10 min under 300 bars; irradiated for 10 min at 254 nm, with an ultraviolet radiation intensity of 6 mW/cm^2 to crosslink the stick; and was finally allowed to rest for 24 h.
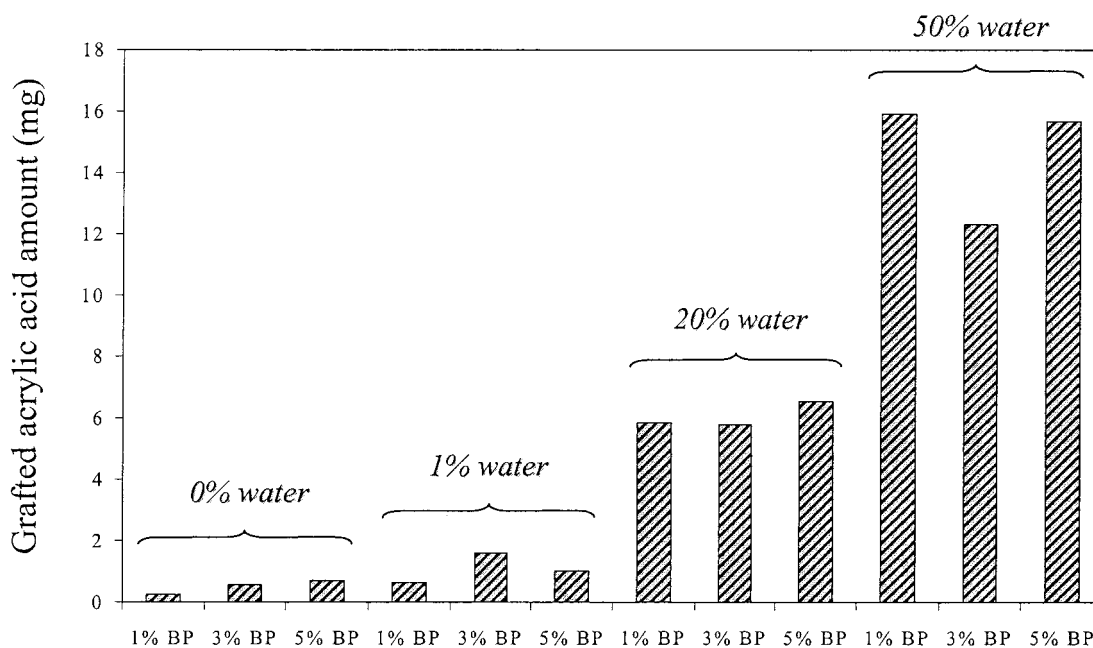

Figure 5   Grafted polyacrylic acid amount as a function of benzophenone and monomer concentrations.

Figure 6 Photochemical reaction rate as a function of benzophenone concentration: (■) 1% (w/w); (♦) 3% (w/w); (▲) 5% (w/w).

By separating the sandwich of the two PE films by T peeling, the stick transfer on the side of the non-pretreated film was visually evaluated. On the other hand, the necessary force to remove the adhesive film from the substrate was determined at 180° by means of a dynanometer.
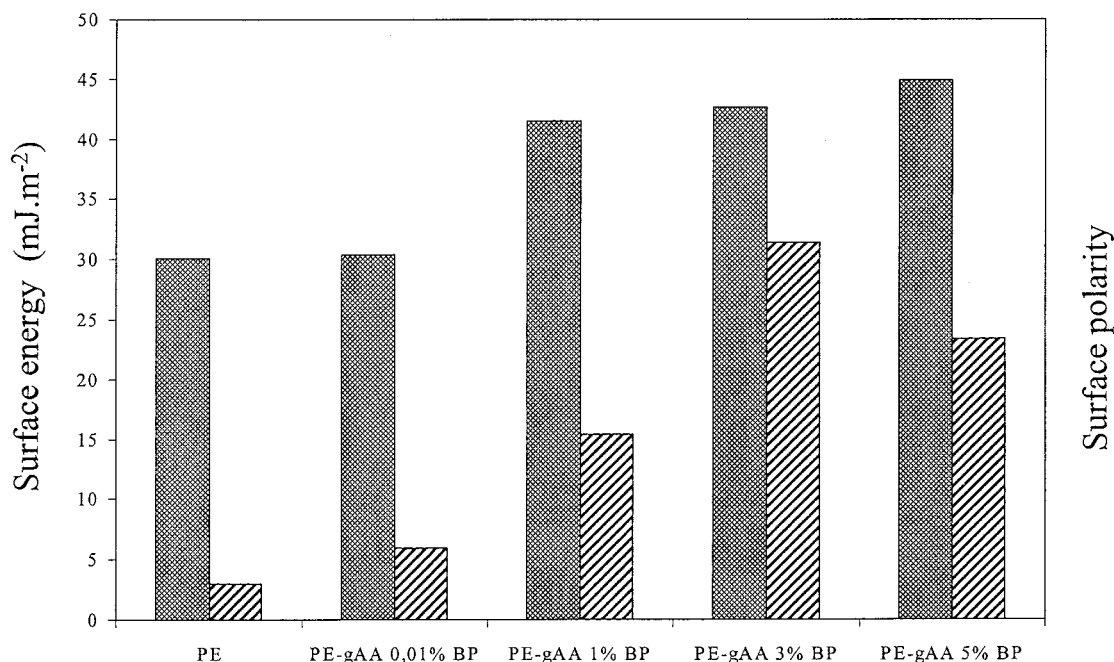
Figure 7 Surface energy (left column) and surface polarity (right column) of grafted films as a function of benzophenone concentration.
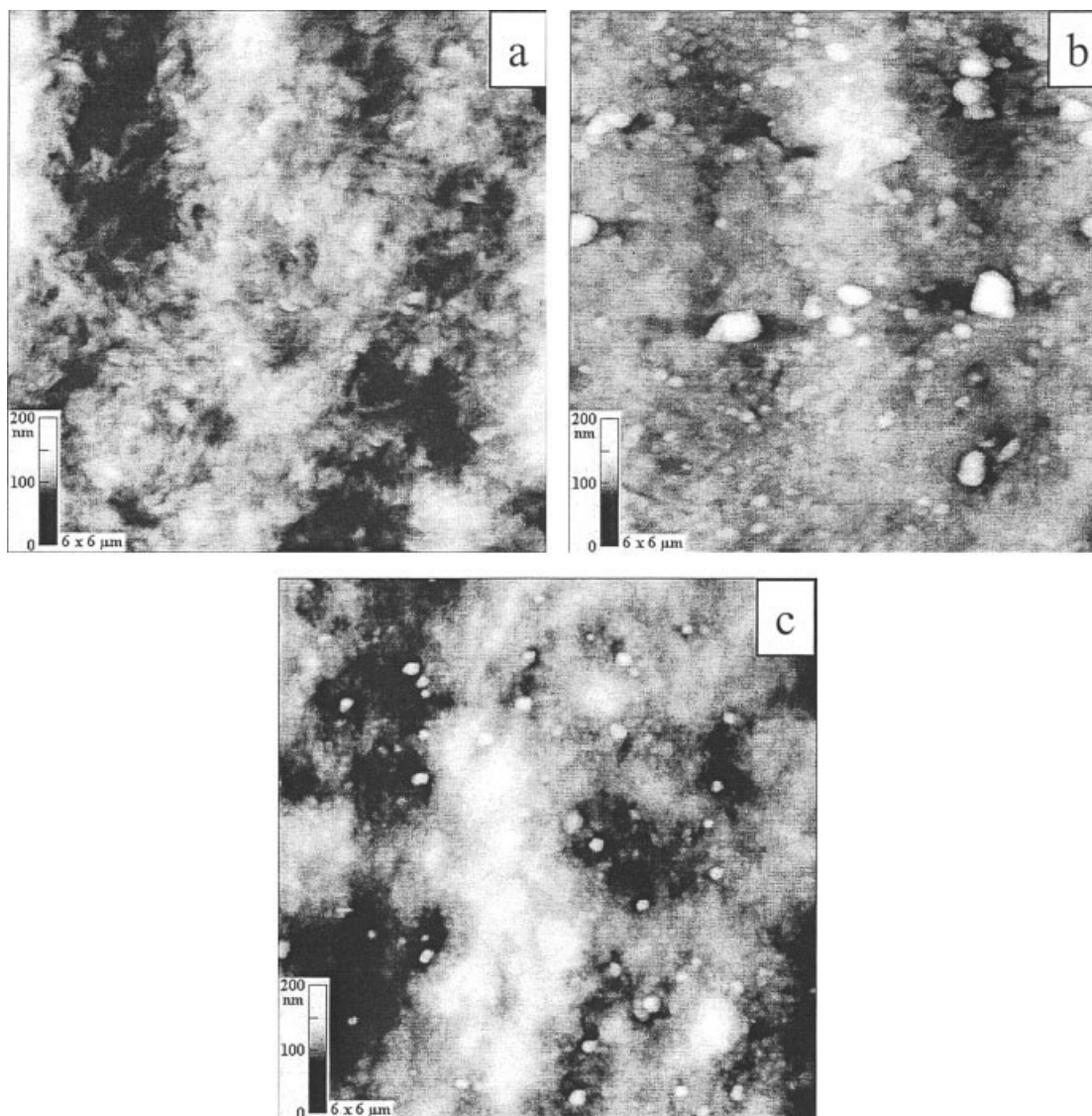
Figure 8 AFM images (6 × 6 μm): (a) original polyethylene film; (b) polyethylene film grafted with acrylic acid in the presence of 0.001% (w/w) benzophenone; (c) polyethylene film grafted with acrylic acid in the presence of 1% (w/w) benzophenone.

RESULTS AND DISCUSSION

Kinetic study of the photografting of acrylic acid onto PE film was first evaluated by RTIR spectroscopy as a function of the nature of the photoinitiator. Three photoinitiators were used: Darocur 1173 and Lucirin TPO are two PI_1 photoinitiators that undergo a homolytic cleavage under UV radiation, and benzophenone is a PI_2 photoinitiator that needs a hydrogen donor such as polyethylene to generate radicals (Fig. 1). Their weight concentrations were 3% (i.e., 0.17 mol L^{-1} for Darocur 1173 and benzophenone and 0.086 mol L^{-1} for Lucirin TPO). The UV radiation was carried out monochromatically at 254 nm, a wavelength that corresponds to the maximum absorbance of these three photoinitiators.

Benzophenone is well known for its efficiency for grafting reactions. Nevertheless, it was shown that PI_1

photoinitiators can also be used for this purpose.[21,22] Indeed, as shown in Figure 2, formation of primary radicals from the photocleavage of PI_1 photoinitiators can lead not only to the homopolymerization of acrylic acid (reactions 1 and 2 or 5), but also to a grafting at the polymer surface after a transfer reaction (reaction 6). For PI_2 photoinitiators, photografting (reaction 4) can immediately proceed because they need to abstract a hydrogen on the polymer surface to create radicals under UV radiation.

Conversions in acrylic double bonds versus irradiation time are shown in Figure 3 for the three photoinitiators in the presence of a PE film. We first observe that conversion in acrylic double bonds does not exceed 90% with PI_1 photoinitiators. Moreover, the reaction rate is much faster with Darocur 1173 and Lucirin TPO than with benzophenone, and this in spite of
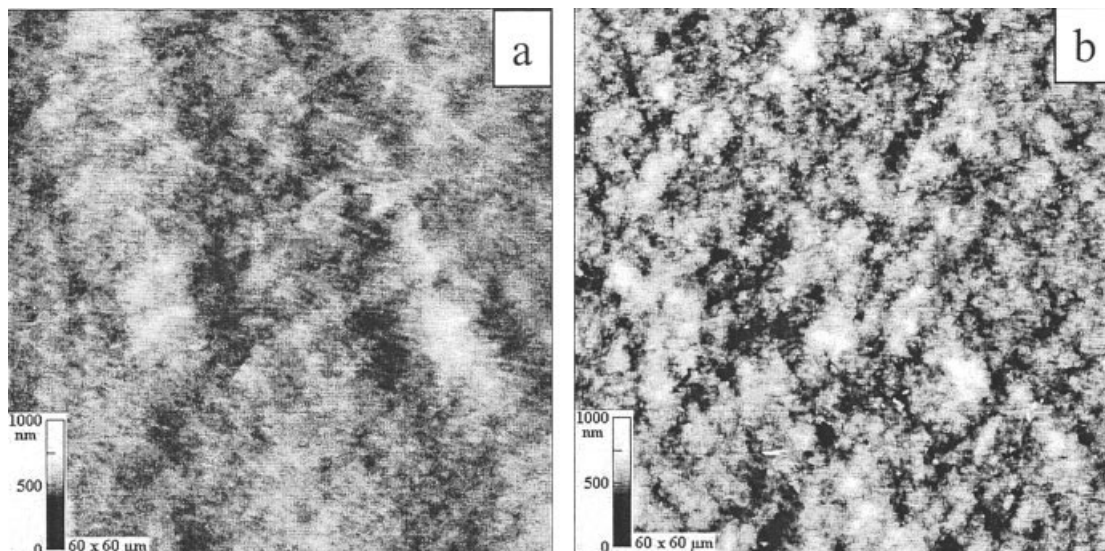
Figure 9 AFM images (60 × 60 μm): (a) original polyethylene film; (b) polyethylene film grafted with acrylic acid in the presence of 1% (w/w) benzophenone.

a molar concentration that is two times lower than that of Lucirin. However, a quantitative yield was obtained only with benzophenone.

After washing, an infrared analysis of the PE film (Fig. 4) reveals that vibration bands of carboxylic group at 1735, 1645, and 1185 cm^{-1}, and hydroxy group at 3200 cm^{-1}, are observed only on the PE film in contact with the mixture of acrylic acid and benzophenone. Thus, it seems that in our experimental conditions, PI_1 photoinitiators did not allow initiation of grafting of acrylic acid onto the PE film surface. There is a competition between homopolymerization and transfer to polyethylene reactions and results seem to show that homopolymerization is favored in the presence of type I photoinitiators. For the following study, we then decided to use benzophenone as the grafting photoinitiator.

In a second experiment, photografting of acrylic acid onto PE film was studied in the presence of benzophenone and as a function of solvent concentration (i.e., as a function of monomer concentration). Here, water was chosen as solvent because of its good solvent properties toward acrylic acid. Moreover, it was previously established as a good solvent for photografting acrylic acid.[7] Determination of the amount of grafted polymer by gravimetry (Fig. 5) was realized as a function of photoinitiator and water percentage. Taking into account the experimental uncertainties on the weighing of samples, we can say in general that the obtained results show a significant increase in the amount of grafted acrylic acid when the water concentration increases (i.e., when the monomer concentration decreases). Indeed, we postulate that water favors transfer reactions, leading to polyacrylic acid (PAA)–ramified chains and consequently to higher amounts of grafted acrylic acid. On the other hand, the photoinitiator concentration does not seem to have a notable influence on the grafted amount.

Monitoring of reaction kinetics by RTIR spectroscopy (Fig. 6) first reveals that polymerization rates vary slightly with the benzophenone concentration when the bulk photopolymerization of acrylic acid (0% water) is carried out. On the other hand, addition of water amplifies this behavior. Indeed, we observe that, in the presence of 20% water, the reaction rate is maximum for 3% benzophenone. The decrease in the maximum polymerization rate for higher photoinitiator concentration can be attributed to the bimolecular termination reaction, by recombination of radicals, that hinders the polymerization reaction of acrylic double bonds. Second, we note that, for a given benzophenone concentration, the photochemical reaction rate logically increases with the acrylic acid concentration. Nevertheless, let us note that incorporation of water into the mixture in the absence of surfactant induces a problem of wettability, and so of grafting heterogeneity of the treated film, which can be a hindrance to its use. In the following investigations, we decided to study the surface properties of photografted films without water.

Measurements of surface energy and polarity of samples photografted with different benzophenone concentration were carried out with water and diiodomethane (Fig. 7), the analysis of which satisfactorily confirmed the grafting efficiency. Indeed, surface energy and polarity increase with the amount of acrylic acid concentration and a maximum for polarity is reached with 3% benzophenone. We note values of surface energy > 42 mJ m^{-2}, crucial for the improvement of adhesive properties of the LDPE film.

TABLE I
Results of T Peeling Test for Different Polyethylene Films

Film 1	Film 2	Stick transfer on the non-pretreated LDPE film
Pristine LDPE	Corona-treated LDPE ($\gamma_t = 42$ mJ m^{-2})	Little
Pristine LDPE	LDPE-g-AA 3% BP after washing	High
Pristine LDPE	LDPE-g-AA 3% BP without washing	Very little

Morphology of polyethylene films grafted with mixtures of acrylic acid in bulk was determined by AFM as a function of benzophenone concentration (Fig. 8). Figure 8(a) is a 6×6-μm image showing the original polyethylene surface. This surface presents the cotton aspect. The 6×6-μm image of polyethylene surface photografted by acrylic acid in the presence of 0.001% benzophenone is given on Figure 8(b). The cotton structure of the original PE film is no longer visible, indicating that grafting occurred over the entire surface of the film. White polymer grains are also locally observed. When the benzophenone concentration increases and reaches 1% [Fig. 8(c)], growing PAA grains are always present but the surface roughness has increased, meaning that grafting polymer thickness has also increased. Thus, grafting of acrylic acid leads to a PAA layer that covers the entire PE surface, as can be seen on larger-scale images (Fig. 9), and of which the thickness depends on the photoinitiator concentration, thus confirming that PAA grows by a classical nucleation process on the entire LDPE surface. The overall topography shows that the PAA grafting leads to higher relief. AFM analyses of films grafted with higher photoinitiator concentrations are no longer of investigative importance because of the too thick grafted polymer layer.

Finally, the efficiency of this method of surface modification was evaluated by an adhesion test. Polyethylene film grafted in the presence of 3% benzophenone was tested only because of its superior surface polarity. Sandwiches of a photocrosslinking acrylic stick between different PE films or metallic substrates were constructed, as shown in Tables I and II, and the irradiation step was carried out as described in the experimental section. After separation of the sandwiches, we already noted that washing the PE-g-AA film significantly influenced the adhesion test. Thus, the presence of acrylic acid homopolymers seems to improve the stick adhesion on the photografted film. Moreover, a photografted film in the presence of 3% benzophenone without washing seems to be superior to a corona-pretreated film ($\gamma_t = 42$ mJ m^{-2}).

CONCLUSIONS

Acrylic acid can be successfully grafted by a continuous process onto polyethylene film in the presence of benzophenone. Study of the influence of photoinitiator and water concentration has shown that the greater their concentrations, the higher the acrylic acid grafted amounts. This was confirmed by AFM analysis, which has shown that the grafted polyacid chains cover all the surface of the polyethylene film with a thickness dependent on the photoinitiator concentration. It was also shown that photografting of acrylic acid is a good method for increasing the adhesive properties of a polyethylene film toward the chosen reference stick. Finally, the photografting process seems to be as competitive as the usual surface-modification techniques such as corona. On the other hand, it has the advantage of being more fully and definitively developed as demand for its use increases.

TABLE II
Results of 180° Peeling Test on Two Metallic Substrates

Metallic substrate	Film	Peeling forces (N)	Stick transfer on the metallic substrate
Inox	Corona-treated LDPE ($\gamma_t = 42$ mJ m^{-2})	2.5–3.5	High
	LDPE-g-AA without washing	>5	Little
Aluminum	Corona-treated LDPE ($\gamma_t = 42$ mJ m^{-2})	1.5–2	High
	LDPE-g-AA without washing	>4	Very little

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