Surface Functionalization of Polyolefin Films via the Ultraviolet-Induced Photografting of Acrylic Acid: Topographical Characterization and Ability for Binding Antifungal Agents

Vanina Costamagna,[1] Daniel Wunderlin,[2] Maider Larrañaga,[3] Iñaki Mondragon,[3] Miriam Strumia[1]

[1]*Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, Córdoba (5000), Argentina*
[2]*Centro de Química Aplicada, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, Córdoba (5000), Argentina*
[3]*Materials and Technologies' Group, Departamento Ingeniería Química y Medio Ambiente, Escuela Universitaria Politécnica, Universidad del País Vasco/Euskal Herriko Unibertsitatea, Plaza Europa, 1, 20018 Donostia-San Sebastian, Spain*

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ABSTRACT: The photoinduced graft copolymerization of acrylic acid with ultraviolet radiation onto films of poly (vinyl chloride), polypropylene, and polyethylene was studied. Benzophenone was used as the initiator for most of the experiments performed. The percentage of grafting was determined by gravimetric measurements, and the characterization of the grafted films was carried out by chemical analysis (Fourier transform infrared spectroscopy, volumetric titration, and dye adsorption). In all samples, the grafted yield increased with the ultraviolet exposure time. High levels of grafting were obtained at room temperature. In addition, optical and atomic force microscopy allowed the topography of the modified films to be studied as a function of the reaction time. The pendant functional groups that were grafted were then used to bind antifungal agents, such as natamycin and crystal violet, and the antifungal properties of the films were demonstrated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2254–2263, 2006

Key words: atomic force microscopy (AFM); films; functionalization of polymers; graft copolymers; polyolefins

INTRODUCTION

In many applications, it is necessary to change or improve some of the polymeric surface properties without modification of the bulk properties of the material. Therefore, there is much interest in the surface modification of polymers to create different and new applications.[1–3] Modified polymer surfaces have a number of improved properties, such as adhesion,[4–6] hydrophilicity,[7] antistatic nature,[8] wearability,[9,10] dyeing ability,[11] and biocompatibility.[12]

The graft polymerization of monomers onto the surfaces of polymers is one of the main efficient processes for inducing modification. Surface grafting can proceed by a free-radical mechanism, which can be generated by several methods, such as different kinds of radiation,[13–15] Ce^{+4} ions,[16] and peroxide initiators.[17] Radiation-induced surface modification is one of the most thoroughly investigated areas that can result in both physically and chemically altered surfaces. Both high-energy radiation (either γ or electron beams) and low-energy radiation [e.g., ultraviolet (UV) light] are frequently used to initiate the surface modification of various polymers, particularly polyolefins.

On the other hand, surface grafting uses versatile techniques to introduce specific functional groups such as amine, imine, hydroxyl, carboxylic acid, sulfate, and epoxy groups onto a broad range of conventional polymeric substrates, most of which have a nonpolar, less reactive surface. Functionalization is achieved by either direct grafting of functional monomers or by postderivatization of graft chains. The introduced functional groups can be used to further reactions through covalent or noncovalent linkages with small or large molecules required for particular applications, such as biomolecular immobilization[18] and antimicrobial activity.[19]

In this work, the heterogeneous surface modification of polyolefin films such as poly(vinyl chloride) (PVC), polypropylene (PP), and polyethylene (PE)

Correspondence to: M. Strumia (mcs@mail.fcq.unc.edu.ar).
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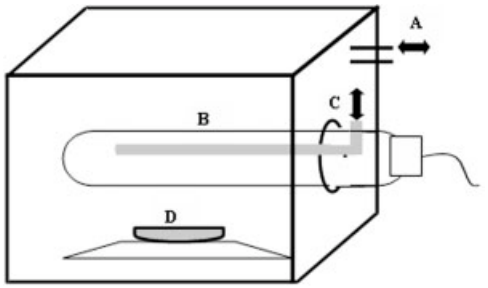

Figure 1 Reactor for surface grafting experiments: (A) N_2, (B) lamp, (C) lamp refrigeration, and (D) substrate.

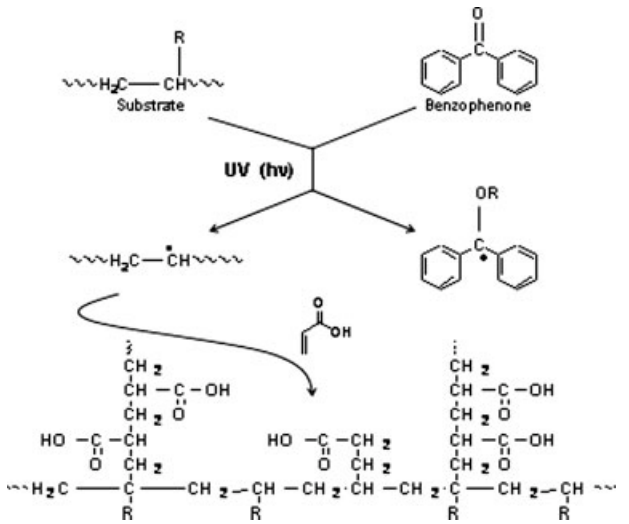

Figure 2 General scheme for the modification of polyolefin films.

was undertaken via the UV-induced photografting of acrylic acid (AA). The goal was to perform a comparative study by means of an efficient, rapid, and economical method suited to yield modified surfaces of different commercial films. The influence of different reaction parameters on the graft yield, such as the type of initiator, presence or absence of a solvent, and irradiation time, was analyzed. Then, the active functional groups present in the surface were used for binding specific organic molecules to impart to the films antifungal activity.

The surface modification of the films with the treatment time was characterized by gravimetric measurements and also by chemical analysis, such as Fourier transform infrared (FTIR) spectroscopy, volumetric titration, and dye adsorption. In addition, the topographical evolution of the film surfaces was followed with optical microscopy (OM) and atomic force microscopy (AFM).

Finally, as crystal violet and natamycin were electrostatically bonded to the functionalized films, their antifungal properties were verified.

EXPERIMENTAL

Materials and reagents

Films of PVC, PP, and PE were kindly provided by Klockner (Córdoba, Argentina), Arcor Flexibles (Córdoba, Argentina), and Vitopel (Córdoba, Argentina), respectively. The thickness was about 29 μm for PVC films, 32 μm for PP films, and 47 μm for PE films.

The following chemicals were commercially acquired: AA (BASF), benzophenone (Fluka AG; Buchs, Switzerland), benzoyl peroxide (Fluka AG), acetone (Cicarelli; San Lorenzo, Argentina), ethanol (Porta; Córdoba, Argentina), NaOH (Cicarelli), $NaH_2PO_4{\cdot}H_2O$ (Cicarelli), $Na_2HPO_4{\cdot}12H_2O$ (Mallinckrodt; St. Louis, Missouri, USA), nutrient agar (Britania; Buenos Aires, Argentina), dye crystal violet (Anedra; Buenos Aires, Argentina), and natamycin (pimaricin [Cultor; Ardsley, New York, USA]). All chemicals were used as received, without further purification.

Graft copolymerization procedure

The reactions were carried out in a photoreactor designed and built in our laboratory, as shown in Figure 1. Films of PVC, PP, and PE (previously washed with distilled water and dried *in vacuo* at room temperature until a constant weight) were

TABLE I
Reaction Parameters and —COOH Equivalents for the Reactions with PVC

Sample	Initiator*	Solvent	Time (min)	Microequiv of —COOH (cm^2)**	Grafting (%)***	Nanoequiv of violet crystal (cm^2)
PVC1	Benzophenone	—	30	—	—	—
PVC2	Benzoyl peroxide	—	60	3.48	6.8	0.093
PVC3	Benzophenone	Ethanol	60	—	—	—
PVC4	Benzophenone	Acetone	1	—	—	—
PVC5	Benzophenone	Acetone	2	6.4	4.4	—
PVC6	Benzophenone	Acetone	5	7.7	19.5	0.080
PVC7	Benzophenone	Acetone	10	26.2	34.1	0.115

* 0.5 mL of a solution 0.2*M* of the initiator in the monomer.
** Equivalents of —COOH determined by titration.
*** Determined by gravimetric measurements.

placed in glass Petri dishes; then, 0.5 mL of a solution (0.2*M*) of the initiator benzophenone in the monomer AA, and 0.5 mL of the solvent (acetone, ethanol, or distilled water) were added. The dish containing the reactive materials was enclosed in the photoreactor and irradiated with UV light (medium-pressure UV lamp, Engenlhard-Hanovia; Slough, England) under a nitrogen atmosphere and at room temperature. This process was performed with different reaction parameters, including the absence or presence of a solvent, the type of initiator, and the time of reaction. All grafted samples were extensively washed before analysis with a NaOH solution (pH 8) and finally with distilled water to remove traces of the unreacted monomer and the homopolymer that formed and to extract remains of the initiator. The samples were dried *in vacuo* at room temperature until a constant weight and finally characterized. PVC films irradiated with a reaction time over 10 min became brittle and hard to manipulate, so they could not be characterized.

Film characterization

Gravimetric measurements

The grafting percentage was obtained by the weighing of the films before and after the grafting reactions were carried out. The grafting percentage was estimated as follows:

$$\text{Grafting (\%)} = \left(\frac{\text{Weight of grafted products} - \text{Weight of substrate}}{\text{Weight of substrate}}\right) \times 100 \quad (1)$$

Chemical analysis

Volumetric titration. The —COOH groups grafted onto the surfaces of the films were determined by volumetric titration with a 0.1*M* NaOH solution.

Dye adsorption. Light absorption of the crystal violet was carried out in a Shimadzu UV 260 recording spectrophotometer (Kyoto, Japan). The adsorption of the dye was performed as follows. The films were immersed in an aqueous crystal violet solution (2.5×10^{-5} *M*) and buffered to pH 4.6 (by the addition of acetic acid and sodium acetate), and the dye adsorption was measured as the difference in the absorption in the crystal violet solution before and after contact with the films with ultraviolet–visible spectrometry at 584 nm (with the previous performance of a calibration curve).

FTIR spectroscopy. The FTIR spectra were made with a Nicolet 5 SXC (Madison, Wisconsin, USA). The FTIR spectra were performed on films in the transmission mode with a resolution of 8 cm^{-1} and 32 scans.

AFM and OM surface analysis

AFM measurements were performed at room temperature in air with a scanning probe microscope (Nanoscope IIIa, Multimode from Digital Instruments; Santa Barbara, California, USA). Tapping-mode height and phase images were recorded with etched silicon probes with a spring constant of 20–100 N/m. The scanning frequency was 1 Hz. The surface height was measured

TABLE II
Reaction Parameters and —COOH Equivalents for the Reactions with PP

Sample	Initiator*	Solvent	Time (min)	Microequiv of —COOH (cm^2)**	Grafting (%)***	Nanoequiv of violet crystal (cm^2)
PP1	Benzophenone	—	30	—	—	—
PP2	Benzophenone	Ethanol	30	—	—	—
PP3	Benzophenone	Ethanol	60	—	—	—
PP4	Benzoyl peroxide	Ethanol	60	—	—	—
PP5	Benzophenone	Acetone	60	—	—	—
PP6	Benzophenone	Water	2.5	—	—	—
PP7	Benzophenone	Water	5	—	—	—
PP8	Benzophenone	Water	7.5	3.9	6.51	0.105
PP9	Benzophenone	Water	10	4.28	12.9	0.127
PP10	Benzophenone	Water	15	6.59	19.8	0.142
PP11	Benzophenone	Water	25	12.03	36.2	0.160

* 0.5 mL of a solution 0.2*M* of the initiator in the monomer.
** Equivalents of —COOH determined by titration.
*** Determined by gravimetric measurements.

TABLE III
Reaction Parameters and —COOH Equivalents for the Reactions with PE

Sample	Initiator*	Solvent	Time (min)	Microequiv of —COOH (cm^2)**	Grafting (%)***	Nanoequiv of violet crystal (cm^2)
PE1	Benzophenone	Water	2	—	—	—
PE2	Benzophenone	Water	3	—	—	—
PE3	Benzophenone	Water	4	—	—	—
PE4	Benzophenone	Water	5	3.2	3.7	0.087
PE5	Benzophenone	Water	10	5.3	13.0	0.112
PE6	Benzophenone	Water	15	18.9	24.0	0.158
PE7	Benzophenone	Water	20	23.8	36.5	0.174

* 0.5 mL of a solution 0.2*M* of the initiator in the monomer.
** Equivalents of —COOH determined by titration.
*** Determined by gravimetric measurements.

as the height difference between the highest and lowest points of the corresponding AFM topographic images.

Optical micrographs of the film surfaces were taken with a Nikon Eclipse E600 W optical microscope (Tokyo, Japan).

Coupling of natamycin and crystal violet

The adsorption of natamycin was performed as follows. The grafted films were immersed in an aqueous dispersion of a 50/50 natamycin/lactose blend (0.25% W/V) buffered to pH 8.0 (by the addition of a phosphate buffer). After 24 h, the films were removed from the dispersion and exhaustively rinsed with phosphate buffer and finally with distilled water to remove the natamycin not ionically bonded to the modified films.

The adsorption of crystal violet was carried out with the same procedure for dye adsorption studies. The films were washed with an acetic/acetate buffer and finally with distilled water to facilitate the removal of unbonded crystal violet.

At last, the films, modified with both antifungal agents, were dried *in vacuo* at room temperature until a constant weight, and their activity was verified through microbiological assays *in vitro*.

Evaluation of the antifungal activity

To evaluate the antifungal activity of the films modified with crystal violet and natamycin, discs of the modified films were placed onto a dish of nutrient agar previously inoculated with a suspension of yeasts. The dish was then incubated at 20 ± 1°C for 5 days in darkness.

RESULTS AND DISCUSSION

Graft copolymerization reactions

The chemical modifications of the surfaces of PP, PE, and PVC films were carried out by radical grafting polymerization initiated by UV light. AA was used as the grafting comonomer. For chemical modifications, variables such as the presence or absence of a solvent, the type of initiator, and the time of reaction were examined. Figure 2 shows the general modification found on different films.

Film characterization

The experimental conditions are shown in Tables I–III for PVC, PP, and PE, respectively. The efficiency of the chemical modification was evaluated by gravimetric measurements and confirmed by the determination of the —COOH groups grafted onto the film surfaces through volumetric titration and dye adsorption. As can be seen in Tables I–III, in all cases, the grafting reactions produced better yields when they were performed in solution rather than in bulk. Therefore, different solvents were tested for optimal grafting yields. On the other hand, for surface modification applications, thick grafting layers are unnecessary and even undesirable because they may change the bulk physical properties of the polymer. Therefore, because the

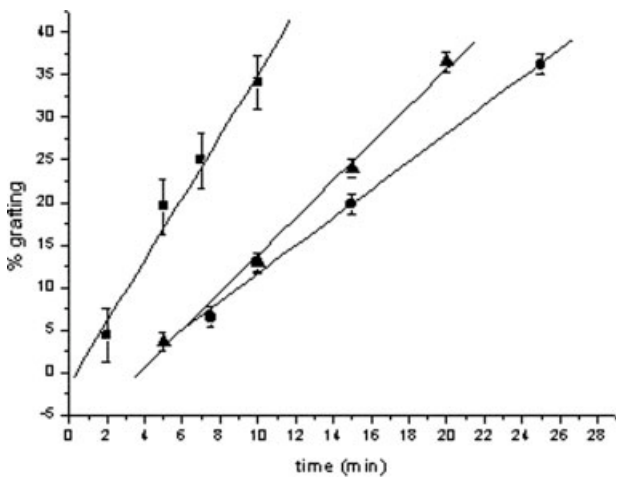

Figure 3 Percentage of grafting (as determined by gravimetric measurements) versus the reaction time. (■) PVC; (▲) PE; (●) PP.

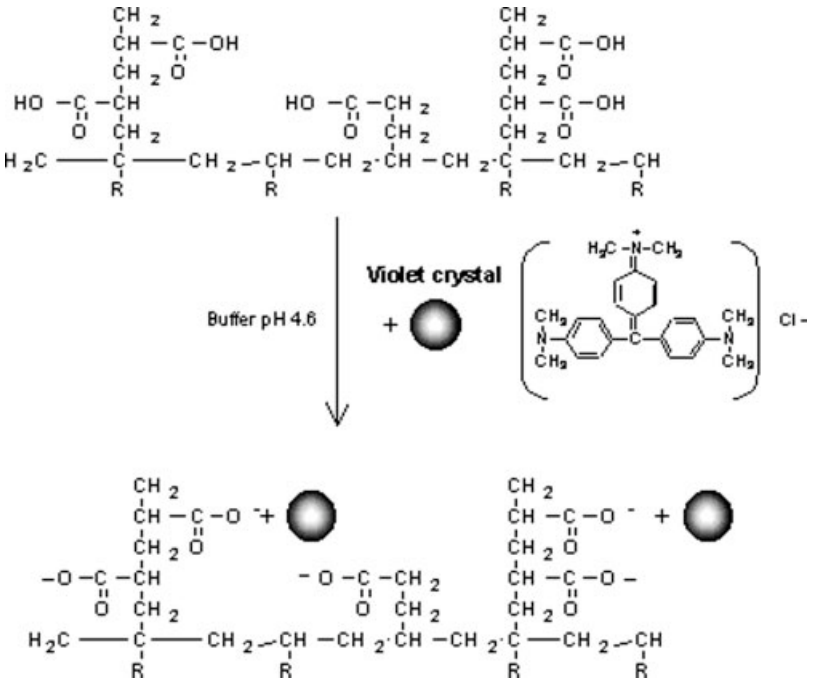

Figure 4 General scheme of dye adsorption for modified polyolefin films.

aim of this study was to modify the surfaces of the films without modifying the bulk material, weak interactions between the solvent and polymer film were desirable. Thus, we used polar solvents (water, acetone, and ethanol) because they have rather small interactions with polyolefins. Besides, the fact that the grafting agent and the grafted chains are soluble in these solvents facilitates their propagation outside the polymer surface; this phenomenon is advantageous because it will help in the growth of the grafted chains outside the film surfaces. In addition, the solvent must be inert to the triplet excited state of the photosensitizer or photoinitiator. It has been demonstrated that neither acetone nor water is reactive to the excited state of benzophenone, so grafting is not inhibited.[20] The best conditions for grafting in PVC films were benzophenone as the initiator and reaction times over 2 min. For PP and PE, the grafting of AA was effective when water was used as the solvent, benzophenone was used as the initiator, and lapses longer than 7.5 and 5 min were used for PP and PE, respectively.

An increase in the grafting yield was seen when the reaction time or exposure to UV increased (Fig. 3). The grafting rate was related to the dissociation energy of the C—X bond of each film, which was about 79, 84, and 95 kcal/mol for X = Cl, X = CH_3, and X = H, respectively. However, this reactivity could be related to the crystalline/amorphous zones ratio of the films,[21] in this case, PVC was the film with more amorphous zones. The ratios for the other films are yet unknown to us.

The quantification of the —COOH groups grafted onto the surfaces of the films showed the same trend observed for gravimetric measurements.

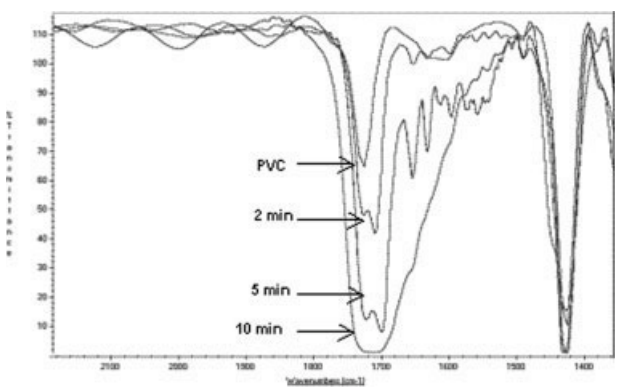

Figure 5 FTIR spectra for PVC and PVC grafted with AA for different reaction times.

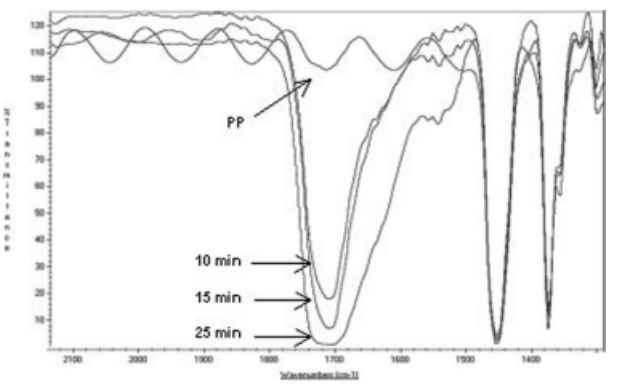

Figure 6 FTIR spectra for PP and PP grafted with AA for different reaction times.

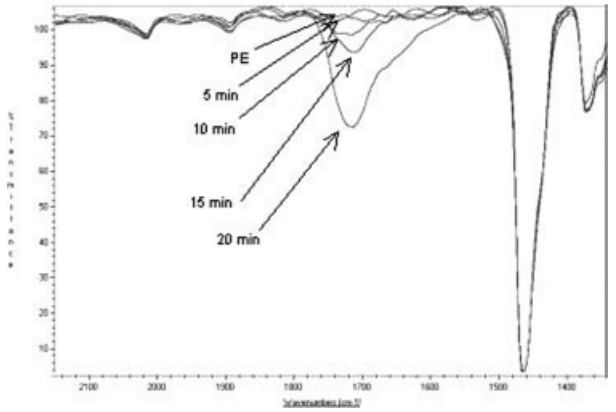

Figure 7 FTIR spectra for PE and PE grafted with AA for different reaction times.

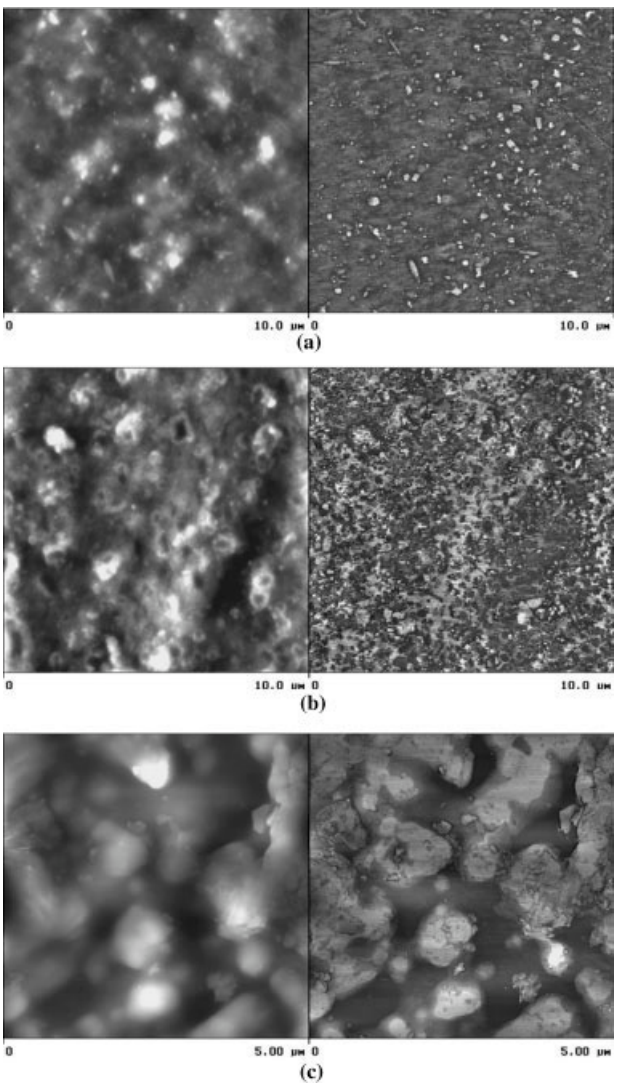

Figure 8 AFM images of (a) a PVC film at a reaction time of 0 min, (b) a PVC film grafted with AA at a reaction time of 5 min, and (c) a PVC film grafted with AA at a reaction time of 10 min.

TABLE IV

	Grafting time (min)				
	0	5	10	15	20
PVC	173	288	1259	—	—
PP	58	—	1959	2410	3571
PE	209	369	674	1677	3349

Although both benzophenone and benzoyl peroxide initiators were assayed in the reactions, grafting was possible or the yield was improved only when benzophenone was used. In PP and PVC films, higher percentages of grafting for the same reaction time were obtained with benzophenone.

Dye adsorption

The available carboxyl groups were evaluated by the ionic bonding of a dye, such as violet crystal. This is a cationic and voluminous dye that was strongly adsorbed by the carboxylic groups of the film surfaces (Fig. 4). As shown in Tables I–III, the concentration of the $—COO^-dye^+$ was lower than those found by titration. This result explains why only the carboxylic groups with no steric hindrance were able to bond to the dye, and indeed this bond ability was lower than that shown with Na^+. These kinds of carboxylic groups probably are available and active

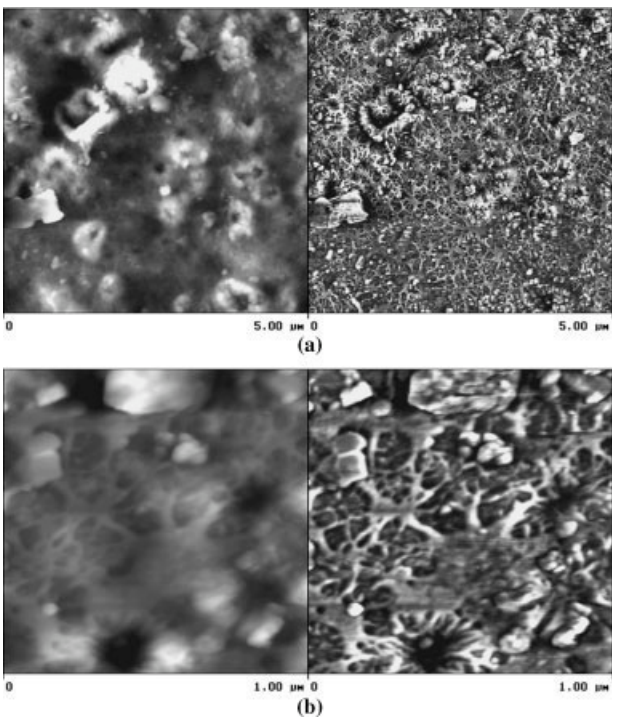

Figure 9 Low-scale AFM images of PVC films after 5 min of treatment: (a) 5 and (b) 1 µm.

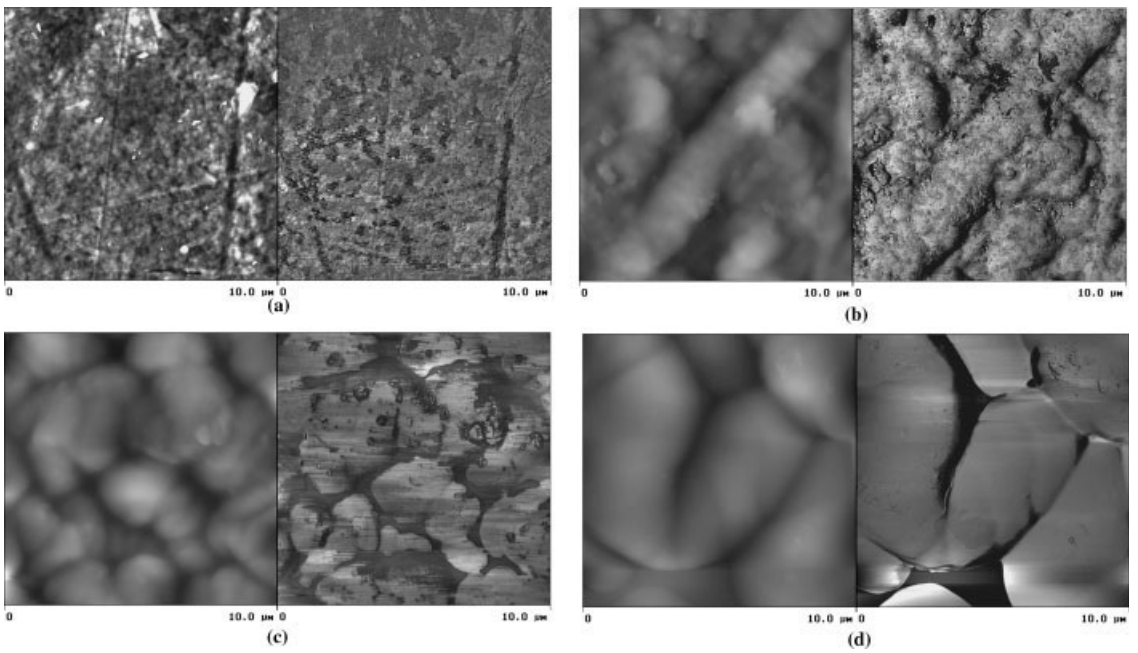

Figure 10 AFM images of (a) a PP film at a reaction time of 0 min, (b) a PP film grafted with AA at a reaction time of 10 min, (c) a PP film grafted with AA at a reaction time of 15 min, and (d) a PP film grafted with AA at a reaction time of 20 min.

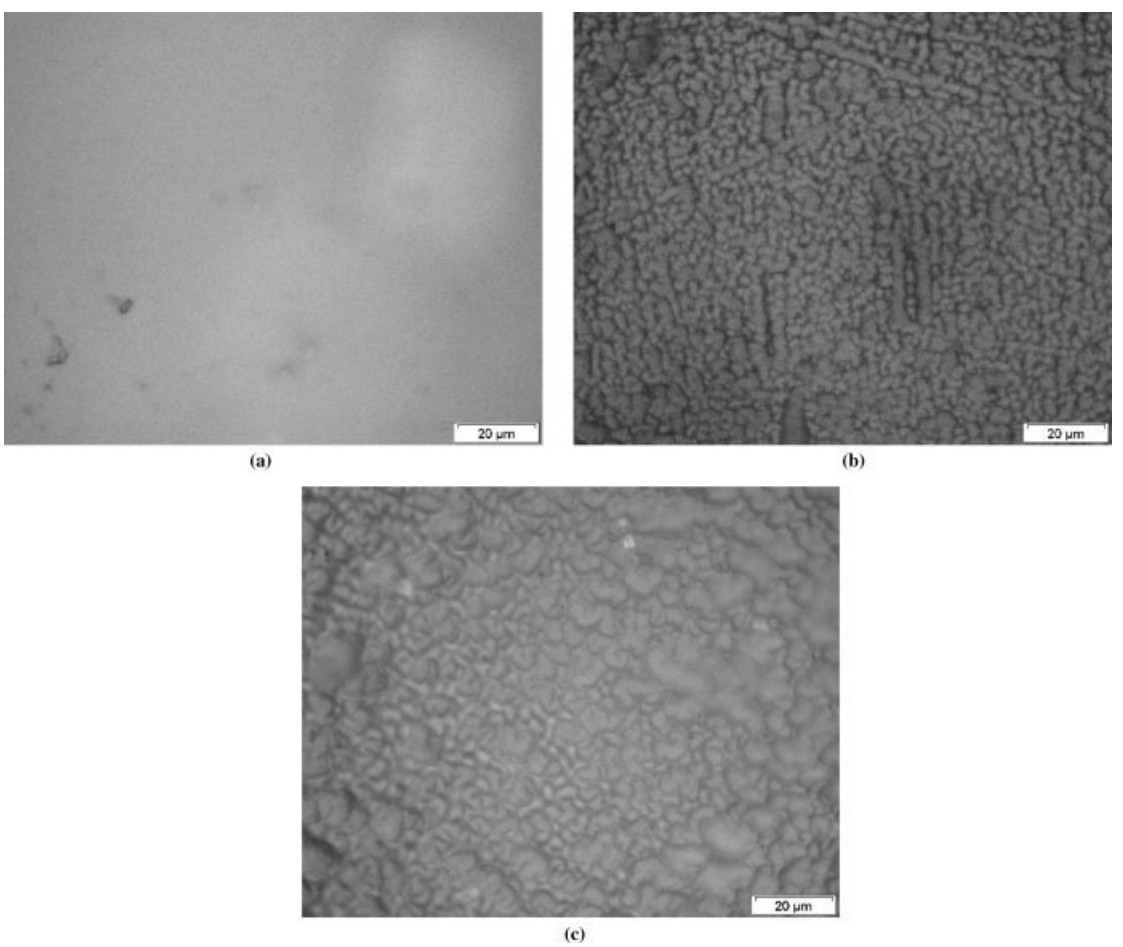

Figure 11 Optical micrographs of (a) a PP film at a reaction time of 0 min, (b) a PP film grafted with AA at a reaction time of 15 min, and (c) a PP film grafted with AA at a reaction time of 20 min.

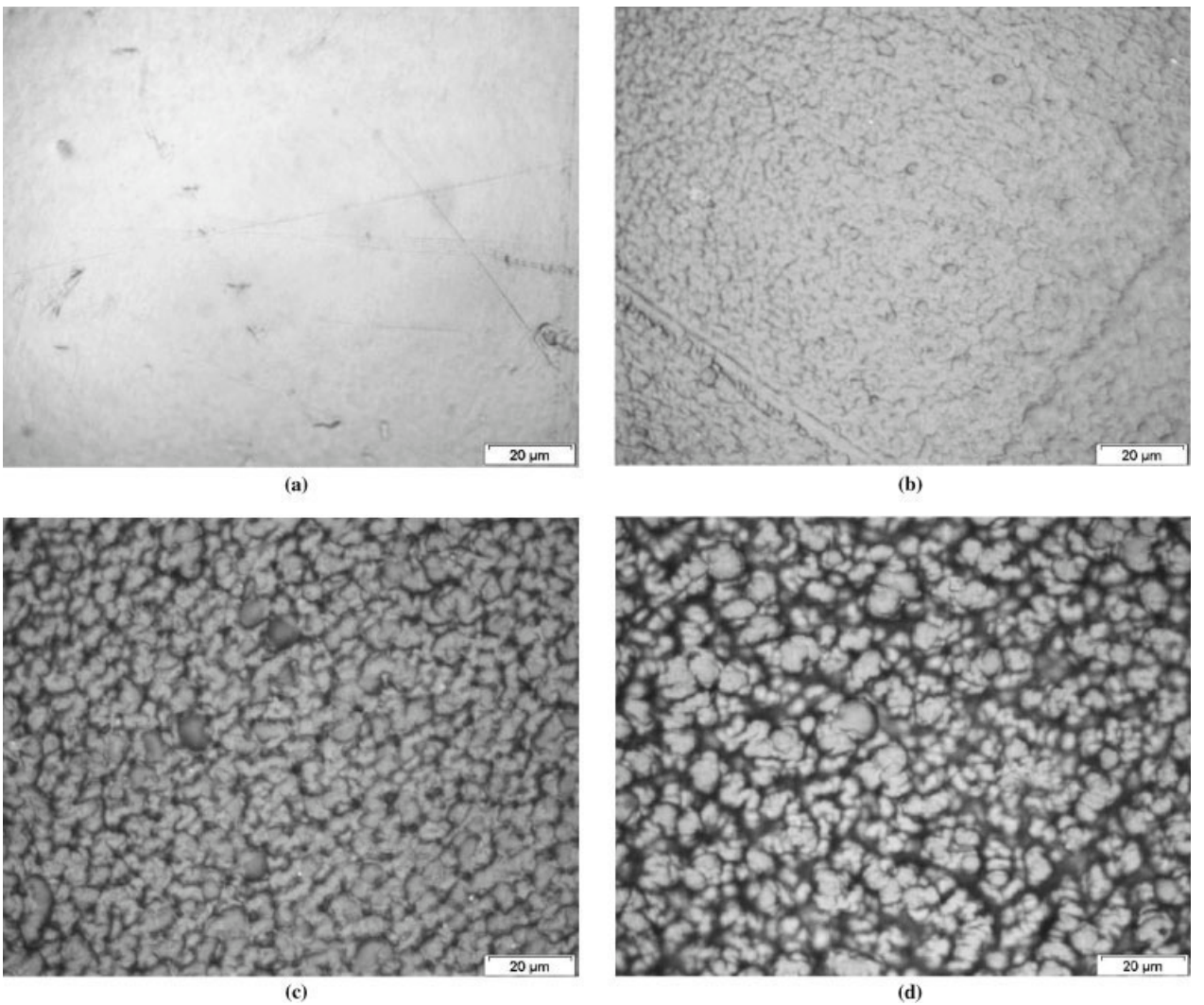

Figure 12 Optical micrographs of (a) a PE film at a reaction time of 0 min, (b) a PE film grafted with AA at a reaction time of 10 min, (c) a PE film grafted with AA at a reaction time of 15 min, and (d) a PE film grafted with AA at a reaction time of 20 min.

sites for further applications and for the bonding of organic compounds with a specific function.

FTIR spectroscopy

The modified films were characterized with FTIR spectroscopy. Representative spectra are shown in Figures 5–7 for PVC, PP, and PE, respectively, at different irradiation times. Typically, intense —C=O absorption (1718 cm^{-1}) characteristic of poly(acrylic acid) was seen in the spectra. The absorption of this band increased when the percentage of grafting rose with the irradiation time. In PVC films, this band overlapped the —C=O absorption of additives used in the preparation of the films.

On the other hand, AA homopolymerization could occur outside the film surfaces. According to this finding, the FTIR spectra of films before the removal treatment showed a larger signal from C=C groups of AA at 1613 and 810 cm^{-1}, revealing the presence of unreacted monomer.

Other typical characteristic bands of base polymers were observed, such as PE peaks at 1472 and 1462 cm^{-1} (CH_2 and CH_3 bending) and at 719 and 729 cm^{-1} (CH_2 rocking) and the main bands of PP at 2850 and 1450 cm^{-1} (CH_2 and CH_3 bending) and of PVC at 1290 and 1250 cm^{-1} (—C—H in CHCl).

AFM and OM surface analysis

The topographical results of chemical grafting onto PVC, PP, and PE films were investigated with microscopic techniques such as AFM and OM. Figure 8(a–c) (10 × 10 μm^2 images) presents AFM height and phase images for PVC film surfaces after different times of grafting with AA. As a result of the chemical treatment, the original featureless topography of

the raw film was made up of growing aggregates. As shown in Table IV, topographic images indicated that the longer the chemical treatment was, the higher the surface rose. Figure 9(a,b) shows lower scale images of the film modified for 5 min. A spider-web-like topography appeared, covering the polymer bulk up to generate the agglomeration shown in Figure 8(b), as chemical reactions proceeded, surely linking the network reactive sites.

Figure 10(a–d) shows AFM images for PP films at different modification times. The evolution of the film surfaces revealed the presence of aggregates that started forming at low reaction times. After collapsing between them, these growing aggregates formed big domains that increased the roughness of the films, as reported in Table IV. These agglomerates could be formed by reaction-induced agglomeration between the carboxyl groups introduced and also by enlargement of the AA chains simultaneously with the grafting reactions.

For PE films, the development of agglomerates seemed to proceed by a pathway similar to that of PVC. After 5 min of AA modification of the film surface, bundlelike domains were present. At longer times, 10 min or so, they grew and linked together, showing features similar to those of PVC on the same scale [Fig. 9(b)]. Indeed, AFM could be used in film modification as a powerful technique to screen the growing domains and also to elucidate how the time and reaction conditions influenced the kind and size of such domains.

For understanding the macroscopic effects of chemical grafting with AA, OM analysis was also performed. Figures 11(a–c) and 12(a–d) show the evolution of surface topographical features of PP and PE, respectively, at different grafting times. After the treatment, both PP and PE films showed the typical bumped texture of a partially crystalline polymer grafted by irradiation-initiated polymerization. As suggested by Johnston and Ratner,[22] the surface topography could result from a competition between the grafting reaction and surface relaxation processes. Moreover, the bumped surface texture arose with different initiation rates in amorphous and crystalline domains, regardless of the substrate used. In all experiments performed with PP and PE and also with PVC, as shown by AFM, the dimensions of the bumps increased with the increase in the treatment time. Both microscopic techniques, AFM and OM, showing topographical features on different scales, allow us to propose a complete scheme of the effects of AA grafting on polyolefin films. Thus, during the earlier stages of grafting, bundlelike domains, possibly formed by several molecules of the grafted chains, appear. Afterwards, they link together, forming a network with a spider-web shape in which further association between the network constitutive groups occurs. As a result, nonhomogeneous domains grow as the time of the grafting treatment increases.

The presence of crystals on the surface of PP and PE could be explained by the use of water as the solvent for the grafting reactions; instead, for PVC, which presented minor crystal domains, the grafting reactions were performed with acetone as the solvent. Water, a more polar solvent, probably favored the interaction between the chains of poly(acrylic acid), leading to the formation of crystalline domains.

Coupling of antifungal agents and evaluation of the antifungal activity

The functionalized films were used to bind different antifungal agents. Dye crystal violet and natamycin were electrostatically bonded to —COOH groups of the grafted chains of the films. Natamycin is a powerful antifungal agent that can be used in food coverings; therefore, its incorporation into the film could be an interesting option for its applications in packaging. Figures 13 and 14 show certain examples of the efficiency of both antifungal-modified films against yeasts. Crystal violet and natamycin effectively inhibited the growth of the microorganisms, as indicated by the clear inhibitory zone under the film discs. The natamycin films showed great clarity and maintained their inhibitory effect for more than 35 days. In all samples, the formation of a clear zone of inhibition around the discs was not observed

Figure 13 (a) PVC film and (b) PVC-*g*-AA showing no inhibition of the growth of yeast and (c,d) PVC-*g*-AA with 19.5 and 34.1% grafting, respectively, containing crystal violet and showing zones of inhibition of yeasts under discs. In all cases, the discs were removed to see the yeast beneath them.

Figure 14 PP film (surrounded by a continuous line) and PP-*g*-AA with 12.9% grafting and natamycin (surrounded by a discontinuous line). There was a clear zone of yeast inhibition under the film containing natamycin.

because all crystal violet and natamycin not electrostatically bonded were removed from the films through several washes performed in adequate solvents; that implied that there was no antifungal agent available to migrate from the modified films and to diffuse into the surrounding agar.

CONCLUSIONS

The optimal conditions to achieve the UV-induced photografting of AA onto PP, PE, and PVC surfaces have been studied. The method is relatively simple, and high levels of grafting can be obtained after a short reaction time at room temperature. The most reactive substrate for irradiation grafting polymerization under our study conditions is PE films.

As a result of the use of water or acetone as the solvent and the hydrophobic nature of the film substrate, grafting is limited to the outermost surface of the polymer. Besides, water creates crystalline grafting domains in the surfaces of PP and PE.

Microscopy techniques such as OM and AFM have been demonstrated to be useful tools for the characterization of modified films and for the description of their topographical evolution.

Electrostatic bonds of crystal violet and natamycin give films interesting antifungal properties for more than 35 days.

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