Surface Modification of Polyvinyl Chloride with Biodegradable Monomers

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ABSTRACT: Graft copolymerization of sucrose acrylate (SA) onto 55 μm films of poly(vinyl chloride)(PVC) was investigated with benzophenone or 2,2′-azoisobutironitrile as the initiator. The grafting reactions were carried out in a closed cell containing the films to be treated with a solution of the sensitizer and the monomer. In this system, ultraviolet light through a quartz window initiated the reaction by exciting the initiator used. The grafting took place on a PVC surface layer, from the solution. The homopolymer formed during copolymerization was removed by washing. The percentage of grafting was determined by gravimetric measurements and by dye adsorption (crystal violet), and the characterization of PVC(g)SA was carried out by the use of infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and thermogravimetric analysis. The weathering behavior of PVC(g)SA was studied with microorganisms in a growing medium, and the degradation was monitored by the weight loss of the films, FTIR, and SEM. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1195–1201, 1997

Key words: surface modifications; photoinduced graft; PVC; sucrose acrylate

INTRODUCTION

Surface modification is one of the active research areas in the field of chemical reactions of polymers. In many instances, the surface properties may even be more important than the bulk properties of the polymer. The former includes biocompatibility, adhesion, wettability, and resistance to biological degradation processes because microorganisms do not have polymer-specific enzymes capable of degrading them, in addition to their hydrophobic surface that inhibits enzyme activity.[1,2]

To change and adapt these properties to other requirements, a number of methods modifying polymer surfaces have been developed and applied. Radiation-induced surface modification is one of the most thoroughly investigated areas and can result in both a physically and a chemically altered surface. High-energy radiation, gamma or electron beam radiation, and low-energy radiation, such as ultraviolet (UV) light, have been used to initiate surface modification.[3,4] Graft polymerization of monomers on the surface of polymers has been used to induce surface modification.

Many types of common plastics were modified by means of grafting reactions. The works reported in the last few years involve modifications of polypropylene, polyethylene, poly(ethyliden therephthalate), and poly(vinyl alcohol) with acrylic monomers, with the aim of improving the surface characteristics, i.e., wettability, adhesion, and biocompatibility.[5,6] In contrast, grafting reactions on polyvinyl chloride (PVC) have been carried out to obtain biomedical polymers prepared, for example, by using photopolyacrylamide-heparin applied to catheters with antithrombogenic activity.[7]

The interest in degradable polymers has in-

creased recently. The need to obtain biodegradable plastics was in direct response to community interest in the increasing content of postconsumer waste plastics in municipal waste streams.

Degradable plastics can play an important role, together with recycling and incineration, in the reduction of the waste stream. Degradable plastics must retain all of the mechanical properties expected by the consumer and then, when placed in the appropriate environment, degrade more rapidly than conventional disposable plastics.[8]

The main objective of this work was to propose a new methodology that involves the surface modification of commercial films, and in particular on the PVC surface, by using biodegradable monomers such as sucrose acrylate (SA) with the purpose of conferring hydrophilic properties due to the presence of their hydroxyl groups, improving the microbial activity. The grafting was induced by UV irradiation through the film, which was in contact with a solution containing the initiator and the monomer. The method used was effective to obtain surface graftings. The effect of biodegradation in films of PVC(g)SA was analyzed through weight loss, molecular changes followed by infrared spectroscopy (FTIR), and superficial changes by scanning electron microscopy (SEM).

EXPERIMENTAL

Materials and Analysis

PVC was supplied by Vitopel. The fine powder was obtained by suspension polymerization.

The following chemicals were commercially acquired and used: acrylic acid (BASF), sucrose (Mallinckrodt), dimethylformamide (DMF) (Merck), and thionyl chloride (Merck). All reagents were purified before use.

The initiators, benzophenone (BP) and 2,2'-azoisobutironitrile (AIBN) (Fluka S.A.), were dissolved in acetone (Merck). The dye, crystal violet, was purchased from Mallinckrodt. Soil samples were obtained from the CLIMA regional waste treatment plant (Córdoba capital-Pvcia, Córdoba-Rep, Argentina).

The FTIR spectra were performed on films with a Nicolet 5 sxc FTIR spectrometer. DTA and TGA were carried out on a Perkin Elmer 1B in a N_2 atmosphere between 25 and 450°C, with linear heating rates of 10°C min^{-1}.

SEM was performed at the Research Centre of Materials and Metrology, following conventional
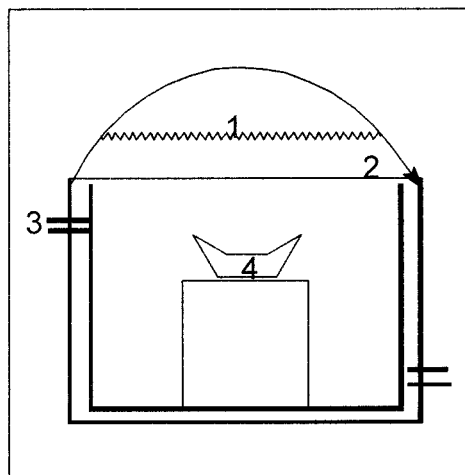

Figure 1 Reactor for surface grafting. (1) lamp, (2) quartz window, (3) N_2, and (4) substrate.

techniques with a Phillips SEM 501 B equipment. Light absorption of the crystal violet was carried out in a Shimadzu UV 260 recording spectrophotometer.

Film Preparation

The films of PVC were prepared by a conventional solvent-casting technique from PVC (powder) dissolved in tetrahydrofurane, with glass Petri dishes as the casting surface. The obtained films of 55 μm were removed after 24 h at room temperature.

Monomer Preparation

Acryloyl chloride was obtained by dropping the acrylic acid over thionyl chloride with a ratio of 1 Eq of —COOH : 1.5 Eq of Cl_2SO, in an ice bath, for 45 min with stirring. The liquid product was purified by distillation. Afterwards, a solution of acryloyl chloride in DMF was allowed to drop over sucrose in DMF, with a ratio of 1 Eq of —COCl : 1 Eq of sucrose. Dropping was made in an ice bath for 40 min, with stirring. Finally, the product was precipitated with toluene, washed, dried, and stored under nitrogen atmosphere.[9]

Graft Copolymerization

The reactions were carried out in a photoreactor constructed in our laboratory (Fig. 1). The substrate was placed in a glass Petri dish, and then 0.5 mL of a solution of initiator (0.2M) (BP or AIBN) and 0.5 mL of monomer were added. The

dish containing the reactives was enclosed in a cell with a quartz window and irradiated with UV light (UV lamp HLF-342 Philips) in nitrogen atmosphere. This process was performed at different times, 3, 4, 5, 8, 10, 13, and 15 min, giving films 1–7, respectively, with BP as the initiator. The same reaction times were used to obtain the films 1–7, respectively, with AIBN. All grafted samples were washed extensively with water to remove the homopolymer formed and then with acetone to take out the rest of the initiator.

Films 1–7 were studied by FTIR. The growth of the grafted layers was measured by determining the adsorption of crystal violet dye on its surface and by gravimetric measurements.

In the first case, films 1–7 were immersed in an aqueous crystal violet solution buffered to pH 4.6 (by the addition of acetic acid and sodium acetate) ($2.5 \times 10^{-5} M$), and the adsorption of the dye was measured, after 48 h at room temperature, by the difference in absorption in the solution before and after each experiment by UV/Vis spectrometry at 600 nm, the previous performance of the calibration curve (Abs. versus concentration).

In the second case, the measurements were performed by weighing the films before and after the copolymerization reactions were carried out. The grafting percentage is expressed as[10]:

$$\% \text{ grafting} = \left(\frac{\text{weight of grafted product} - \text{weight of substrate}}{\text{weight of substrate}} \right) 100 \quad (1)$$

Film 7 was analyzed by SEM, TG, TGA, and biodegradation assays.

Biodegradation Assays of PVC(g)SA

Five soil samples from the CLIMA regional waste treatment plant were collected. The basal medium for the cultivation of soil samples was prepared in distilled water containing soybean (20% w/v) and NaCl (5% w/v). It was autoclaved for 15 min and filtered through sterile gauze, with the finality of removing solid particles, completing the sterilization at 115°C for 20 min more (final pH, 7.5).

Each soil sample was diluted with sterilized basal medium. The cultivation was carried out at 25°C for 48 h; then, the PVC(g)SA films were exposed for their degradation.

The culture soil was placed in a box, with sterile desiccated and preweighed samples of film 7 and PVC (by duplicate). The box was placed outside in an open field. The different samples were removed at different incubation times (7, 15, 30, 45, and 60 days) and rinsed with distilled water, to remove the microbial growth or any soil residues, dried, and weighed to determine their percentage of weight loss. In addition, the samples were checked by FTIR and SEM.

RESULTS AND DISCUSSION

The reason for the modification of a polymer on its surface to increase the hydrophilicity is in most cases a necessity to improve wettability, adhesion, and biocompatibility. In our case, the surface modification was made to improve the interfacial phenomenon between the microorganism and the PVC surface, through the incorporation of SA.

It is know that biodegradation mechanisms can be initiated only on the surface and that their rate depends on the surface area modified with the biodegradable material, that is, on the number of sites per unit area.[11] The overall disintegration mechanism of a film in room medium involves degradation processes and deterioration that include chemical and physical changes. It is thus possible to suggest that surface biodegradation occurs along with oxidations, which are started by the free radicals generated by additives and some impurities present in the polymer; these free radicals can propagate in the polymer matrix, and the oxygen present in the environment reacts with such radicals and forms a radical hydroperoxide, which abstracts a proton from the polymer matrix and thus forms a hydroperoxide group inside the polymer. This group can dissociate by heat or light, yielding more initiated species and thus leading to the formation of free radicals. The propagation steps can be associated with bond breakage of the polymer. Also, crosslinking reactions occur as a result of the interaction of radicals, leading to a decrease of their mechanical properties.[12] Once the superficial biodegradation process is over, the film thickness diminishes, turning into a weakening of its mechanical properties.

We have worked particularly with PVC. The replacement of Cl atoms for SA molecules produces decay of the mechanical properties of a PVC(g)SA film.[13]
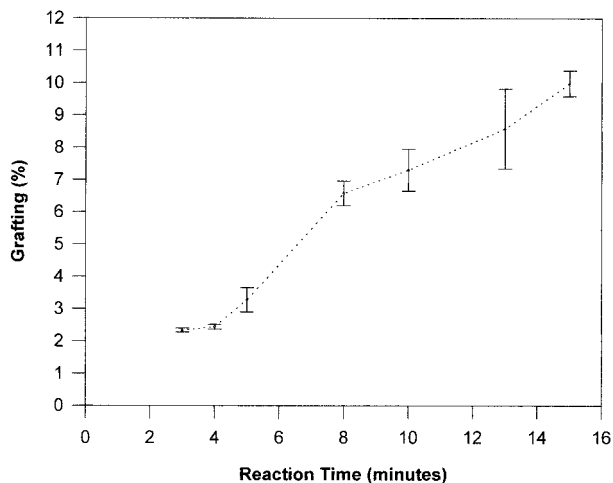
Figure 2 Extent of grafting (%) versus reaction time for films 1–7, with BP as the initiator.

Scheme 1

Figures 2 and 3 (% grafting versus reaction time) were obtained by gravimetric measurements, showing the results of PVC(g)SA graft copolymerizations with BP and AIBN, respectively, as the initiator. Although both BP and AIBN could be used as initiators in the reactions, the copolymerization reaction improved the yield when BP was used, obtaining a higher percentage of grafting at lower reaction times.

The BP initiator reacts as shown in Scheme 1. It adsorbs UV light, and the aromatic ketone group is excited to a singlet state, which by an intersystem crossing (ISC) reverts to a triplet state, abstracting chlorine from the polymer and forming a polymer radical.[14] This (PVC) adds
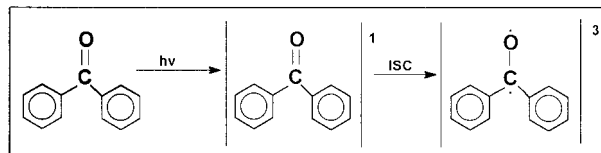
monomer (SA) and forms grafted chains as a layer on the surface.

Figure 4 compares the degradation rates of both products. It is clearly observed as a multistep degradation process for PVC as well as PVC(g)-SA. The characteristic temperatures reported for each decomposition are as follows: initial decomposition temperature (T_i) and maximum rate of weight change (T_m) (the maximum peaks of the DTG curves). For PVC, the T_i is 248°C and the T_m values are 301 and 317°C. For PVC(g)SA, the main process occurs at lower temperatures with $T_i = 114$°C and $T_m = 260$, 280, and 293°C. This indicates that all degradation steps are influenced by the modification introduced in the original structure of PVC.

In Figure 5 are shown the FTIR spectra of the PVC and modified PVC. The PVC spectrum exhibits characteristic bands at 616 and 669 cm^{-1} (—C—Cl). The PVC(g)SA spectrum shows a relative decrease of the bands corresponding to the signal (—C—Cl) and the following additional bands; 1,720 cm^{-1} ($\backslash$C=O) and 3,450 cm^{-1} (—OH), which show a relative increase in films 1–7, as can be seen in Figure 6, when the time is

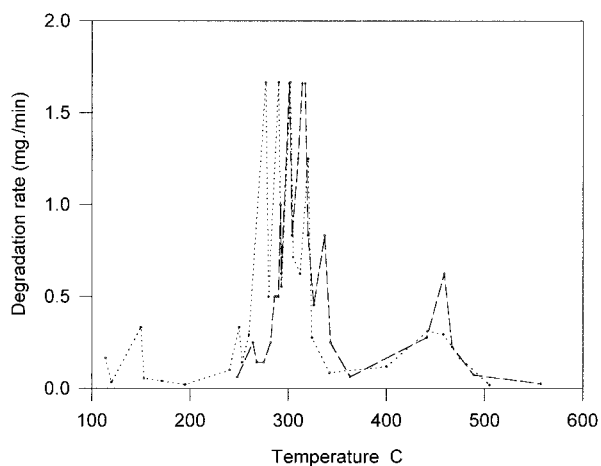**Figure 3** Extent of grafting (%) versus reaction time for films 1–7, with AIBN as the initiator.

Figure 4 DTG curves of (——) PVC and (---) PVC(g)SA : film 7.
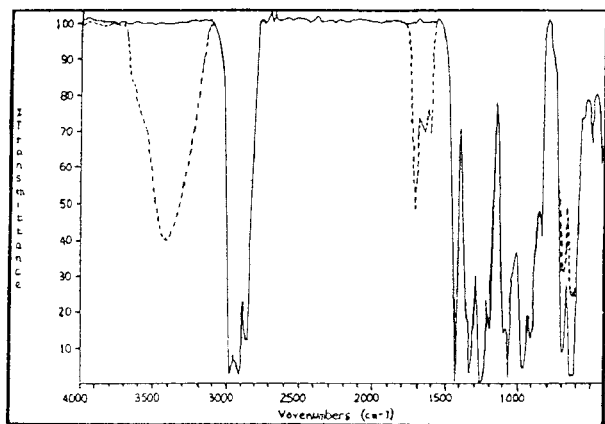
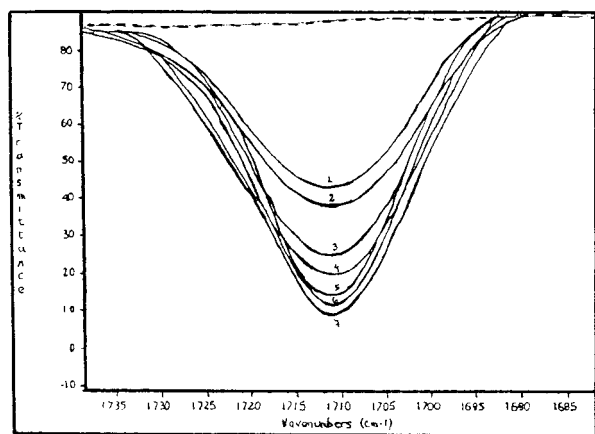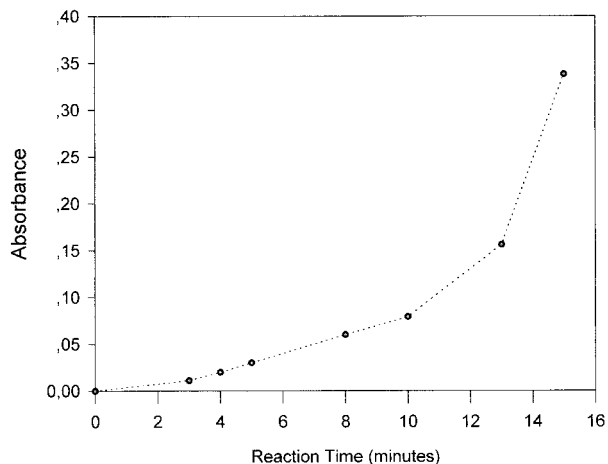**Figure 5** Infrared spectra of (——) PVC and (---) PVC(g)SA : film 7.

Figure 7 Kinetics of surface grafting of PVC with SA by photografting with BP as the initiator, measured as an increase of absorbance at 600 nm after dipping the films in an aqueous solution of crystal violet.

reached. These spectral data are in good agreement with the data presented in Figure 2 (percentage of grafting from the modified polymer).

On the other hand, the growth of the grafted layer as a function of time could be studied after the dye adsorption on the grafted surface. Crystal violet is strongly adsorbed by hydrophilic surfaces. Therefore, it can be correlated with the percentage of grafted SA.

The kinetics of the grafting on the PVC surface, as can be observed in Figure 7, showed a nonlinear growth value, probably due to competitive reactions between grafting and homopolymerization. After an initial copolymerization on the polymer surface, the monomer in excess can either be grafted or homopolymerized.

To observe the type and magnitude of the grafting reaction that took place on the polymer sur-
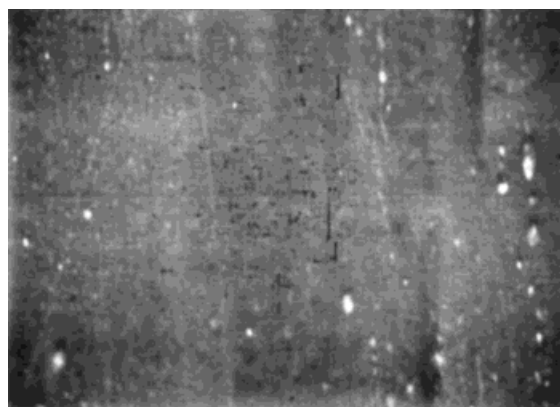

(a)

(b)

Figure 6 Increase of the new signals: (a) —OH of PVC-(g)SA : films 1–7, (b) —CO of PVC(g)SA : films 1–7.
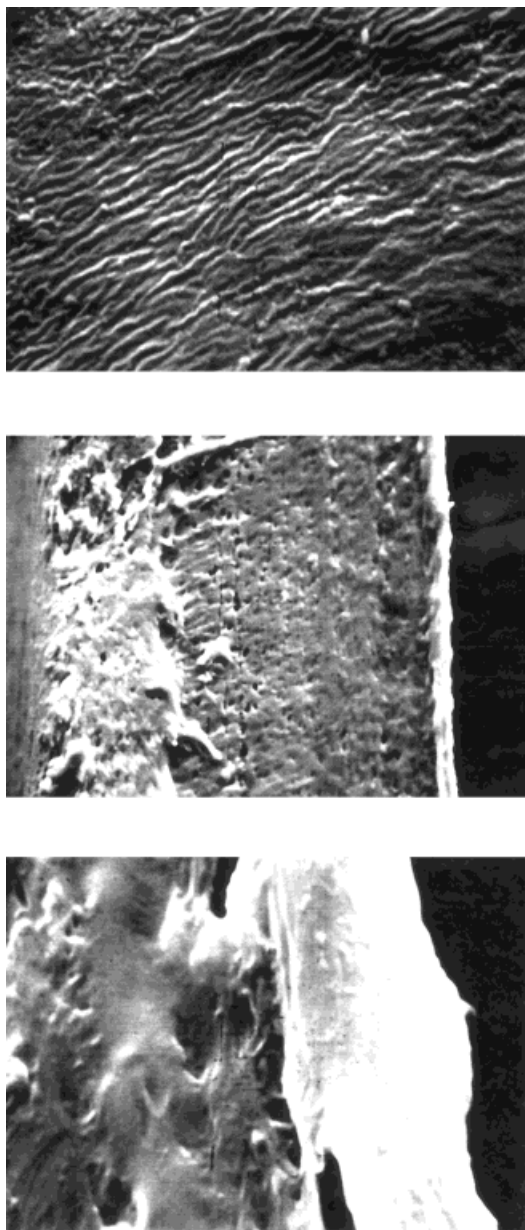

Figure 8 Unmodified PVC surface (×640) by SEM.

Figure 9 PVC(g)SA (film 7) by SEM: (a) PVC(g)SA surface (×640), (b) PVC(g)SA cross-section (×640), and (c) PVC(g)SA cross-section (×5,000).

face, SEM observations of cross-sections and surfaces of the original and modified PVC were carried out. The grafting processes determined a modification of the appearance of PVC films. The clear PVC surface is shown in Figure 8. In Figure 9, a layer of SA distributed onto the PVC surface is shown.

A preliminary report indicated that the utilization of the starch portion of a copolymer with polymethyl acrylate by different fungi increases the

Table I   Weight Loss of PVC(g)SA (Film 7) After Microbiological Assays, Over 60 Days

Sample	Time (days)	Weight Loss	
		g	%
PVC(g)SA-film 7	7	0.044	4.9
	15	0.063	7
	30	0.113	12.5
	45	0.125	13.8
	60	0.135	15
PVC-control	7	ND[a]	ND
	15	ND	ND
	30	0.002	0.22
	45	ND	ND
	60	0.003	0.33

[a] ND, not determined.

surface area of the polymethyl acrylate, thereby increasing its susceptibility to microbial degradation.[15] PVC is not biodegradable; the weight loss observed after 60 days (0.25%) is insignificant compared with that observed for the PVC modified (Table I), indicating that the weight loss observed, for the last material, is attributable to the modification of PVC with SA.

Table I gives the weight loss of the PVC(g)SA (film 7) during the microbiological degradation for 60 days. The extent of weight loss for the PVC-modified films was 15%.

The FTIR spectra of the graft copolymer show a series of characteristic absorbance peaks. These can be assigned to a specific structure in the compounds and used to follow the loss of those structures[16] when the products are submitted to degradation processes.
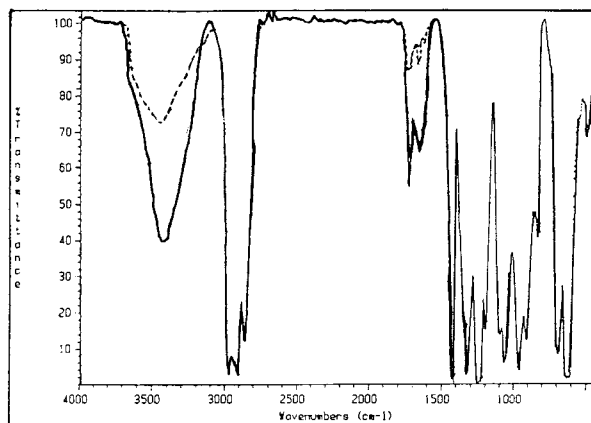

Figure 10 Infrared spectra of PVC(g)SA (——) before and (- - -) after 15 days of incubation.
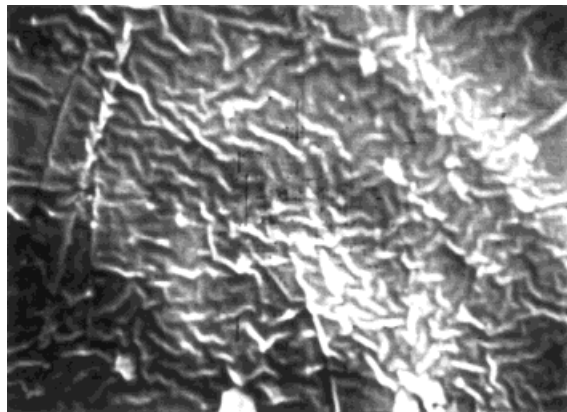
Figure 11 PVC(g)SA, after 15 days of incubation, by SEM.

Figure 10 shows PVC(g)SA spectra, which have been taken before and after 45 days of incubation, in which a significant diminution of characteristic signals of hydroxyl and carboxyl groups can be observed. Figure 11 shows SEM of the surface of the PVC(g)SA film after the 45 days (incubation period). The surface of the degraded film is apparently blemished by the microorganism.

CONCLUSIONS

The method using BP to achieve grafting of SA onto the PVC surface was studied, and a good level of grafting was obtained after only a few minutes of reaction. AIBN was also used in this surface modification technique, but a lower grafting percentage was obtained. By using this method, we succeeded in introducing hydroxyl groups onto a PVC surface, changing their hydrophobic properties, which normally hinders the enzymatic activity of microorganisms. The data obtained by microbiological assays show that the microorganisms present in the soil samples from the CLIMA regional waste treatment plant were able to utilize the PVC modified as a source of carbon, thus providing significant evidence about the biodegradability of these films in a soil environment.

PVC is frequently used as a packaging material, with a high percentage in waste disposal streams. Our society produces many commercial products of fully synthetic materials. From the promising results obtained in this study about the

surface biodegradation, it is our intention to apply these investigations to other commercial films that lack halogen groups in their structure.

The copolymerization of synthetic backbones with natural side chains could be considered as a way of producing compounds more sensitive to degradation in a natural environment. We believe that this type of model could be useful to the development of material that can meet not only engineering but also biodegradation requirements.

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