

Surface Modification of Poly(propylene) by Photoinitiators: Improvement of Adhesion and Wettability

P. Castell,¹ M. Wouters,² G. de With,¹ H. Fischer,³ F. Huijs²

¹Laboratory of Solid State and Materials Chemistry, Department of Chemical Technology and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

²Department of Polymer Technology, TNO Industrial Technology, P.O. Box 6235, 5600 HE, Eindhoven, The Netherlands

³Divisie Modellen en Processen, TNO TPD, P.O. Box 595, 5600 AN Eindhoven, The Netherlands

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ABSTRACT: Different benzophenone-type photoinitiators were photografted onto poly(propylene) (PP). The polymer surfaces were analyzed by means of contact angle measurements, UV spectroscopy, and FTIR-ATR. The modified samples showed a better wettability and higher surface energies, increasing from 26 mN/m for pure PP to 36 mN/m for the modified samples. The UV spectrum of the modified PP films showed two absorption bands that could be related to the grafted initiator. The effect of irradiation time and photoinitiator concentration was investigated. Different acry-

lates were grafted efficiently onto the modified polymer surfaces. FTIR-ATR and contact angle measurements confirmed the presence of the grafted chains. The surface energy of the grafted surfaces of samples increased to 70 mN/m, depending on the type of acrylate used. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2341–2350, 2004

Key words: adhesion; modification; photografting; poly(propylene) (PP); wettability

INTRODUCTION

In many applications plastic materials suffer mechanical impacts and other conditions that lead to a loss in transparency and therefore to a reduction in the performance of the material. To avoid these problems and to give plastics the desired surface finish, different coatings have been developed. However, polyolefins have a hydrophobic, chemically inert surface. These surfaces cause problems in several applications because of their inertness with respect to their adhesion, coating, painting, coloring, laminating, and so forth, thus limiting the applicability of polyolefins. Because of their lack of functionalities these materials require a chemical¹ or physical² treatment before a coating can be successfully applied. This implies a tailoring of the surface properties of these materials.^{3,4}

Thus, modification of the surface properties of polymeric materials has been an important field of investigation in the past to satisfy the continuously increasing commercial demands for polymeric materials with specific properties.

In industry the main methods of improving adhesion on polyolefins are based on chemical modification of the interfacial polymer chains with polar groups as hydroxyl, carbonyl, and carboxylic acid

groups.⁵ Another approach is the use of block copolymers as primers, incorporating a special type of polyolefins composed of a polyolefin-like part and a polar part that interact or react with the desired material, thus increasing the adhesion on the polyolefin.⁶

Chemical methods without solvents have been widely used for the surface modification of polyolefinic materials from an economical point of view. Flame treatment⁷ and plasma treatment such as corona,^{8–10} low-pressure glow discharges,¹¹ and others have been described previously and are used especially in the automotive industry. Such surface-modification techniques are difficult to control, often cause problems with respect to uniformity and reproducibility, and present extra disadvantages (i.e., they require a short time between treatment and application of the coating). Free-radical grafting has also been used on an industrial scale. This process is performed during extrusion of the material and involves the formation of free radicals along the backbone of the olefin.^{12,13} However, such materials often show a degradation of mechanical properties attributed to side reactions such as chain scission. Furthermore, the grafted material is composed of a mixture of modified and pure material and the adhesion improvement depends on the surface arrangements and the diffusion of chains. A review by Rätzsch¹⁴ discusses all the radical reactions on poly(propylene) (PP).

The use of UV radiation offers an excellent alternative because of its simplicity and cleanness. Photoini-

Correspondence to: P. Castell (p.castell-muixi@tue.nl).

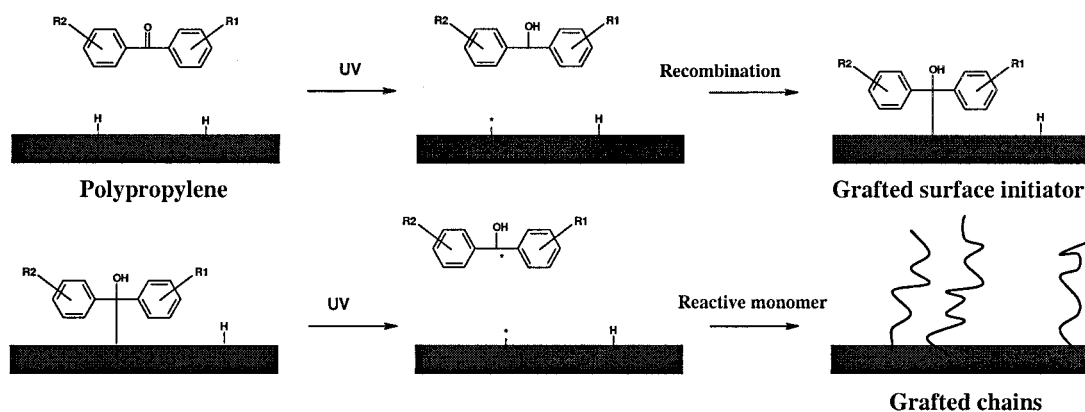


Figure 1 Grafting of reactive monomers onto PP surfaces using a two-step method.

duced grafting is known to be a useful technique for the modification or functionalization of polymeric surfaces because photochemically produced triplet states on carbonyl groups can abstract hydrogen atoms from almost all polymers, thus generating radicals. Therefore, high concentrations of active species can be produced locally at the surface without altering the bulk properties of the polymer. In addition to the simplicity of the procedure, the equipment cost is lower for UV irradiation than for ionizing irradiation. This technology has been applied to modify the surface of various polymers,^{15,16} especially polyolefins,^{17–26} and to improve adhesion and surface wettability. As mentioned previously this technique requires the use of photoinitiators that generate radicals on the surface by proton abstraction; for this purpose different photoinitiators have been used, such as benzophenone (BP), 4-chlorobenzophenone, and hydroxycyclohexylacetophenone. In a second step, the initiation of the polymerization of different monomers occurs at the reactive sites generated on the solid surfaces, resulting in the grafting of the monomers on the surface.

Homopolymerization of the applied monomer competes with the grafting. The approach proposed by Bowman et al.²⁷ has solved this problem. The grafting polymerization in their study is performed in two steps. In a first step the BP abstracts one proton from the surface of the substrate to form semipinacol radicals and radicals in the surface itself. These radicals recombine with the surface radicals to form a so-called surface initiator, which is stable and can be stored for further usage. The surface initiators can react in a second step with a monomer solution initiating the polymerization under the presence of UV light. The formation of homopolymer is reduced because the semipinacol radicals generated have a very short lifetime and prefer to recombine or terminate growing chains (see Fig. 1).

In this article we describe the surface modification and characterization of PP with some BP derivative

photoinitiators. For this purpose we used some commercial photoinitiators. The grafting of the initiators on the surface improved the wetting and the adhesion behavior of the PP. We studied the effect of temperature, concentration, irradiation time, and solvents on the surface properties of the modified polymer surfaces.

EXPERIMENTAL

Materials

The poly(propylene) sheets (PP, 10 cm × 10 cm × 2 mm) used were supplied by Vink Kunststoffen (Didam, The Netherlands). The surface was cleaned with acetone and ethanol before use. Dichloromethane was distilled under reduced pressure; acetone, methanol, ethanol, and toluene were used as received from Aldrich Co. (Milwaukee, WI). The photoinitiators benzophenone (BP), 4-methoxybenzophenone, 4-hydroxybenzophenone, benzyl, and 9-fluorenone were used as received (Aldrich). The acrylic acid, pentaerythritol triacrylate, and 2-hydroxyethyl acrylate were used as purchased from Aldrich.

General methods

¹H-NMR and ¹³C-NMR spectra were recorded at room temperature on a Varian Gemini 400 MHz spectrometer (Varian Associates, Palo Alto, CA), deuterated with tetramethylsilane as an internal reference.

Contact angle measurements

The contact angles of water and diiodomethane were determined using a contact angle measuring apparatus (Krüss, Hamburg, Germany) and the software Drop Shape Analysis 1.0. The surface energy was calculated using the values of the contact angle of the

water and diiodomethane (average of 10 droplets) by the Owens–Wendt–Rabel–Kaeble method.²⁸

FTIR-ATR

The presence of the initiator as well as the acrylates grafted on the surface were identified with FTIR spectroscopy with an attenuated total reflectance modulus (ATR; IR spectrometer; Bio-Rad, Hercules, CA). The samples (size 20 × 20 mm) were placed between the diamond crystal (refractive index 2.5) and a stainless-steel cover with a variable pressure, to ensure good contact between the sample and the crystal. Usually 20 scans with a resolution of 4 cm⁻¹ were collected.

UV spectroscopy

The UV absorption spectra of the photoinitiators were measured in a Hitachi UV/vis U-2001 spectrophotometer (Hitachi, Osaka, Japan) using chloroform as solvent. The spectra of the pure PP and the modified PP were recorded directly on the films about 100 μm thick.

Grafting of the photoinitiator

The photoinitiator films were prepared by dissolving the correct amount of photoinitiator in methanol, dichloromethane, acetone, or toluene, and applying them onto PP sheets with a wire bar, resulting in a film thickness of 30 μm. The solvent was evaporated and the samples were then irradiated with UV light at 20 cm distance from the source with a high-pressure mercury lamp (H-type, 400 W, Osram GmBH, Berlin, Germany) in a UVA Cube (from Dr. Hönle AG, Gräfelfing, Germany), under a nitrogen atmosphere. The irradiation times were varied between 10 and 600 s and the UV doses were measured using a UV Power Puck radiometer (Electronic Instrumentation and Technology, Sterling, VA). The samples irradiated were washed with ethanol and acetone and dried overnight. On storage the samples were covered with aluminum foil to prevent photodegradation.

Grafting of acrylates

Acrylic acid, pentaerythritol triacrylate, and 2-hydroxyethyl acrylate were grafted onto pure and modified PP sheets at room temperature. Thin films of the different acrylates were applied using a wire bar of 100 μm and a quartz plate (2 mm thick) to cover the whole sample to ensure a good contact between the acrylate and the PP and also to prevent oxygen inhibition. The grafting was initiated by UV light with irradiation times between 30 and 300 s. After irradiation the samples were cleaned using boiling water in the case of acrylic acid, whereas acetone or ethanol

was used for the other acrylates. The samples were dried overnight under vacuum before any measurements.

RESULTS AND DISCUSSION

Surface modification

The irradiation of a BP-type initiator excites the molecule to a triplet state. This excited molecule can abstract a proton from the PP in the absence of another source and generate a radical on the surface.²⁷ These radicals can recombine with the semipinacol radicals also generated, as explained previously in Figure 1. The generation of a chemical bonding between the initiator and the surface results in grafted species, which are called “surface initiators” because they can generate radicals by exposure to UV light. The covalent bonding can be broken and the radicals on the surface are regenerated again, as shown in the same figure.

The minimal concentration required to obtain complete coverage of the surface was estimated, assuming that all the molecules of benzophenone lie flat on the surface. The minimal concentration required to fully cover the surface was approximately 0.002 wt %. Thus, in the conditions used in our experiments, the complete coverage of the surface was ensured.

A series of experiments was performed to evaluate the different factors affecting the grafting reaction:

- Influence of the UV irradiation on surface properties of the PP.
- Influence of the solvent: acetone, dichloromethane, and toluene were tested as solvents to form the film of the initiator.
- Concentration of photoinitiator.
- Possible inhibition effect of oxygen: irradiation under both air and nitrogen were studied.
- Nature of the photoinitiator.

Surface analysis

Contact angle measurements

One of the most sensitive techniques used to analyze the outer layers of the polymer surfaces is the measurement of the contact angle. The surface energy extracted from such experiments provides us information about the properties of the polymer such as wettability, heterogeneity, and surface mobility.

There are different methods of evaluating the contact angles. They can be divided into two main groups, static and dynamic measurements. In the first case the measurement takes place on the solid/liquid interface, which is not in motion. In the second case the liquid is in motion with respect to the solid phase. In our studies we will use the static measurement of the

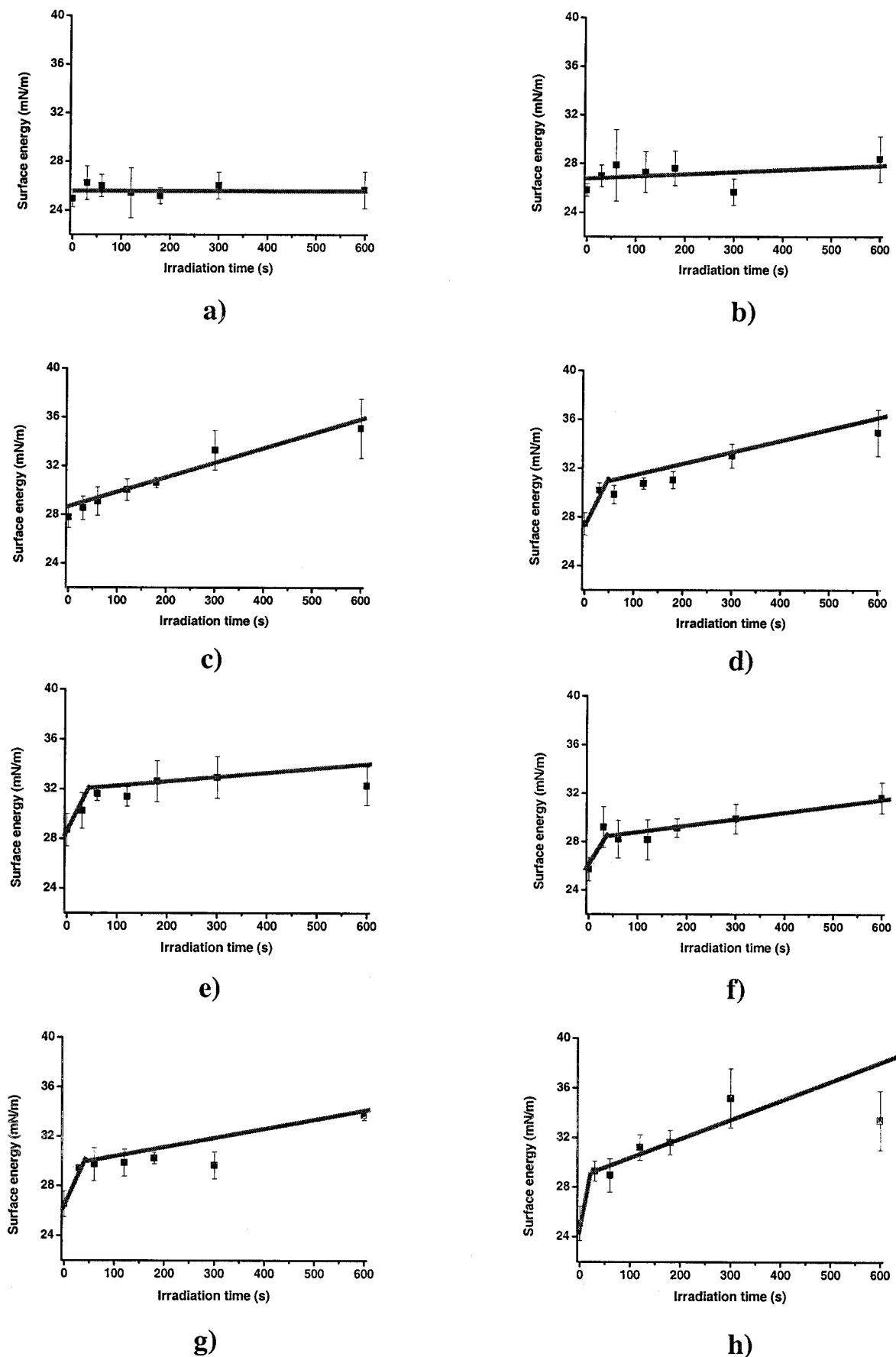


Figure 2 Surface energy of the PP versus irradiation time: (a) no photoinitiator, (b) 0.5 wt % BP, (c) 1 wt % BP, (d) 2 wt % BP, (e) 5 wt % BP, (f) 10 wt % BP, (g) 15 wt % BP, and (h) 25 wt % BP. The lines drawn are a guide to the eye.

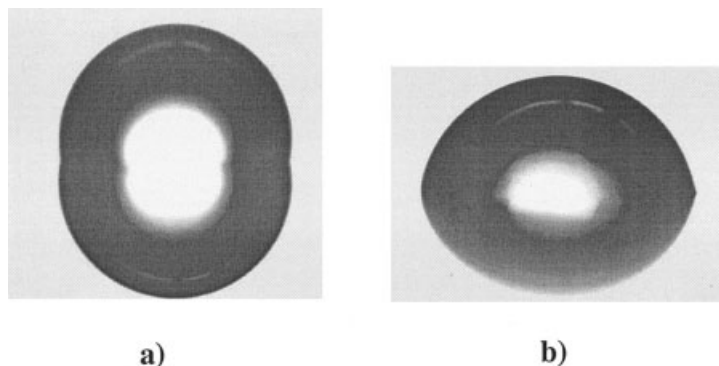


Figure 3 Contact angle of water on (a) pure PP and on (b) 600 s irradiated PP covered with a film obtained from a 5 wt % solution of BP.

contact angle of water and diiodomethane to calculate the surface energy as described in the experimental section.

The surface energy of the untreated PP has been determined to be in the range between 26 and 29 mN/m, and the initial contact angle displayed in contact with water is about 103°.

The effect of irradiation on pure PP samples was almost negligible and no significant differences in the surface energy were observed during the irradiation [Fig. 2(a)]. The use of different solvents (acetone, dichloromethane, and toluene) had no effect on the surface energy. Similar values were obtained for all the solvents tested and toluene was chosen as the solvent because it dissolves all the photoinitiators used.

BP solutions of 0.5 to 25 wt % in toluene were prepared; a film 30 μm thick was applied to the PP and irradiated from 30 to 600 s. No significant differences in the surface energy can be observed when 0.5 wt % of BP is used [Fig. 2(b)]: the surface energy of the PP remains almost constant, indicating that no changes occurred on the surface. However, a significant increase in the value of the surface energy as well as a decrease in the contact angle of water can be observed at higher concentrations [Fig. 2(c)–(h)]. The increase in the surface energy is produced during the first 60 s of irradiation and, after that, the value remains almost constant. The increase from 26 to 34 mN/m is a clear indication that some changes had occurred in the surface: the initiator can abstract protons from the surface and react with the originated radicals, resulting in the grafting of the initiator on the surface. Further analysis of the surface is required to prove the presence of the initiator. The contact angle of water decreased from 103 to 80–90°, indicating that the appearance of hydrophilic groups on the surface originated from the grafted initiator (Fig. 3).

The presence of oxygen during irradiation has an inhibition effect, given that no differences in the surface energy were observable after irradiating in air. Only on irradiation under nitrogen is an increase in

surface energy observable that can be associated with the grafting of the photoinitiator, as we will prove later. The inhibition effect of oxygen in the grafting reaction of BP has been observed by different authors. Yang and Rånby²⁰ concluded that the scavenging interaction of oxygen with the primary free radicals formed is responsible for the inhibition effect of the oxygen in the grafting reaction using BP-type photoinitiators.

Other photoinitiators were tested under the same conditions and the resulting modified PP sheets were analyzed. The initiators tested were 4-hydroxybenzophenone, 4-methoxybenzophenone, benzyl, and 9-fluorenone.

To evaluate the efficiency in the grafting reaction of the different initiators, different PP sheets were modified using solutions of the different initiators in toluene. The concentration used was 5 wt % in all cases, and the irradiation time was from 30 to 600 s. The surface energy of the modified surfaces was evaluated and used to compare the different efficiencies of the photoinitiators. It was found that the methoxy derivative led to values of surface energies comparable to those obtained by using BP. For all the other initiators tested the differences in the surface energies were almost negligible, indicating that low grafting occurred under the conditions studied. Samples treated with 4-methoxybenzophenone showed the same tendency during irradiation time as described previously for BP. Surface energies were attained, in this case of 36 mN/m, that can be related to the different polarities of the two initiators or the different scattering patterns of the initiators, as explained by Yang and Rånby²⁰ (Fig. 4).

The initiators most commonly used for grafting acrylates or other monomers onto PP are BP and its derivatives.^{22,24} To our knowledge there are few studies that compare the efficiency of different photoinitiators. DeSimone et al.²¹ published a study on the grafting of styrene onto PP, comparing the effect of BP

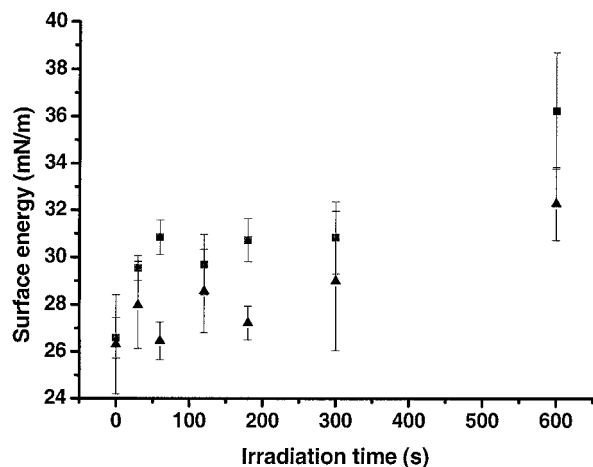


Figure 4 Surface energy of the PP versus irradiation time using: (■) 5 wt % 4-methoxy-benzophenone as photoinitiator and (▲) 5 wt % BP.

and benzoin ethyl ether and concluding that the BP is more active than the other initiator.

Yang and Rånby²⁰ studied the effect of different initiators (benzophenone, benzyl, and fluorenone) on the photografting efficiency of different acrylates on polyethylene (PE) films. They concluded that the grafting efficiency of BP is largely independent of the concentration used; on the other hand, fluorenone shows the greatest dependency on concentration. The efficiency decreased concomitantly with the decrease in initiator concentration. Finally, benzil showed an intermediate behavior. This effect is explained by Rånby as the scattering

effect of the photoinitiator. In the UV coating industry, the scattering effect of the photoinitiator is an important variable to balance the curing with the coating thickness. In their photografting system the intensity of the UV light that reaches the interface depends on the absorption and the scattering of the light. The stronger the scattering effects, the weaker the intensity of the light that reaches the surface, resulting in less grafted polymer. Rånby proved that BP has the least scattering effect and was the most effective initiator in the photografting reaction. In our study the screening effects produced by scattering could be responsible for the lower reactivity of some of the initiators studied. Benzophenone and 4-methoxybenzophenone are the most effective initiators in the conditions used in our study.

Nuclear magnetic resonance

The solutions that were used to clean the surfaces after treatment were analyzed by means of ¹H- and ¹³C-NMR. The solutions obtained were evaporated to dryness under reduced pressure and the residue obtained was dissolved in CDCl₃. The spectra of the residues obtained when no initiator was applied showed only traces of acetone used in the cleaning procedure. Thus, the solvent used for applying the initiator does not dissolve the PP or any of the additives that the PP could contain. The solutions obtained from the modified samples with BP showed BP as the only residue from the reaction (Fig. 5). A large excess of BP was used, thus ensuring complete coverage of the surface.

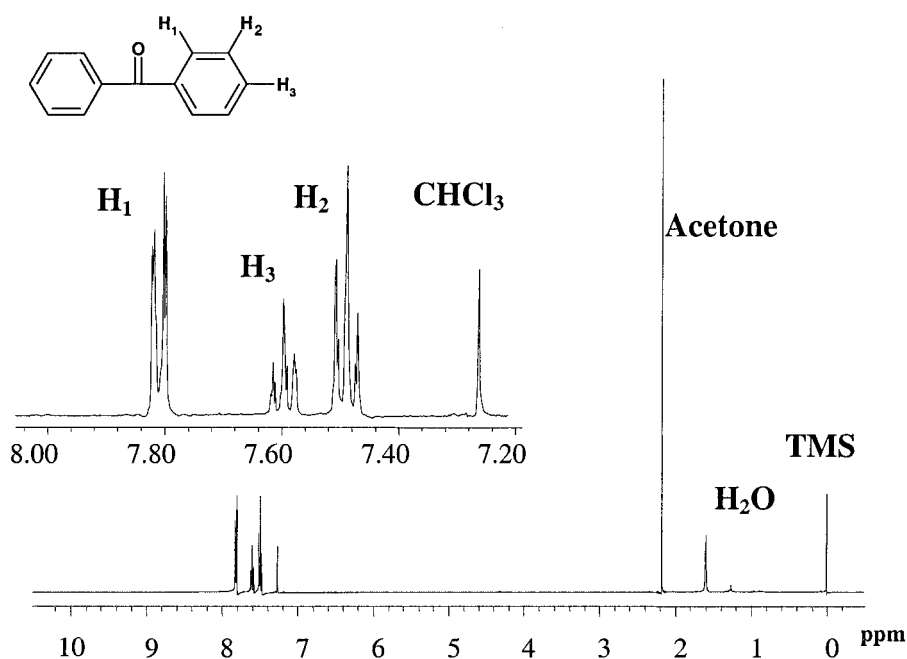


Figure 5 ¹H-NMR spectra in CDCl₃ of the residue obtained in cleaning the PP covered with a film of 5 wt % BP irradiated for 600 s.

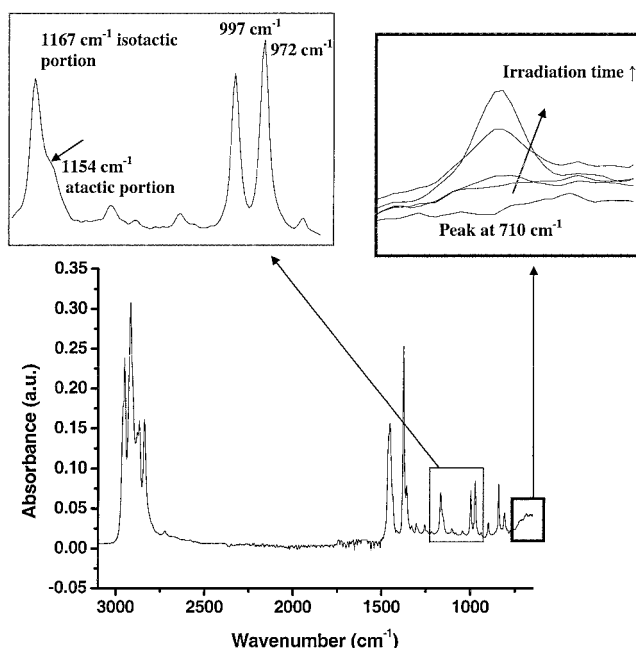


Figure 6 IR spectra of the used PP. Inset: variation absorption peak at 710 cm^{-1} versus irradiation time on samples grafted with 5 wt % BP solution.

Attenuated total reflectance infrared spectroscopy (FTIR-ATR)

The pure and the modified PP sheets were studied using FTIR-ATR spectroscopy. FTIR-ATR is a very surface selective technique and allows the study of the modification of the outermost layer of the PP surface.²⁹ In this technique the surface to be analyzed is placed in contact with an IR-absorbing material with a high refractive index (ATR crystal). The radiation beam penetrates the sample and part is reflected. The spectrophotometer measures the attenuated radiation as a function of the wavelength, obtaining the spectral characteristic for the sample. Depending on the angle of incidence of the beam the analyzed depth is different (from 1 to $20\ \mu\text{m}$), allowing the study of surfaces and their composition.

The resulting spectra of the pure PP showed characteristic bands at 2953 , 2916 , 2872 , 2839 , 1452 , 1375 , and 1358 cm^{-1} , associated with the stretching and bending of methylenic and methynic groups. The band at 1167 cm^{-1} was attributed to the isotactic portion and also those present at 997 and 972 cm^{-1} . They are used to quantify the tacticity.³⁰ All these bands showed the high isotacticity of the PP used (Fig. 6).

There are a few differences observable for the spectra obtained from modified PP surfaces, as follows: (1) a broad band centered on 3400 cm^{-1} that may be attributed to either humidity or hydroxylic groups from the semipinacol radicals; (2) a band at 1640 cm^{-1} that may come from the same hydroxylic group; (3) a band at 710 cm^{-1} that can be attributed to the bending

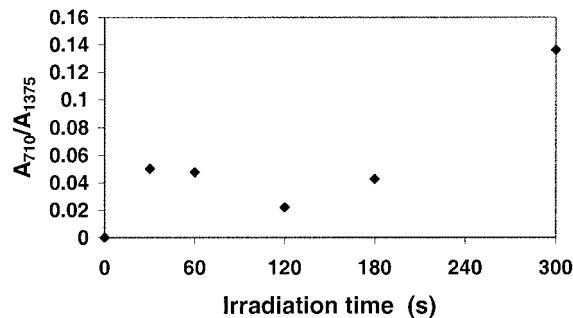


Figure 7 Variation of the area ratio of the 710 and 1375 cm^{-1} peaks (A_{710}/A_{1375}) in modified PP with a solution of 5 wt % BP versus irradiation time.

of an aromatic ring. We measured the IR spectra of all the surfaces modified with a 5 wt % BP film irradiated from 30 to 600 s. The integration of the band at 710 cm^{-1} , compared with the reference band corresponding to the bending vibration of the methyl group (1375 cm^{-1}), yielded the results shown in Figure 7. The peak intensity at 710 cm^{-1} increased with increasing irradiation time, indicating that the amount of aromatic ring is higher. This proves again the grafting of the initiator to the surface (Fig. 7). These results are in accordance with results obtained by the surface energy measurements: the surface energy increases concomitantly with the increase in irradiation time and, by FTIR-ATR, we can observe a higher content of phenyl rings. The signal at 710 cm^{-1} is an indication that the initiator is covalently grafted onto the surface.

UV spectroscopy

For the absorption experiments transparent PP films were used as substrates. These substrates were grafted with photoinitiator using a solution of 5% of BP in toluene as described in the experimental section.

The irradiated PP has no absorption bands in the UV region, nor does the nonirradiated sample. However, the modified samples with BP present an absorp-

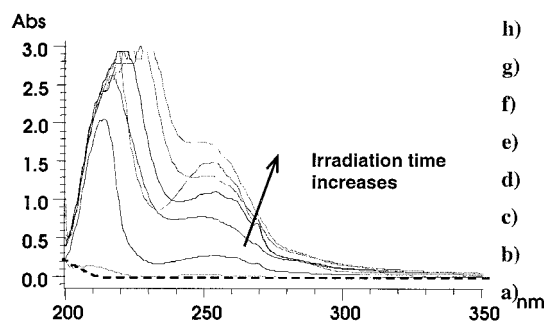


Figure 8 UV absorption spectra of (a) a PP film, (b) a film covered with a layer of BP irradiated 0 s, (c) 30 s, (d) 60 s, (e) 120 s, (f) 180 s, (g) 240 s, and (h) 300 s.

tion band around 250 nm and a higher intensity band centered at 220 nm (Fig. 8). These two absorption bands could be related to the grafted initiator and the concentration increases with the irradiation time until the maximum value after 300 s of irradiation is reached. The presence of this absorption in the UV region, even after washing the modified PP substrates with abundant acetone, is a clear evidence that the initiators are covalently grafted onto the surface.

Although we have attempted to use other techniques such as DRIFT, XPS, and AFM to prove the grafting and to determine the thickness of the grafting layer, no clear conclusions could be obtained from the results. In all cases some differences were observed for the modified samples: higher oxygen content and some characteristic signals originating from groups corresponding to the photoinitiator were observed, but in some cases the high noise and in other cases the low differences make a correct quantification very difficult.

Time stability

One of the main problems of industrial methods used to modify the surface of PP is the stability of the modified surface. The plasma treatment is widely performed on polyolefins and other polymeric substrates but, depending on the nature of the substrate, the plasma treatment is more or less effective. It is well known that the plasma treatment is more effective on PE than in PP, attributed mainly to the nature of the PP surface. Moreover, even when the PP surfaces can be modified, like other polyolefin surfaces, they generally have a tendency to reorganize and reconstruct, thus losing their surface properties.^{31–34} This reorganization is time dependent and this is the main reason for the poor time stability of the plasma modification of PP. The problem of poor time stability can be compensated by using grafting methods where a functional group is attached to the surface. To be able to modify the surface properties of PP for long periods of time is interesting from an application point of view. The modification of the PP could be done by the supplier and the final user could buy the modified PP and use it as needed.

To study the time stability of the modification, different samples of PP were modified with a solution of 5 wt % of BP irradiated for 600 s and stored in the dark. Surface energy of the samples was monitored during a period of 3 weeks, and was found to be almost constant at about 37 mN/m, during the first days after modification, and after 3 weeks the value decreased to only 35 mN/m (Fig. 9). The surface energy of the pure PP is 26 mN/m, so the changes observed are significant. The grafting of photoinitiators onto PP results in a stable modification of the surface properties. Modified samples can be stored

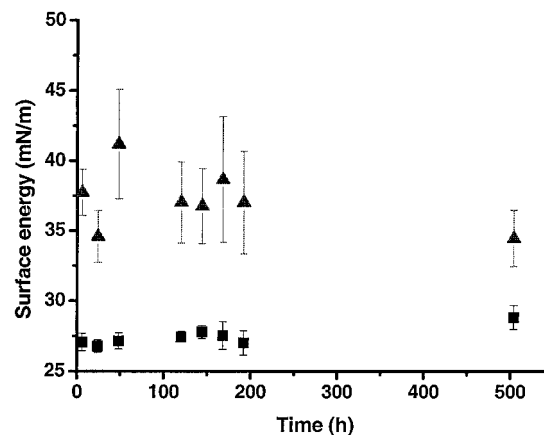


Figure 9 Surface energy of (■) nonmodified PP and (▲) modified PP sheets with 5 wt % BP solution versus time.

and used with the same effectiveness even after 3 weeks after their preparation.

Grafting of acrylates

To prove further the presence of the grafted initiator onto the modified PP substrate we used the modified samples as substrates to graft onto some acrylic monomers. The initiator present on the surface can generate radicals upon UV radiation and initiate the polymerization, as we discussed earlier. As a result we were able to obtain grafted chains of polymers on the surface.

The acrylic monomers chosen were acrylic acid, 2-hydroxyethyl methacrylate, and pentaerythritol triacrylate. To verify the grafting reaction the acrylates were grafted onto both pure PP and modified PP. Also an acrylate containing 1 wt % of BP was grafted onto pure PP as control. For the irradiation experiments the surface was covered with a quartz plate that had the same size as that of the PP sheet to ensure good contact of the pure PP with the different acrylates. The thickness of the acrylate films was approximately 100 μm .

The irradiation occurred in the UVA Cube, as described in the experimental section. The irradiated samples were washed with adequate amounts of solvent, extracted for at least 4 h, and dried overnight. The surface energy of all the samples was measured using the contact angle of water and diiodomethane, as described earlier.

The surface energy of the pure PP samples did not change significantly and remained almost constant around 28 mN/m with irradiation time, although in the case of the modified samples a large increase was observed even in the first 20 s of irradiation. The surface energy increased from 30 to 70 mN/m as the contact angle of water decreased from 100 to 20° in the

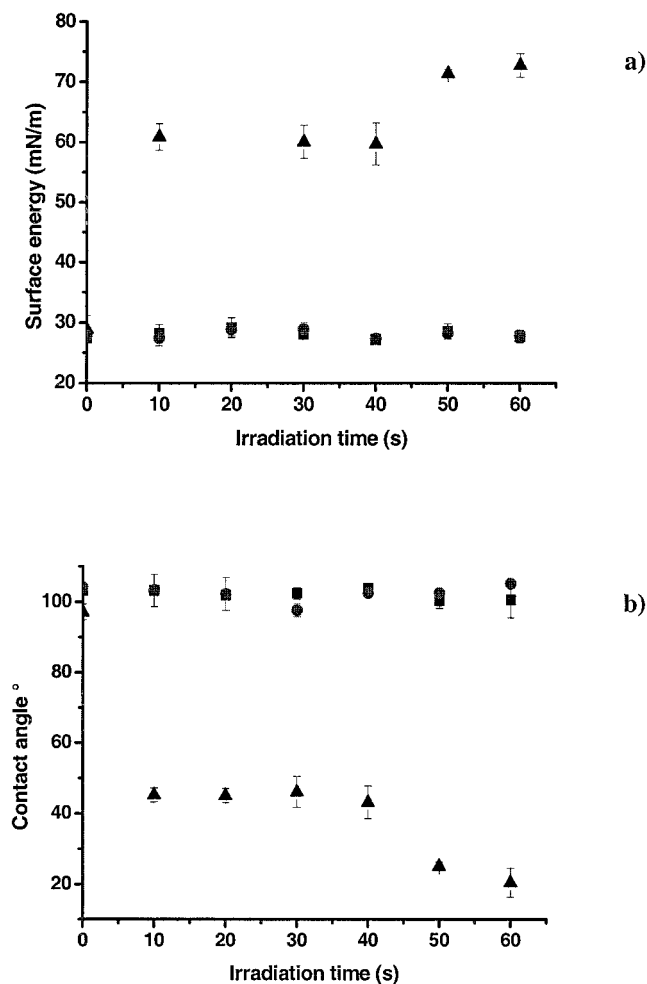


Figure 10 (a) Surface energy versus irradiation time of the PP grafted with acrylic acid: (■) pure PP, (●) pure PP (acrylic acid + 1 wt % BP), and (▲) modified PP with BP. (b) Contact angle (water) versus irradiation time of (■) pure PP, (●) pure PP (acrylic acid + 1 wt % BP), and (▲) modified PP with BP.

case of acrylic acid (Fig. 10). Decker et al.²² reported the grafting of acrylic acid on PP films using UV light. In their study they measured by IR spectroscopy the grafting of acrylic acid by the appearance of a characteristic band at 1670 cm^{-1} . The contact angle of water was also measured and a decrease from 90 to 30° was measured when acrylic acid was grafted; the thickness of the grafted acrylate was estimated to be about 2000 nm . The surface energy increased from 24 to 60 mN/m ; other acrylates were studied with similar values of surface energy and contact angle of water. Bergbreiter et al.³⁵ described the grafting of acrylic acid on PP using an etching oxidation. In their study they reported a decrease of the contact angle of water on PP from 105 to 20° when acrylic acid was grafted on the surface.

When other acrylates were used the same tendency was observed. The sample containing acrylic acid and

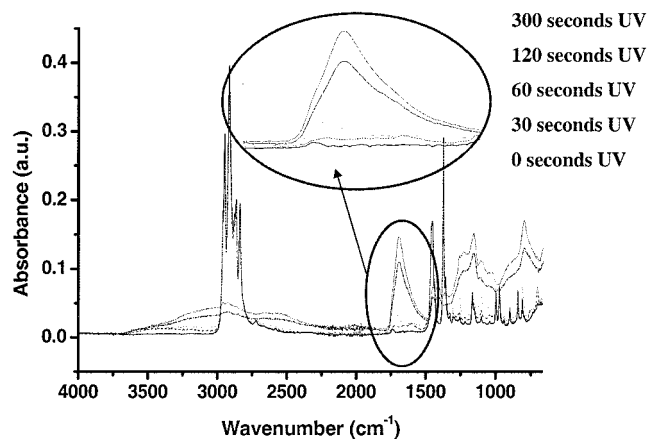


Figure 11 FTIR-ATR spectra of the modified PP grafted with acrylic acid irradiated for different irradiation times.

BP as initiator had a low grafting efficiency, which can be attributed to the affinity of the monomer to the different generated radicals, the surface radicals, the macromolecular radicals, and the semipinacol radicals, which have increasing polarity in this order. Acrylic acid is a polar monomer and therefore will have a better affinity with the semipinacol radicals initiating the polymerization, leading to homopolymerization and a low grafting of polymeric chains. In our study we observed that the acrylates react with only the modified samples because of the presence of the grafted initiator in the surface reaching surface energies of 58 mN/m in the case of 2-hydroxyethyl acrylate and 64 mN/m when triacrylate was used.

The increase in surface energy can be attributed to the grafting of the acrylates onto the treated surfaces as a result of the higher content of polar groups. The amount of grafted acrylate chains onto PP increases with irradiation time as the surface energy values increase, reaching a maximum value after about 60 s of irradiation. The fact that the acrylates do not graft onto pure PP samples proves the effect of the grafted photoinitiator on the modified PP surface, as expected. The grafted chains could not be washed from the surface using organic solvents, indicating the covalent bonding between the surface and the acrylate.

All modified samples were studied using FTIR-ATR to identify the groups on the surface. The spectra of the irradiated samples showed characteristic bands from the polymer grafts (Fig. 11).

The spectra of the nonirradiated samples presented no significant differences with the pure PP but the irradiated samples showed new peaks (broad band centered at 3000 , 1700 , and around 1200 cm^{-1}) that can be associated with the grafted chains of polyacrylic acid. The increase of the intensity of these bands can be explained by the increase of the thickness of the grafted layer with irradiation time.

CONCLUSIONS

The grafting of benzophenone-type photoinitiators onto poly(propylene) substrates was achieved using UV light. As soon as the UV light strikes the sample, and the concentration of initiator is beyond 2 wt %, the covalent bonding of the photoinitiator onto the surface is observed. The solvent used has no effect on the grafting reaction, whereas oxygen results in inhibition of the grafting. The reactivity of different photoinitiators was studied: 4-methoxybenzophenone and benzophenone were found to be the most active initiators in our study.

Contact angle measurements, FTIR-ATR, and UV spectroscopy proved the presence of the initiator on the surface, of which the concentration increased with increasing irradiation time. In most cases it reached a plateau after about 60 s of irradiation; where the maximum amount of initiator is grafted onto the surface, longer irradiation times have no further effect on the surface energy values.

Grafting of different acrylates onto the modified PP samples as substrates was possible because the initiator on the surface can act as a polymerization center, leading to grafted chains on the surface with covalent bonding between the growing chains and the surface itself. The amount of grafted chains increased with increasing irradiation time, reaching a maximal value around 60 s.

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