

Study of Wettability and Improvement of Adhesion of UV Curable Powder Coatings on Polypropylene Substrates

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ABSTRACT: Different benzophenone type photoinitiators were photografted onto polypropylene. The polymer surfaces were analysed 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 polypropylene up to 36 mN/m for the modified samples. Different acrylates 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 samples increased then up to 70 mN/m depending of the

type of acrylate used. Finally UV curable powder coatings were applied onto the modified polypropylene substrates and the adhesion was improved. Adhesion was measured by pull-off tests and values of ~ 0.20 MPa were obtained for pure polypropylene while the modified polypropylene reach pull-off values of 2.00 MPa. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3348–3358, 2007

Key words: surface modification; photografting; contact angle measurements; UV curable powder coatings; adhesion; polypropylene

INTRODUCTION

There has been an upward trend in the amount of plastics that are being used in industries such as automotive, sporting goods, medical, and electronic. This trend has been influenced by the drive to reduce weight and lower system-costs through design flexibility, increased process efficiency, and increased part performance. Unfortunately, many polymeric materials have a poor tendency to bond to other materials because of their inherent inert chemical structure and thus require a pretreatment for coating, laminating, or bonding.

Chemical or physical modification of the surface properties of polymeric materials is undoubtedly a fascinating field for research as well as a practical way to improve their value.

Conventional and modern methods of surface preparation now provide the ability to bond plastics that were not capable of being bonded previously. This is especially relevant to low energy surfaces such as polypropylene (PP), and other olefinic materials. Because of their lack of functionalities these

materials require a chemical¹ or physical² treatment before their final application. This requires tailoring of the surface properties of these materials.^{3,4} In industry the main methods to improve adhesion on polyolefins are based on chemical modification of the interfacial polymer chains with polar groups as hydroxyl, carbonyl, and carboxylic acid groups.⁵ There are several methods described to modify the surface of the PP, such as the use of block copolymers,⁶ flame treatment,⁷ plasma and corona treatment,^{8–10} and low-pressure glow discharges,¹¹ among others. Such surface modification techniques are difficult to control, and often cause problems regarding uniformity and reproducibility combined with another disadvantage i.e., they require a short time between treatment and application of the coating.

Free radical grafting has also been used for surface modification 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 degradation of mechanical properties due to side reactions such as chain scission. Furthermore, the grafted material is composed of a mixture of modified and pure material, and consequently, the adhesion improvement depends on the surface arrangements and the diffusion of chains. A review by Rätzsch¹⁴ discusses all the radical reactions on PP.

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Another possibility is the grafting of functional monomers using UV radiation. This has been widely described in literature.^{15–26} The use of UV radiation offers an excellent alternative to the free radical approach because of its simplicity and cleanness. Photoinduced grafting is known to be a useful technique for the modification or functionalisation of polymeric surfaces since 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 interfering the bulk properties of the polymer. In addition to the simplicity of the procedure, the equipment cost is lower for UV irradiation than for ionising irradiation.

This UV technology has been applied to modify the surface of various polymers^{27,28} especially polyolefins^{15–26} in order 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, hydroxycyclohexylacetophenone, and others. In a second step the initiation of the polymerisation of different monomers occurs at the reactive sites generated on the solid surfaces resulting in the grafting of the monomers on the surface.

During the grafting reaction of different monomers onto a polymeric surface, the homopolymerisation of the applied monomer is competing with the grafting reducing the overall grafting reaction yield. The approach as proposed by Bowman and coworkers²⁹ has solved this problem. The grafting polymerisation in their study is performed in two steps. In the first step 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 polymerisation under the presence of UV light. The formation of homopolymer is reduced since the semipinacol radicals generated have a very short lifetime and prefer to recombine or terminate growing chains. In a previous article we had described the photografting of photoinitiators on the surface of PP to increase its surface energy and wettability.³⁰ The grafted photoinitiators can generate radicals in the surface of the PP upon exposure to UV light. These radicals in the surface of the PP not only increase the wettability of the PP but also generate covalent bonds between the surface and a reactive monomer applied onto the polymeric surface.

The same approach can be used to apply coatings onto modified PP surfaces. The wettability of the modified samples is higher and the generation of radicals on the surface will generate covalent bonds between the surface and the reactive coating applied on the surface. The main problem of coating PP can be solved using the modified PP substrates.

In this article we describe the application of UV curable powder coatings onto PP using a two-step process. In the first step the surface of the PP is modified by photografting of different photoinitiators. While in the second step a powder coating is applied and cross-linked using UV light at moderate temperatures.

The grafting of commercial and some synthesized initiators on the surface will improve the wetting and the adhesion behavior of the PP. We have studied the surface properties of the modified polymer surfaces before applying a powder coating onto it. The final properties of the cured coating are also studied focusing this work onto the adhesion of the coating onto the modified PP surface.

EXPERIMENTAL SECTION

Materials

The PP sheets (PP) (10 cm × 10 cm × 2 mm) used in this study were supplied by Vink Kunststoffen (Didam, the Netherlands). The surface was cleaned with acetone and ethanol before use. All solvents that were used in this study were used as received, unless otherwise noted, and were supplied by Sigma Aldrich Chemie B.V. (Zwijndrecht, the Netherlands). For the surface modification reaction, the photoinitiators BP, 4-hydroxybenzophenone, 2,4-dihydroxybenzophenone, 2,3,4-trihydroxybenzophenone, and 2-hydroxy-4-octyloxy-benzophenone were used as received from Sigma-Aldrich Chemie B.V. (Zwijndrecht, The Netherlands). Dichloromethane was distilled under reduced pressure, while 18-crown-6, potassium carbonate, and ω -bromooctane were used without any further purification (all chemicals were purchased from Sigma-Aldrich Chemie B.V., Zwijndrecht, the Netherlands) in the synthesis of the initiators with aliphatic chains. The monomeric acrylates, acrylic acid, pentaerythritol triacrylate, and 2-hydroxyethyl acrylate, were used as purchased from Aldrich. The binders of the powder coating formulations were based on unsaturated dimethacrylate polyesters that were commercialized by UCB Chemicals under the trademark Uvecoat[®]. Uvecoat 1000 and Uvecoat 9010 were kindly supplied by UCB Chemicals (Drogenbos, Belgium) and used as received. The photoinitiator in these formulations, Irgacure 651 (IC651), was supplied by Ciba Speciality Chemicals (Groot-Bijgaarden, Belgium) and used without any further purification.

Synthesis of initiators with aliphatic chains

As precursor of the initiator with aliphatic chains the corresponding hydroxyl BP derivative was used. This precursor (5 mmol) was mixed in acetone (50 mL) together with ω -bromooctane (equimolar with respect to the hydroxyl functionality), potassium carbonate (25 mmol), and 18-crown-6 (0.5 mmol). This mixture was heated and refluxed for 24 h. After this time the reaction was completed as observed by TLC using toluene/acetone (9/1) as eluent. The solvent was evaporated and the remaining solid was dissolved in chloroform and washed three times with 100 mL water. The organic phase was evaporated under vacuum to obtain a solid that was recrystallized from heptane and dried under vacuum. The purity of the modified BP was confirmed by ^1H - and ^{13}C -NMR analysis.

Grafting of the photoinitiator

The photoinitiator was dissolved in a proper solvent (e.g., methanol, dichloromethane, acetone or toluene depending on functional groups). The solution was applied on a PP sheet using a wire bar resulting in a film thickness of 30 μm . The solvent was evaporated and the samples were subsequently irradiated with UV light at 20-cm distance from the source with a high-pressure mercury lamp (H type, 400 W) in a UVA Cube from Dr Hönle, under a nitrogen atmosphere. The irradiation times were varied between 10 and 600 s and the UV doses were measured using an UV Power Puck radiometer. The samples irradiated were washed with ethanol and acetone and dried overnight. On storage, the samples were covered with aluminium foil to prevent photodegradation.

Grafting of acrylates

Acrylic acid (AA), pentaerythritol triacrylate (PETA), and 2-hydroxyethyl acrylate (HEA) were grafted on pure and modified PP sheets at room temperature. Thin films of the pure acrylates were applied using a wire bar of 100 μm . A quartz plate (2-mm thickness) was used 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 and exposure times were varied between 30 and 300 s. After irradiation the samples were cleaned (removing unreacted monomer by dissolution) using a proper solvent, i.e., boiling water in the case of acrylic acid while acetone or ethanol was used for the other acrylates. The samples were dried overnight under vacuum prior to any measurement.

Powder coating procedure

Preparation of the powder. The unsaturated polyesters used in this study were commercialized by UCB chemicals under the trademark Uvecoat. In our studies we used a mixture composed of two unsaturated polyesters, an amorphous and a semi-crystalline resin. The amorphous resin (Uvecoat 1000) is characterized by a glass transition temperature (T_g) of $\sim 47^\circ\text{C}$ and a relatively high viscosity (1000 mPa.s at 200°C). The semi-crystalline resin (Uvecoat 9010) is characterized by a melting point (T_m) of $\sim 85^\circ\text{C}$ and a very low viscosity (<10 mPa.s at 200°C). Both resins were mixed using the proportion described in the literature as the one that offers the best performance, i.e., 75 wt % Uvecoat 1000 and 25 wt % Uvecoat 9010.

To mix the two resins with the initiator and some other additives, all the components were ground using an Alpine 100 UPZ pin mill and extruded using a twin-screw extruder from APV at 80°C and 250 rpm. After extrusion the mixture was ground again and sieved to obtain a powder with a particle size below 150 μm .

Fluidized bed. The powder coating was placed inside a round recipient (half filled with powder) were compressed dry air at a pressure of 1 Pa was introduced through a porous plate. Under these conditions the powder is fluidized and behaves as a liquid. The PP preheated sheets at temperature $\sim 100^\circ\text{C}$ were dipped in the fluidized powder for the period of a few seconds. Under these conditions coatings with a thickness of 100 μm were obtained after curing.

UV curing. The samples were irradiated in a closed cabinet UVACube (Dr. Hönle), which was equipped with an H type UV lamp (400 W). The cabinet was equipped with a home-built heating plate that allows curing at controlled elevated temperatures. The whole compartment can be flushed with air or dry nitrogen to evaluate the influence of the atmosphere on the curing reaction. The UV doses were measured using an UV Power Puck radiometer. All powder coatings studied in this contribution are cured at 100°C under a nitrogen atmosphere and were irradiated for 60 s (corresponds to an UV dose of $20 \text{ mW}/\text{cm}^2$).

Characterisation

UV spectroscopy

UV absorption spectra of the photoinitiators were measured using a Hitachi UV/Vis U-2001 spectrophotometer. The spectra of the pure PP and the modified PP were recorded directly on the films of $\sim 100 \mu\text{m}$ thickness.

Contact angle measurements

Contact angles of water and diiodomethane were determined using a contact angle measuring appara-

tus (Krüss) 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, and Kaeble method.

Contact angle measurements on polymer melts

The determination of the surface tension development as a function of temperature was carried out by a conventional contact angle microscope (G10, Krüss). A drop of the polymer melt is formed at elevated temperature on a sample holder in a measurement chamber equipped with a heating element (Linkam, TMS93). During the measurement, pictures of the drop were taken at a fixed time interval using a CCD camera. A drop shape analysis program then fits the profile of the drop contour and provides the values of the contact angle, the drop volume, and the surface tension. The contact angle is taken at both sides of the drop and is averaged.

Typically, about 10 mg of polymer was used for the size of the sample holder used in our equipment. After placing the sample in the measurement chamber the temperature was raised with a heating rate of 10°C/min. A sequence of pictures was acquired (one picture every 30 s) after the polymer was melted and equilibrated. The measurement always started with an isotherm during 30 min after which the temperature was lowered with a cooling rate of 5°C/min to the next temperature of measurement. Each temperature of measurement was kept for 30 min during which the pictures were taken.

FTIR-ATR

The infrared spectra were recorded with attenuated total reflectance (ATR) using a Bio Rad FTS 3000MX Excalibur spectrometer with a MTC detector. The spectrometer was equipped with a Golden Gate™ Diamond ATR Top-Plate (Specac). The samples of size 20 × 20 mm² 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.

Pull-off measurements

A Universal tensile tester machine model 112.10kN.L (TesT GmbH) was used to monitor the force required to detach the coating from the substrate. The tensile tester was controlled with a model 810 control and display electronics (TesT GmbH).

An aluminium stud of 0.5 cm² was glued on top of the coating using an epoxy based glue. The glue was dried during 24 h at room temperature. The coating was sanded slightly to increase the adhesion of the stud. After the curing time the excess of glue was removed and the coating was cut around the stud until reaching the surface of the substrate to obtain a constant contact area in all the samples studied. The experiments were performed using the standards described in the ASTM-D 4541.³¹

The sample was mounted in a home-built sample holder and the stud fixed to a flexible wire to ensure a good alignment. The conditions used in the experiments were a speed of 1 mm/min and a maximum force of 450 N (95% of the maximum value of the load cell used). A preload force of 1 N is used in all the experiments. The force and displacement were monitored during the pull-off experiment. The maximum force required to pull apart the coating can be related to the adhesion of the coating to the substrate used. All the experiments were repeated on at least 25 samples to obtain the average value and its standard deviation.

RESULTS AND DISCUSSION

Surface modification

The irradiation of a BP type initiator excites the molecule to a triplet state. This excited molecule can

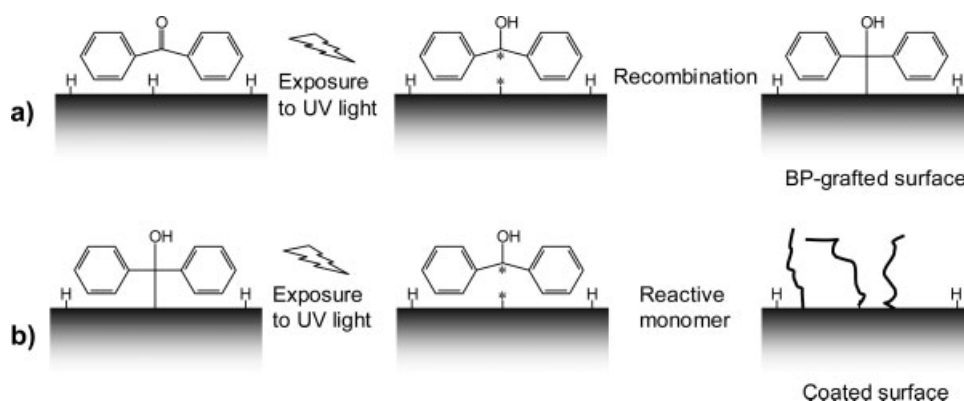


Figure 1 Modification of PP surfaces using a two-step grafting method.

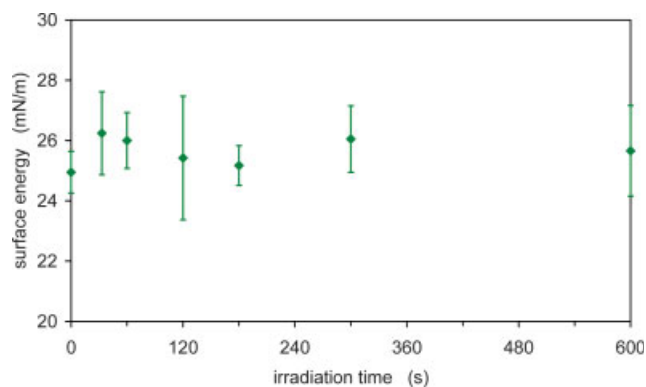


Figure 2 Variations in surface energy of the pure PP substrate as a function of irradiation time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

abstract a proton from the PP surface in the absence of another source and generate a radical on the surface.²⁹ These radicals can recombine with the semipinacol radicals, as explained in Figure 1(a). Stable species are formed with a covalent bond between the initiator and the PP surface.

These grafted molecules are called “surface initiators.” These grafted initiators can generate radicals by exposure to UV light, the covalent bond can be broken by the effect of the UV light and the radicals on the surface are regenerated again as is shown in the same figure [Fig. 1(b)].

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 substrate.
- Influence of the solvent for the photoinitiator during the surface grafting onto the PP.
- Concentration of photoinitiator.
- Nature of the photoinitiator.

Covalent grafting of BP

Contact angle measurements

One of the most sensitive techniques used to analyse the outer layer of 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 to evaluate 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 contact angle of water and diiodome-

thane to calculate the surface energy as described in the experimental section. The surface energy of the untreated PP has been determined to be ~ 26.5 mN/m with no significant differences between the different batches of PP. This value is in agreement with the values obtained in a previous study that determined that the surface energy of pure PP was in the range of 26–29 mN/m depending on the batch used.³⁰ The effect of the irradiation on pure PP samples was almost negligible and no significant differences in the surface energy were observed during irradiation (see Fig. 2).

The use of different solvents for the grafting procedure, i.e., acetone, dichloromethane and toluene, produces no differences on the surface energy of the PP, this result is in agreement with the conclusions obtained in a previous study.³⁰ Similar values were obtained for all the solvents tested and toluene was chosen as the solvent since it dissolves all the photoinitiators that are used in this article.

To study the effect of surface coverage 0.5 up to 25 wt % solutions of BP in toluene were prepared; a film of 30 μm thickness was applied on 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; the surface energy of the PP remains almost constant indicating that no measurable changes took place on the surface. However, a significant increase in the value of the surface energy as well as decrease in the contact angle of water can be observed at higher concentrations of BP in the irradiated formulation.

The most significant increase in the surface energy is produced during the first 60 s of irradiation and after that, the value remains almost constant for concentrations of BP below 5 wt %. When concentrated BP solutions are used for the surface modification of the PP, the surface energy increases with increasing irradiation time, but to a lesser extent than in the first 60 s of irradiation (Fig. 3).

The increase from ~ 26 up to 34 mN/m for the BP-grafted PP, is a clear indication that some changes had occurred at the surface. Further analysis of the surface is required to prove the presence of the BP. The contact angle of water decreases from 103° to $\sim 80^\circ$; this is already an indication of the presence of

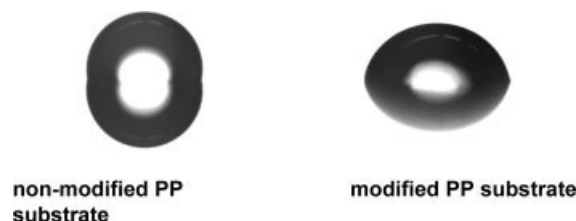


Figure 3 Effect of irradiation and the presence of BP on the contact angle of water.

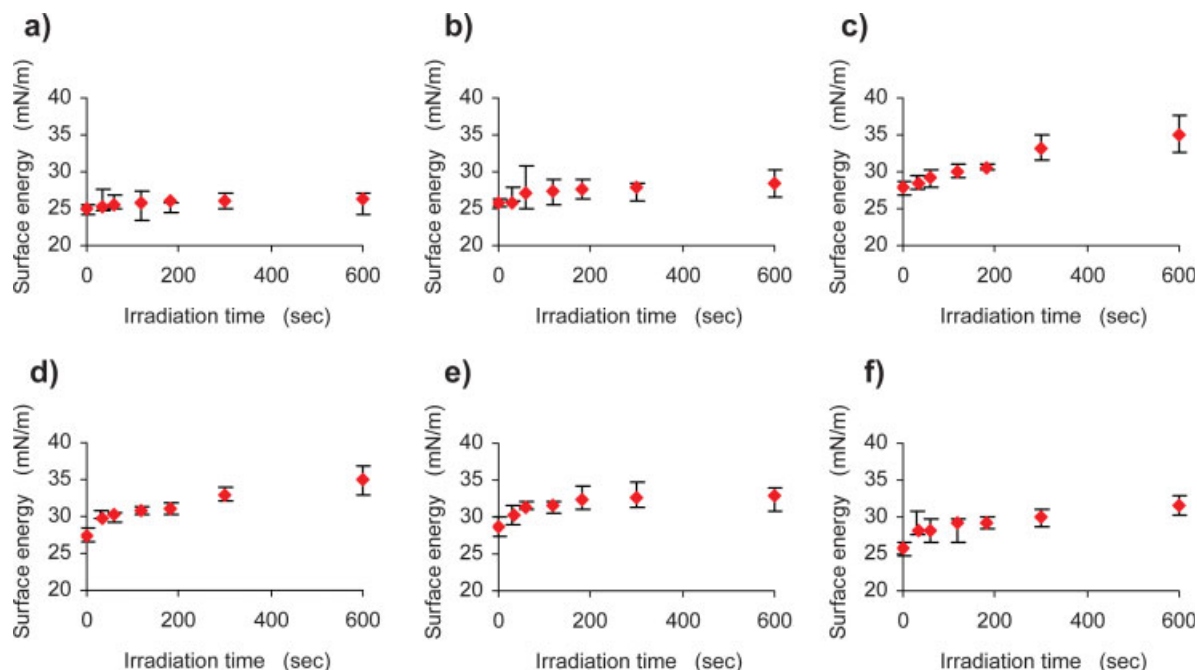


Figure 4 Surface energy of the PP vs. irradiation time for different concentrations of BP. (a) no photoinitiator, (b) 0.5 wt % BP, (c) 1 wt % BP, (d) 2 wt % BP, (e) 5 wt % BP, (f) 10 wt % BP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

hydrophilic groups on the surface originating from the grafted initiator (Fig. 4).

The presence of oxygen during the grafting reaction has an inhibiting effect. This conclusion was drawn from surface modification experiments in air, since no differences in the surface energy are observable after irradiation in air even for concentrated BP solutions. In a nitrogen atmosphere a significant increase in surface energy was observed 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 Ranby^{18–20} has concluded that the scavenging interaction of oxygen with the primary free radicals that are formed is responsible for the inhibition of the grafting of BP type photoinitiators.

ATR 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 of the PP surface.³² In this technique the surface to be analysed 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 analysed depth is

different (from 1 to 20 μm) 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 to the stretching and bending of methylene and methyne groups. The band at 1167 cm^{-1} is associated to the isotactic groups as well as the bands present at 997 and 972 cm^{-1} . They are used to quantify the tacticity.³³ All these bands showed the high isotacticity of the PP used in this study (Fig. 5).

There are a few differences observable for the spectra obtained from modified PP surfaces when compared with the “virgin” PP. These differences are

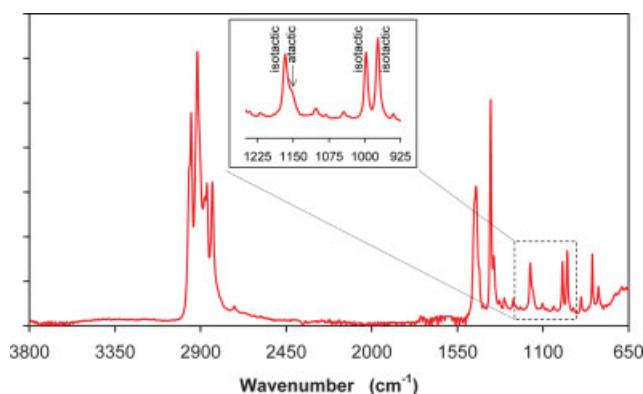


Figure 5 FTIR spectrum of the PP substrate as used in this study. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

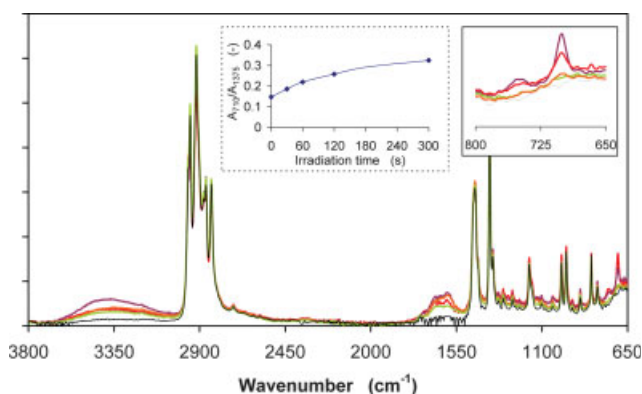


Figure 6 FTIR spectra of modified PP substrates by using a 5 wt % solution of BP at different irradiation times. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

1. a broad band centered on 3400 cm^{-1} that may be attributed to hydroxyl groups from the semipinacol radicals and/or hydrogen bonded water to these hydroxyl groups.
2. a band at 1640 cm^{-1} that may come from the same hydroxyl group.
3. a band is present at 710 cm^{-1} that can be attributed to the bending 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} in comparison with the reference band corresponding to the bending vibration of the methyl group (1375 cm^{-1}), yielded the results shown Figure 6.

The peak intensity at 710 cm^{-1} is increasing with increasing irradiation time, indicating that the amount of aromatic rings is higher. This proves again the grafting of the initiator to the surface. For the other areas the results are comparable, as shown in the Figure 7.

These results are in accordance with the ones obtained by the surface energy measurements; the surface energy increases as the irradiation time does

and by FTIR-ATR we can observe a higher content of phenyl rings. The signals in the FTIR spectra are an indication that the initiator is covalently grafted onto the surface.

UV spectroscopy

For these 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. There is no difference in treating the surface for thick or thin substrates.

The irradiated PP has no absorption bands in the UV region nor does the nonirradiated sample. However, the modified samples with BP present an absorption 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 solvent is clear evidence that the BP is 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 of the grafted BP onto the PP substrate

One of the main problems of industrial methods to increase the polarity of the PP surface is the stability

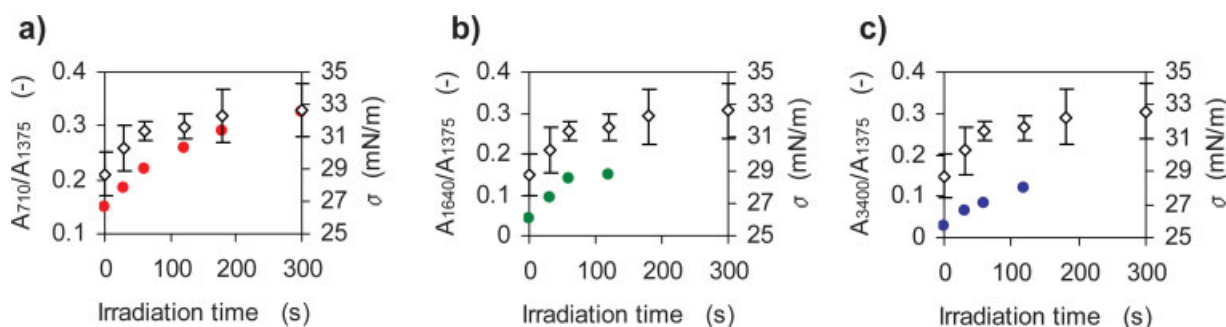


Figure 7 Comparison of the experimentally determined surface energy of the modified PP \diamond and relative FTIR absorption at (a) 710 cm^{-1} \bullet (b) 1640 cm^{-1} \bullet , and (c) 3400 cm^{-1} \bullet vs. different irradiation times using a 5 wt % solution of BP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

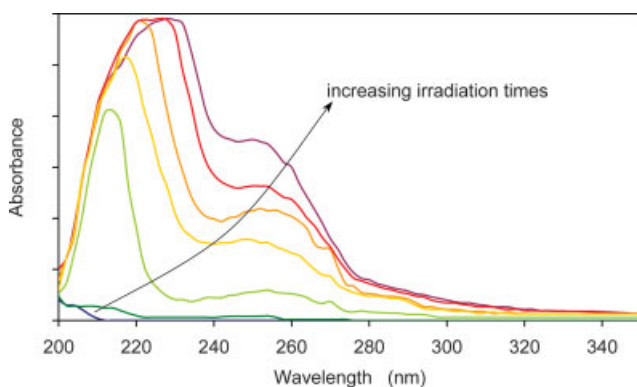


Figure 8 UV absorption spectra of a PP film, and films covered with a layer of BP irradiated for 0, 30, 60, 120, 180, 240, and 300s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of the modified surface. For plasma treatments it is well known that the modified surface of the polymer is stable only for a limited period of time and after that the surface loses its hydrophylic nature.³⁴ 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 when they need to.

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. Their surface energy is monitored during a period of 3 weeks. The surface energy of the samples was found to be almost constant at about 37 mN/m, during the first days after modification and after 3 weeks the value dropped only to 35 mN/m (Fig. 9). The surface energy of the pure PP is ~ 26.5 mN/m so the changes observed are significant. The grafting of photoinitiators onto PP results in a stable modification of their surface properties. Modified samples can be stored and used with the same effectiveness even after 3 weeks after their preparation.

Proof of reactivity by postgrafting of low molecular weight acrylates

Grafting of acrylates onto the modified PP substrates

To prove further the presence of the grafted initiator, and the remaining activity of the grafted photoinitiator on the modified PP substrate we have used the modified samples as substrates to graft some acrylic monomers. The initiator present on the surface can generate radicals upon UV radiation and initiate the polymerisation, as we have discussed before. As a result we will obtain grafted chains of polymers on the surface.

The acrylic monomers chosen were AA, 2-HEA, and PETA.

To check the grafting reaction the acrylates were grafted on pure PP and on modified PP. Also an acrylate containing 1 wt % of BP was grafted on pure PP as control. For the irradiation experiments the surface was covered with a quartz plate that has the same size as the PP sheet to ensure good contact of the pure PP with the different acrylates. The irradiated samples were washed with the adequate solvent, extracted for at least 4 h to remove unreacted acrylate from the surface, and dried overnight.

The surface energy of all samples was measured using the contact angle of water and diiodomethane, as described before.

The surface energy of the pure PP samples does not change significantly and remains almost constant around 26.5 mN/m with irradiation time but in the case of the modified samples a large increase is observed even in the first 20 s of irradiation. The surface energy increases from 30 to 70 mN/m as the contact angle of water dropped from 100° to 20° in the case of AA (Fig. 10). The sample containing AA and BP as initiator in the formulation that was applied onto untreated PP has a low grafting efficiency as well as in the case of pure AA on untreated PP. It 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. The acrylic acid is polar monomer and therefore will have a better affinity with the semipinacol radicals initiating the polymerisation leading to homopolymerisation and a low grafting of polymeric chains. In our study we have observed that the acrylates only react with the modified samples due to the presence of the grafted initiator in the surface reaching surface energies of 70 mN/m for AA, 58 mN/m in the case of HEA, and 64 mN/m when the PETA was used.

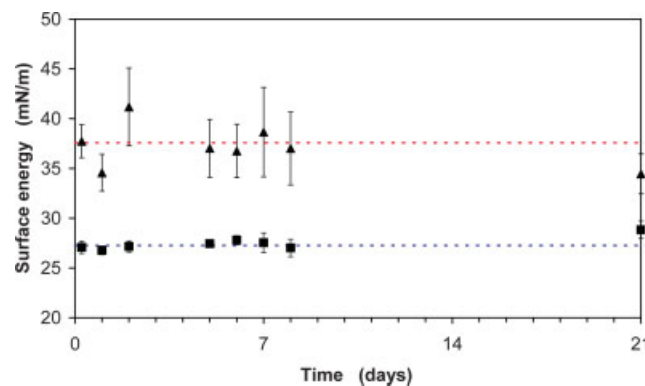


Figure 9 Surface energy vs. time of ■ nonmodified PP and ▲ modified PP sheets using a 5 wt % BP solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

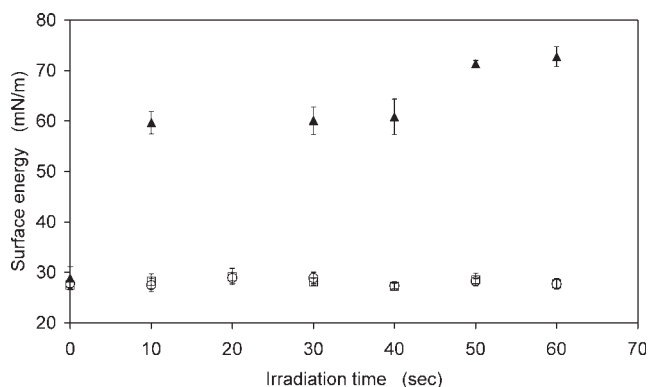


Figure 10 Surface energy vs. irradiation time of the PP grafted with acrylic acid □ pure PP, ○ pure PP (AA + 1 wt % BP), and ▲ BP-grafted PP.

The increase in surface energy can be attributed to the grafting of the acrylates onto the treated surfaces due to 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 approximately after 60 s of irradiation. The fact that the acrylates do not graft on 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.

Powder coating BP-grafted PP samples

As described in the experimental part, a mixture of two unsaturated polyesters was used as the powder coating binder. The effect of temperature, type, and concentration of initiator on the kinetics of curing was studied previously by a combination of UV rheology, DSC, and FTIR studies.³⁵ The powder coating was applied onto the PP using a fluidized bed as explained in the experimental section. The conditions of curing used in this study were isothermal cure at 100°C using 2.5 wt % IC651 during 60 s of irradiation under nitrogen (20 mW/cm²). Under these conditions a conversion of double bonds is ~ 70%.

For the wettability study, the development of the surface tension of the polymer melt was studied on a cured and uncured formulation. It can be seen in Figure 11 that the surface tension of the melt has a larger temperature dependence in the uncured state than in the cured state. This is expected as mobility of functional groups is much lower in the cured material. From this figure it can also be seen that surface tension increases upon curing.

One of the limitations of the usage of coatings on polyolefins is their poor adhesion as we had men-

tioned before. The adhesion of two materials can be measured in two ways; in term of *forces*, defining adhesion by the maximum force per area exerted to separate the two materials or in terms of *work energy*, defining the adhesion as the work done in separating or detaching two materials.

There is a large collection of techniques described in literature, these techniques range from inexpensive to very sumptuous and from primitive to very sophisticated. There is no single technique, which will be acceptable to everyone or will be applicable to all coating-substrate combinations. For relative purposes all techniques can be used and will be able to rank or discriminate cases of poor adhesion. It is widely realized that the selection of the adhesion test methods must be selected on the basis of the hand; nature of the substrate-coating, etc...

No universal test is available; the different tests yield results that are different in nature.

In our study we had decided to use a pull-off method to measure the adhesion. In this method a loading fixture, commonly called dolly or stud, is glued on top of the surface of the coating. A special device is then used to apply an increasing force until the coating or the glue fails. The pull is perpendicular to the surface, so the tensile strength is being measured.

Coatings were applied on different pretreated PP substrates. The effect of grafting and/or sanding was evaluated. Figure 12 shows the pull-off force required to detach the coating from the different substrates.

It can be clearly seen that the adhesion of the coating on pure PP is very low, forces of ~ 20 N are required (0.30 MPa) to detach the coating. In all these experiments a failure between the coating and the substrate is observed. The BP-grafted PP present higher adhesion; values of ~ 30 N are measured (0.60 MPa). Also in these samples the same failure mode was observed in all the samples evaluated. A positive effect of sanding the PP substrate prior to

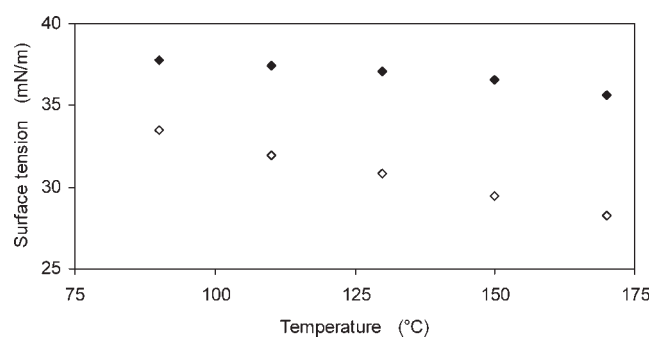


Figure 11 Development of the surface tension of the powder coating formulation, as applied onto the PP substrates, as a function of temperature ◇ uncured coating formulation ◆ cured coating formulation.

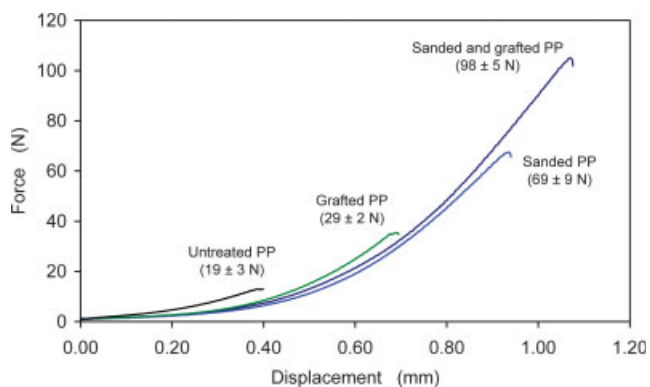


Figure 12 Pull-off force measured to detach the cured coatings from different substrates. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

coating or grafting, using 400 grit sandpaper, was observed as could be expected as a result of an increase in the roughness of the substrate. In the

case of a sanded substrate a value approximately of 70 N is measured (1.40 MPa). Finally the samples that are sanded and afterwards modified with the grafting procedure described in this article showed the best adhesion. Forces ~ 100 N are obtained (2.00 MPa). These values of adhesion are in the range of acceptable levels for coatings on plastics.

When performing a crosscut adhesion test on these types of samples, a value of 5 for the pure PP and the grafted PP was observed. The sanded samples showed a better adhesion, the sanded PP had a 4 while the sanded and grafted PP leads to a 1 that means an acceptable adhesion. It has to be stated here that the crosscut adhesion test is a rather difficult test to perform on polymeric substrates.

Effect of modification of BP-moiety

The effect of structure (or polarity) of the surface grafted BP derivative on the adhesion was also tested

TABLE I
Summarized Results of Surface Energy Values and Adhesion of UV Curable Powder Coatings on Different PP Substrates Grafted With All the Initiators Studied

	SFT (mN/m)	Disperse (mN/m)	Polar (mN/m)	Disp/tot	Structure of the BP derivative	Force (N)	Stress (MPa)
Uncured coating	40.61	40.12	0.49	0.988	—	—	—
Cured coating	41.34	40.72	0.62	0.985	—	—	—
PP	25.2	24.45	0.75	0.970	—	19	0.38
Ini1	33.87	33.1	0.77	0.977		98	1.96
Ini2	32.43	30.7	1.73	0.947		62.1	1.24
Ini3	31.02	30.24	0.78	0.975		100.6	2.01
Ini4	32.51	30.87	1.64	0.950		76.7	1.53
Ini6	31.02	30.12	0.9	0.971		93.1	1.86
Ini7	33.27	33.02	0.25	0.992		69.2	1.28
Ini8	30.42	30.3	0.12	0.996		71.1	1.42
Ini9	24.18	23.67	0.51	0.979		71.6	1.43
Ini10	36.71	35.85	0.86	0.977		59.9	1.2

within this research. The thickness of the applied powder coating (containing 2.5 wt % IC651 and cured at 100°C in N₂ atmosphere) was ~ 100 µm. For the powder coating formulation as used, the surface energy of the uncured as well as the cured coating was determined, these results are shown in the table below.

Some of the modified BP initiators have no significant effect on the adhesion of the powder coating while others showed increased adhesion with respect to the untreated PP. The results are summarized in the Table I.

On the basis of these results it can be concluded that the requirements for good adhesion of the UV curable powder coating formulation is a surface energy of the substrate of ~ 32 mN/m in combination with a disperse/total fraction of ~ 0.98 to obtain good adhesion (i.e., forces of at least 90 N are needed for failure).

CONCLUSIONS

The grafting of BP type photoinitiators onto PP substrates was achieved using UV light. As soon as the UV light hits the sample and the concentration of initiator is beyond 2 wt % the covalent bonding of the photoinitiator onto the surface is observed. Contact angle measurements, FTIR-ATR, and UV spectroscopy proved the presence of the initiator on the surface, of which the concentration of grafted moieties increases with increasing irradiation time. In most of the cases it reaches a "surface saturation plateau" after ~ 60 s of irradiation, where the maximum amount of initiator is grafted on the surface. Longer irradiation times seemed to have no further effect on the surface energy values.

Grafting of different monomeric acrylates on the modified PP samples as substrates was possible since the initiator on the surface can act as a polymerisation center leading to grafted chains on the surface with covalent bonding between the growing chains and the surface itself. The amount of grafted chains increases with increasing irradiation time and reaches a maximal value around 60 s.

UV curable powder coatings were applied efficiently onto PP substrates and cured with UV light at relatively low temperatures. The adhesion of the coatings was measured with a pull-off test. Coatings applied on pure PP showed a very poor adhesion. The grafting of BP derivatives on the PP increases the adhesion of the coating. Finally sanding the PP

and grafting BP derivatives onto it prior the application of the coating lead to coatings with an acceptable value of adhesion ~ 2.0 MPa.

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