

# Optimization of Adhesion Properties of Polypropylene by Surface Modification Using Acrylic Acid Photografting

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**ABSTRACT:** Polypropylene is one of the most widely used plastic materials because of an excellent balance between properties, processability, and cost. Nevertheless, polypropylene is characterized by very low surface energy, and this has a negative effect on adhesion properties. The use of polypropylene in technological applications requires, in many cases, a surface pretreatment to modify surface activity, thus enhancing good adhesion levels. In this work, we have used photopolymerization of acrylic acid (AA) monomer on polypropylene surface by using UV radiation. This enables photografting of AA (highly polar) on polypropylene topmost layers, thus having a positive effect on overall surface activity of polypropylene surface and, consequently, adhesion properties can be remarkably improved. We have evaluated the influence of the exposure time to UV radiation on wettability changes and adhesion properties. Wettability changes

have been studied by contact angle measurements and subsequent surface energy calculation. Chemical changes produced by photopolymerization of AA have been followed by Fourier transformed infrared spectroscopy. Mechanical characterization of adhesion joints has been carried out in two different ways: peel and shear. Fractured surface of adhesion joints has been characterized by scanning electron microscopy. The overall results show a remarkable increase in mechanical properties of adhesion joints for exposure times of about 180 s, which represents an interesting time from an industrial point of view. Therefore, photopolymerization process is highly useful to increase adhesion properties of polypropylene. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3256–3264, 2010

**Key words:** UV photopolymerization; polypropylene; acrylic acid; adhesion properties

## INTRODUCTION

Among the wide variety of thermoplastic materials, polypropylene is one of the most used at industrial level and continuously it finds growing uses. It is classified as a “commodity” plastic with excellent balanced properties (physical, mechanical, electrical, and chemical) and easy processing. So that it is not only used in low-technology sectors but also in medium- to high-technology applications such as automotive or medical devices. Polypropylene, as other polyolefins, is characterized by high chemical inertness, as a consequence of its nonpolar nature, and this fact results in very low wetting properties. For this reason, polypropylene finds enormous difficulties for different industrial processes such as painting and adhesion, which are highly related to surface wetting properties.

The main problem regarding polypropylene adhesion is due to its low surface roughness; this fact, together with its nonpolar nature, leads to poor adhesion properties; so that adhesion joints with polypropylene show relatively low mechanical performance. Hence, in most cases, it is necessary to carry out a surface pretreatment to modify surface wetting properties. There are several technologies to promote surface changes and improve adhesion behavior. Physical processes such as plasma technologies (corona plasma, cold plasma, atmospheric plasma, etc.) are interesting solutions from a technical point of view. They increase surface activation by the action of the plasma gas, which is able to promote chain scission and subsequent free radical formation. After chain scission, two main processes can occur: one mechanism is surface activation by insertion of polar groups (mainly oxygen-based species) into free radicals. The second mechanism is characterized by changes in surface roughness as a consequence of chain scission that leads to formation of low-molecular-weight oxidized material, which can be removed from surface, thus promoting changes in surface topography. These processes are highly advantageous from a technical and environmental point of view; despite this, they are expensive and

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this restricts their use at industrial level. Other interesting technologies to promote surface activation are based on the use of chemical processes. In these, the contact between the polymer surface and certain chemical induces surface activation. Among the wide variety of chemical processes, those based on the use of ultraviolet radiation to carry out surface grafting of an organic monomer (photopolymerization process)<sup>1,2</sup> are interesting from an industrial point of view as their implementation requires low costs and optimum results are obtained in a relatively low exposure time (around 200 s or less). This process consists on polymerization of an organic monomer [such as acrylic acid (AA) or vinyl acetate (VAc)] on a polymeric substrate. First, it is necessary to activate the polymer surface to provide interlock points for the grafted monomer. These processes can be achieved by using an initiator such as benzophenone (BP)<sup>3</sup> and light exposure, mainly ultraviolet radiation.<sup>4-6</sup> Furthermore, this process allows the use of wide variety of combinations by using different polymer substrates (films, nonwovens, fibers, small parts, etc.)<sup>7</sup> and different monomers [AA, VAc, styrene, maleic anhydride, methyl methacrylate, *n*-butyl vinyl ether, polyvinylpyrrolidone, and acrylonitrile (AN)]. The overall effects of these processes are mainly surface activation by grafting monomers (usually polar monomers) into polymer surface and subsequent change in surface topography. All this has a positive effect on wetting properties of polypropylene, thus increasing surface free energy.<sup>8,9</sup> The use of different monomers can lead to a remarkable increase in flame retardancy, paint ability, and adhesion properties. The photopolymerization process can be carried out in a single-step way; in this, the monomer and the photoinitiator are mixed together with the appropriate solvent, and then they are deposited simultaneously onto the polymer surface.<sup>10</sup> Also, this process can be carried out in a two steps or sequential process; in a first step, the initiator is deposited onto the polymer surface and after this, the activated surface is covered with the monomer.

The photopolymerization process can be applied to a wide variety of polymer substrates. It is preferable to use the substrate in a film form as it allows high homogeneity. This process is very useful to modify surface activity of low polarity or nonpolar polymers such as polyolefins, but it can also be used on polytetrafluorethylene and conductive polymers such as polypyrrole or polyaniline.<sup>11-18</sup>

Many of the monomers are used in a liquid state, which enables deposition and dispersion on the polymer substrate. These monomer structures are mainly based on the presence of double bonds (C=C). Many of the monomers for photopolymerization are based on a vinyl structure such as AA,

VAc, methyl methacrylate, AN, and styrene.<sup>19-28</sup> These monomers are usually dissolved in an organic solvent to control monomer concentration. Among the wide variety of organic solvents, acetone, benzene, methanol, chloroform, and cyclohexane are widely used. Other solvents reported in a less extent are tetrahydrofuran, dimethylformamide, ethyl acetate, and *n*-hexane.

Benzophenone is the most used photoinitiator. Photoinitiators act as free electron donors and they provide a bridge for grafting monomers onto polymer surface.

In this work, we have modified polypropylene surface by a single-step photopolymerization process using ultraviolet radiation. As a monomer, we have used AA and BP as an initiator. We have evaluated the influence of the radiation exposure time on the overall improvement of adhesion properties. Surface wettability changes have been evaluated by contact angle measurements and subsequent surface free energy calculation. Chemical changes produced by the photopolymerization process have been characterized by Fourier transformed infrared spectroscopy (FTIR), and finally, adhesive joints have been characterized using shear and peel tests to establish the influence of the exposure time to UV radiation on mechanical performance of adhesion joints.

## EXPERIMENTAL

### Materials

As polymer-based substrate, it was used a polypropylene commercial grade ISPLEN<sup>®</sup> PB 180 G2M provided by Repsol YPF. This is a heterophase copolymer with high fluency, which is appropriate for injection molding. Its flow rate is 20 g/10 min, and its density is 0.905 g/cm<sup>3</sup>. Sheets of 160 × 60 × 2.2 mm<sup>3</sup> were injection molded with a Mateu&Sole, model Meteor 270/75 (Mateu&Sole, S.A., Barcelona, Spain). The injection temperature was fixed to 230°C. To obtain maximum homogeneity, samples sizing 10 × 10 mm<sup>2</sup> were cut with a hydraulic press Melchor Gabilondo, model KCK-15A (Melchor Gabilondo S.A., Vizcaya, Spain).

The monomer used for photopolymerization process was an AA monomer extra pure and stabilized with a purity of 99.5%. This monomer was supplied by Acros Organics (Acros Organics, Geel, Belgium). As photoinitiator, it was used BP with a quality for synthesis supplied by Scharlau Chemie S.A. (Scharlab S.L., Barcelona, Spain). Both monomer and photoinitiator were dissolved in chloroform with 0.6% ethanol supplied by BDH Prolabo VWR (BDH Prolabo VWR, Fontenay-sous-Bois, France).

### Photopolymerization process

The photopolymerization process was carried out using ultraviolet radiation in a UVASPOT 1000RF2 supplied by Honle UV Technology (Honle Spain, S.A., Barcelona, Spain). This is provided with a high-pressure mercury lamp with a power of 1000 W and a wavelength in the 300–400 nm range. Prior to photopolymerization process, AA monomer was diluted in chloroform (1 : 4—AA/chloroform volume ratio). After that 5 wt % of BP was added.

The operating procedure was the following: first, samples sizing  $10 \times 10 \text{ mm}^2$  are washed in distilled water to remove impurities and dried at room temperature in a vacuum desiccator. These samples are placed in a Petri dish, and after this, the solution containing AA and BP is added until polypropylene sample is fully covered with the monomer solution. Once the monomer solution has been applied, the Petri dish is covered with a glass lid to guarantee invariable atmosphere and to avoid gas emanation during the process. Once this stage is completed, the Petri dish is placed on aluminum shelve 20 cm below the mercury lamp and it is ready for UV radiation. The exposure time varied in the 30–240 s. After exposure to UV radiation, samples were washed with distilled water to remove the presence of non-grafted monomer or oligomers and finally dried at room temperature in a vacuum desiccator.

### Wettability characterization and surface free energy calculation

Wettability changes were characterized by contact angle measurements using a EasyDrop Standard goniometer model FM140 (KRÜSS GmbH, Hamburg, Deutschland) with a measurement range from  $1^\circ$  to  $180^\circ$  with a precision of  $\pm 0.1^\circ$ . This equipment is supplied with a video capture kit and analysis software (Drop Shape Analysis SW21; DSA1). Four different test liquids were used for contact angle measurements and surface free energy calculation: diiodomethane (stabilized, >99% purity) supplied by Acros Organics (Acros Organics, Geel, Belgium), formamide (reagent grade ACS), and glycerol (>99% purity) supplied by Scharlau Chemie S.A. (Scharlab S.L., Barcelona, Spain) and double distilled water. At least 10 measurements were carried out for each sample, and average values were calculated. The maximum error did not exceed 3%.

Surface free energy values were calculated using the Owens-Wendt method, which takes into account the dispersive (nonpolar) and polar contribution to the total surface free energy value. This method requires, at least, two different test liquids. As we have described earlier, we have selected four different test liquids with different polar and dispersive

behavior. The Owens-Wendt method considers the following expression:

$$\begin{aligned} \gamma_1 \times (1 + \cos(\theta)) / 2(\gamma_1^d)^{1/2} \\ = (\gamma_s^p)^{1/2} \times [(\gamma_1^p)^{1/2} / (\gamma_1^d)^{1/2}] + (\gamma_s^d)^{1/2}, \end{aligned}$$

where  $\theta$  is the contact angle,  $\gamma_1$  is the total surface free energy of the liquid, and  $\gamma_s$  represents the surface free energy of the solid. The terms with subscripts “d” and “p” refer to the “dispersive” and “polar” component of the surface free energy, respectively. We can see in an easy way that the previous equation can be expressed as a linear expression ( $y = a + bx$ ). So that we can represent  $(\gamma_1^p)^{1/2} / (\gamma_1^d)^{1/2}$  versus a  $\gamma_1(1 + \cos \theta) / (\gamma_1^d)^{1/2}$ . Then, the slope of the line will be  $(\gamma_s^p)^{1/2}$  and the  $y$ -axis intercept will be  $(\gamma_s^d)^{1/2}$ . The total solid surface free energy ( $\gamma_s$ ) will be calculated as the sum of the polar ( $\gamma_s^p$ ) and dispersive ( $\gamma_s^d$ ) component.

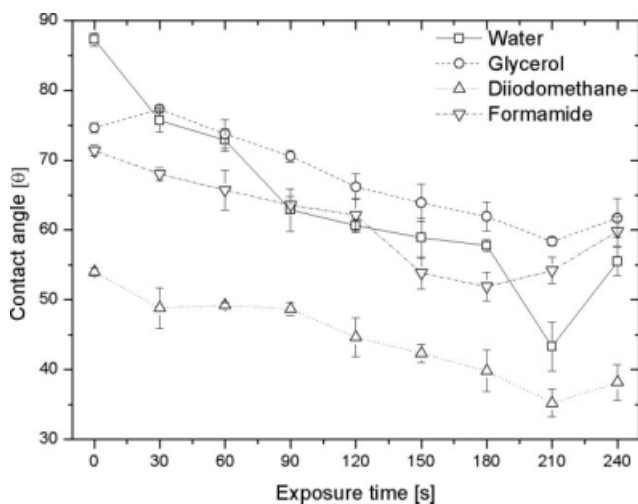
### Characterization of chemical changes

Chemical changes were studied using FTIR with attenuated total reflectance (ATR) accessory. The FTIR spectrometer was a Perkin Elmer, mod FTIR Spectrum BX (PerkinElmer España, S.L., Madrid, Spain), and the ATR accessory model was MIRacle supplied by Pike Technologies (PIKE Technologies, Madison, USA). Samples were directly placed in the ATR accessory, and 10 scans were performed in the 4000–800  $\text{cm}^{-1}$  wavenumber range with a resolution of 2  $\text{cm}^{-1}$ .

### Characterization of adhesion joints

Adhesive joints between two polypropylene sheets were prepared using a polyurethane-type adhesive commercial grade 801 supplied by Adhesivos Kefren (Adhesivos Kefren S.A., Alicante, Spain). It is a high-density monocomponent polyurethane based on 4,4'-diphenyl diisocyanate. The appropriate amount of adhesive was dosed into polypropylene surface. Adhesive joints were subjected to pressure to avoid displacements and after 24 h, adhesive joints were ready for mechanical characterization.

Two types of mechanical tests (shear and T-peel) were performed with a universal test machine Elib 30 (S.A.E. Ibertest, Madrid, Spain). Shear tests were carried out following the guidelines of the ISO 13445 standard; square samples sizing  $25 \times 25 \text{ mm}^2$  were prepared and were subjected to AA photografting as described earlier with different exposure times. After that adhesion joints PP–PP were prepared with an adhesion length of 10–12 mm; the crosshead speed was fixed to 50  $\text{mm min}^{-1}$ . At least five samples for



**Figure 1** Variation of the static contact angle for four different test liquids in terms of the exposure time to UV radiation with acrylic acid as monomer for photografting.

each exposure time were tested, and average values of maximum shear strength were calculated.

T-peel tests ( $180^\circ$ ) were carried out following the UNE-EN 1895. Rectangular samples  $200 \times 25 \text{ mm}^2$  in size were prepared, and after that they were subjected to UV photopolymerization with different exposure times. Once samples were pretreated, it was added the polyurethane adhesive to form PP-PP adhesion joints. An adhesive length of 125 mm was fixed, and the crosshead speed was  $300 \text{ mm min}^{-1}$ . At least five samples for each exposure time were tested, and average values of T-peel strength were calculated.

Characterization of fractured surfaces from T-peel and shear tests was carried with a scanning electron microscope FEI model Phenom (Fei, Oregon, USA). Before sample observation, samples were covered with a gold-palladium alloy in a Sputter Coater EMITECH mod. SC7620 (Quorum Technologies, East Sussex, UK).

## RESULTS AND DISCUSSION

### Characterization of wetting changes

As we have described earlier, changes in wettability are directly related to surface changes. We have evaluated changes in wettability by contact angle measurements with four different test liquids in terms of the exposure time to UV radiation. Figure 1 shows a plot evolution of the static contact angle ( $\theta$ ) for the four test liquids in terms of the exposure time to UV radiation with AA as monomer for photopolymerization.

We can clearly observe a decreasing tendency for contact angle as the exposure time increases. This could be related to surface interlocking of polar

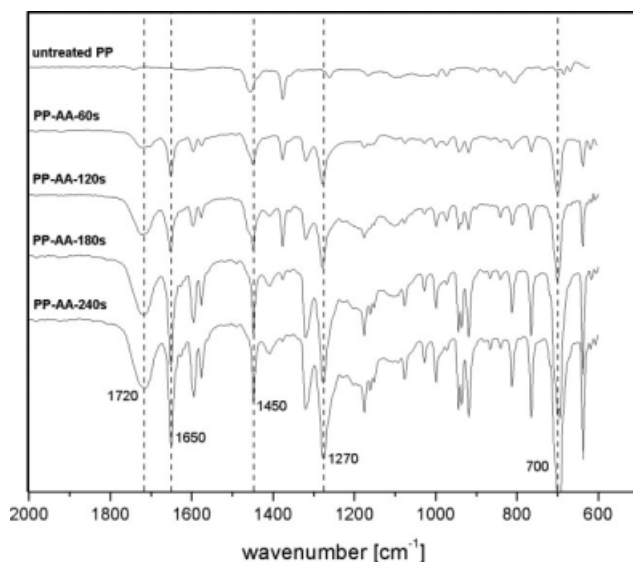
groups coming from the photopolymerized monomer. The evolution of the curves regarding the different test liquids follows similar tendency. In the case of water as test liquid, the contact angle is reduced from  $87.3^\circ$  up to  $43.3^\circ$ , which represents a percentage decrease of about 50%. We can observe a significant decrease at about 210 s followed by a sharp increase at 240 s. This could be related to experimental error as confirmed by error bars in Figure 1, which are greater for 210 s than to other exposure times. Despite this, the trend is clearly distinguishable showing a minimum at about 180–210 s followed by a slight increase for longer exposure times. When using diiodomethane as test liquid, the initial contact angle for the untreated polypropylene is located around  $54^\circ$ , and this value is reduced up to  $36^\circ$  for exposure times in the 180–210 s range as detected using water as test liquid. We can see that the contact angle decreases progressively up to exposure times of about 180 s, and after that it seems to remain almost constant (even we can observe some increase in contact angle values, which could be representative for surface degradation).

The use of four different test liquids allows calculation of surface free energy values. We have used the Owens-Wendt method and the values are summarized in Table I. We can observe values of the total surface free energy ( $\gamma_s$ ) together with the polar ( $\gamma_s^p$ ) and dispersive contribution ( $\gamma_s^d$ ).

As expected, we can observe an increasing tendency in total surface free energy values. The initial surface free energy of polypropylene, which is around  $31.4 \text{ mJ m}^{-2}$ , increases up to values of  $46.7 \text{ mJ m}^{-2}$  for an exposure time of 210 s, and this fact represents an important increase in surface free energy. It is important to remark the evolution of the polar component [ $\gamma_s^p$ ] of the solid surface energy. The initial value is very small (around  $3.0 \text{ mJ m}^{-2}$ ) because of the low polar nature of the untreated polypropylene, and this value is remarkably

**TABLE I**  
Surface Free Energy Values (Total [ $\gamma_s$ ], Polar Component [ $\gamma_s^p$ ], and Dispersive Component [ $\gamma_s^d$ ]) of Polypropylene Surface Modified with Photopolymerized Acrylic Acid in Terms of the Exposure Time to UV Radiation

Exposure time (s)	$\gamma_s$ ( $\text{mJ m}^{-2}$ )	$\gamma_s^p$ ( $\text{mJ m}^{-2}$ )	$\gamma_s^d$ ( $\text{mJ m}^{-2}$ )
0	31.4	3.0	28.4
30	31.8	7.1	24.7
60	33.0	8.8	24.2
90	35.6	15.1	20.5
120	37.8	15.6	22.2
150	40.5	16.3	24.2
180	41.8	16.4	25.4
210	46.7	25.3	21.4
240	41.1	17.5	23.6



**Figure 2** Comparative FTIR-ATR spectra of untreated polypropylene and photopolymerized polypropylene with different exposure times to UV radiation.

increased up to values of about  $25.3 \text{ mJ m}^{-2}$  for an exposure time of 210 s. This is due to the grafting of a polar monomer (AA) onto polypropylene surface. Regarding dispersive component, we can observe a slight decrease from  $28.4 \text{ mJ m}^{-2}$  up to values in the  $20\text{--}25 \text{ mJ m}^{-2}$  range. Therefore, we could expect that the main acting mechanism of the photopolymerization process is surface activation by grafting AA (highly polar) in the topmost layers of polypropylene. This is in agreement with the remarkable increase in the polar component of the solid surface energy. On the other hand, the slight variation on the dispersive component of the solid surface energy could be representative for small changes in surface topography.

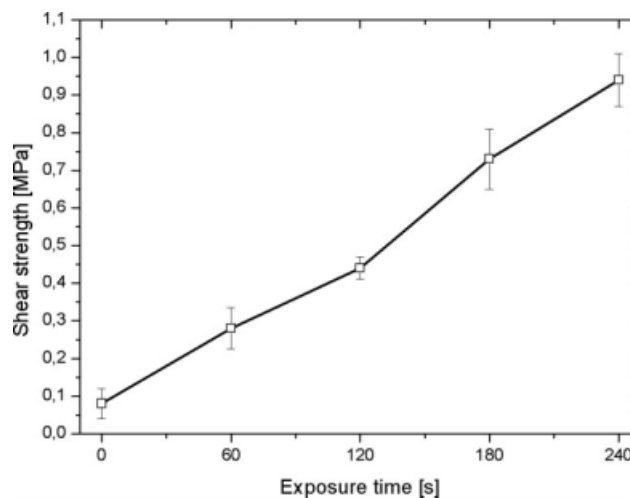
To evaluate surface chemical changes produced by the photopolymerization process, we have used FTIR. Figure 2 shows different FTIR-ATR spectra of untreated polypropylene and UV-photopolymerized polypropylene for different exposure times.

From observation of these spectra, we can see that untreated polypropylene does not show any peak band attributable to oxygen-containing species. If we observe the spectra of the photopolymerized polypropylene samples, we can see typical absorbance peaks and bands attributable to carboxylic groups mainly located at  $1720$ ,  $1650$ , and  $700 \text{ cm}^{-1}$ . Furthermore, the effect of the exposure time is clearly distinguishable in a qualitative way as their intensity increases as the exposure time to UV radiation increases. We can also observe the presence of  $\text{CH}_3$  and  $-\text{CH}_2-$  groups (main peak at  $1450 \text{ cm}^{-1}$ ), which correspond to polypropylene and some of the grafted parts. Photopolymerization is a complex process characterized by different reactions (polypropyl-

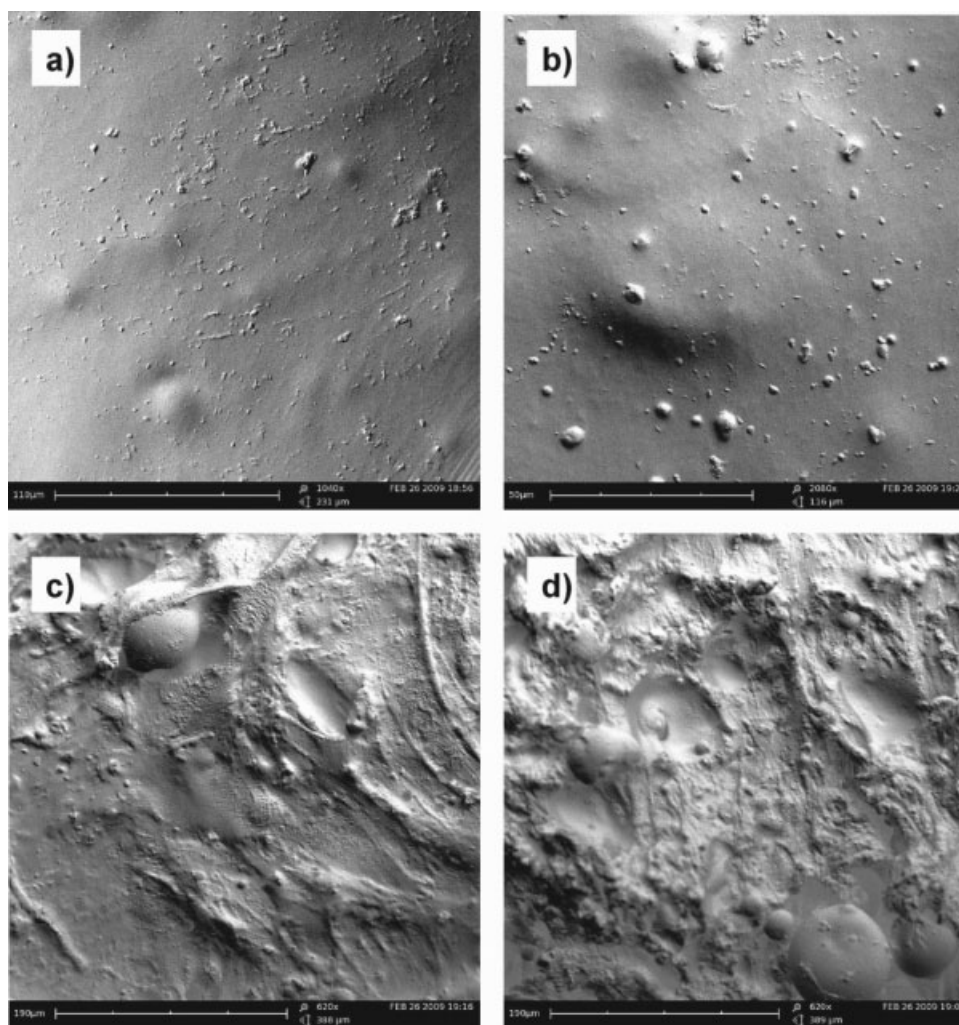
ene chain scission, monomer activation, initiator action, interlock of monomer onto polypropylene chains, etc.); so that other oxygen-containing species could be obtained in this process. As FTIR-ATR spectra show, presence of ester groups ( $\text{C}-\text{O}-\text{C}$ ) is evident with a peak at about  $1270 \text{ cm}^{-1}$ . In a similar way, as the exposure time increases, the intensity of these peaks increases.

### Characterization of adhesion joints

As we have described earlier, the photopolymerization of AA onto polypropylene surface promotes a remarkable increase in surface wettability. This is mainly due to surface interlocking of polar groups from AA monomer. This improvement in surface wettability could lead to an increase in adhesion properties of polypropylene. PP-PP adhesion joints have been characterized in shear and T-peel conditions. Figure 3 shows the plot evolution of the maximum shear strength of PP-PP adhesion joints in terms of the exposure time to UV radiation. As expected, we observe similar tendency to that observed for solid surface energy. As the exposure time increases the shear strength increases. The initial value of the shear strength of PP-PP adhesion joints (untreated polypropylene) is close to  $0.08 \text{ MPa}$ , and as we can observe in Figure 3, this value is remarkably increased up to values of  $0.94 \text{ MPa}$  for a UV exposure time of 240 s. Thus, photopolymerization of AA has a positive effect on final performance of PP-PP adhesion joints. Furthermore, we can observe high dependence of adhesion properties on the UV exposure time during the photopolymerization process, which is in accordance to the results described earlier regarding surface wettability. If we observe the average values of shear strength for



**Figure 3** Variation of the maximum shear strength of PP-PP adhesion joints in terms of the UV exposure time during photopolymerization of acrylic acid.

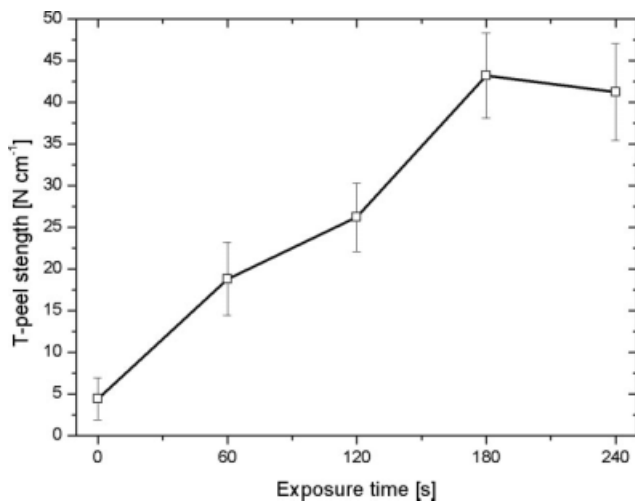


**Figure 4** SEM microphotographs of fractured surfaces (shear tests) of PP-PP adhesion joints with different UV exposure times during photopolymerization of acrylic acid; (a) 60 s [ $\times 1040$ ], (b) 120 s [ $\times 2080$ ], (c) 180 s, and (d) 240 s [ $\times 620$ ].

exposure times of 180 and 210 s, we see an increasing tendency but if we take into account the error bars, the shear strength could slightly increase or even remain almost constant, and this is in accordance to the evolution of the contact angles and surface energy in terms of the exposure time as described earlier.

The effect of the UV exposure time during photopolymerization of AA can also be detected through the observation of scanning electron microscopy (SEM) microphotographs of fractured surfaces obtained from the shear tests of PP-PP adhesion joints. Figure 4(a,b) shows the fractured surface of PP-PP adhesion joints for UV exposure times of 60 and 120 s, respectively. We can observe in a clear way quite smooth surfaces; this is because the polyurethane adhesive has not joined appropriately the two polypropylene sheets and after the shear test it is peel off the surface in an easy way, thus resulting in very smooth surface, which is representative for an “adhesive fracture type.” Figure 4(c,d) shows the

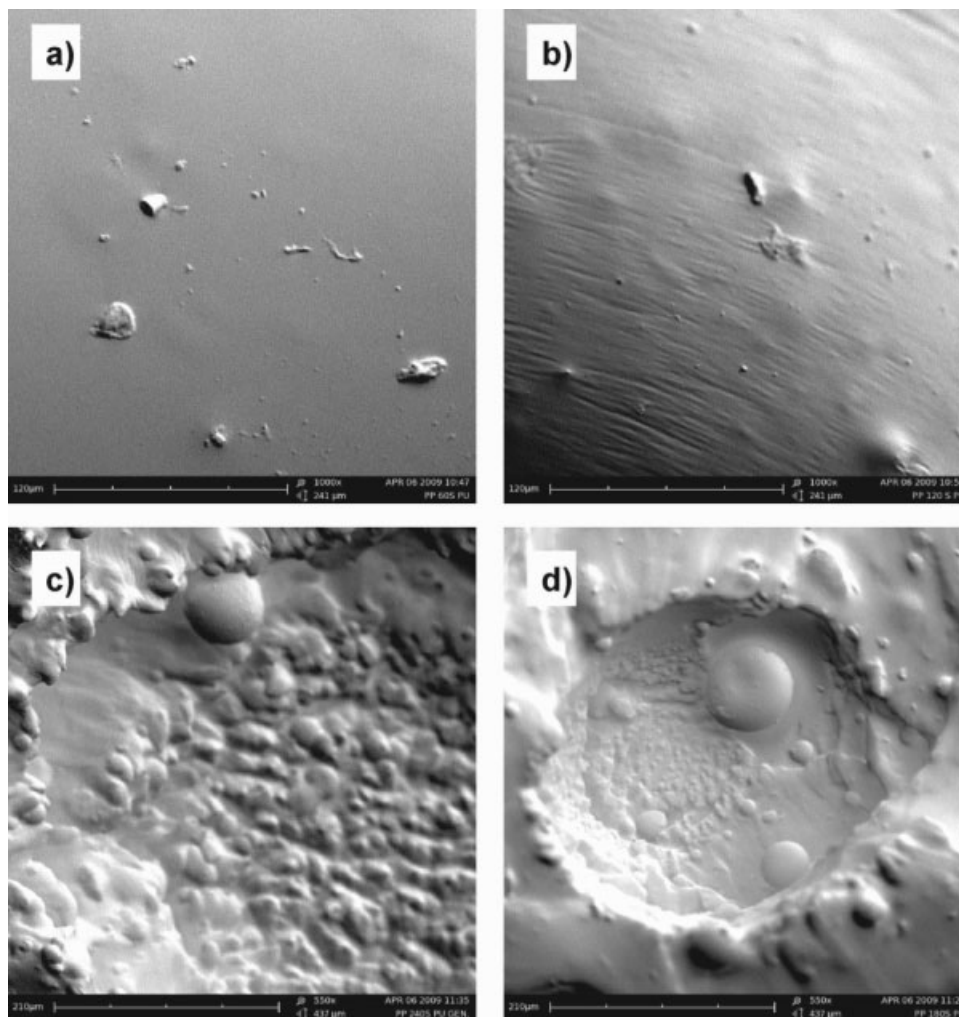
SEM microphotographs of fractured PP-PP adhesion joints with UV exposure times of 180 and 240 s. In a qualitative way, we can observe a remarkable difference regarding samples with exposure times of 60 and 120 s. For long exposure times, the photopolymerization process leads to surface grafting of AA monomers onto polypropylene surface, thus increasing polarity. All these polar groups are capable to interact with the adhesive to form strong adhesion joints; so that during the shear test, the adhesive is strongly linked to polypropylene surfaces and once certain shear strength is reached it breaks, but a great amount of adhesive remains adhered to polypropylene surface and this leads to high surface roughness. This is a “cohesive fracture type.” For short exposure times, the amount of AA grafted to polypropylene surface is small, and PP-PP adhesion joints do not reach the maximum performance, thus resulting in an adhesive fracture. As the exposure time increases, the amount of AA photopolymerized onto polypropylene surface increases, and this



**Figure 5** Variation of the T-peel strength of PP-PP adhesion joints in terms of the UV exposure time during photopolymerization of acrylic acid.

allows strong interactions with the polyurethane adhesive; thus, the fractured surface is a mix between adhesive and cohesive type (the cohesive type increases as the UV exposure time increases).

PP-PP adhesion joints have also been characterized in T-peel ( $180^\circ$ ) conditions. Figure 5 shows the evolution of the T-peel strength in terms of the UV exposure time during photopolymerization of AA. We observe similar tendency to that observed for shear tests. The initial T-peel strength of PP-PP adhesion joints (untreated polypropylene) is located around  $4.43 \text{ N cm}^{-1}$ . This value is considerably increased up to values of  $41.2 \text{ N cm}^{-1}$  for UV exposure times of 240 s (which represents a percentage increase higher than 930%). As the wetting properties increase, the mechanical response of PP-PP adhesion joints increases. UV exposure times in the 180–210 s represent good balance between overall adhesion properties and quickness (from an



**Figure 6** SEM microphotographs of fractured surfaces (T-peel tests) of PP-PP adhesion joints with different UV exposure times during photopolymerization of acrylic acid; (a) 60 s [ $\times 1000$ ], (b) 120 s [ $\times 1000$ ], (c) 180 s [ $\times 550$ ], and (d) 240 s [ $\times 550$ ].

industrial point of view). If we observe the average values of the T-peel strength in the 180–240 s range, we see a slight decrease but if we take into account the statistical distribution of the T-peel strength with the error bars, T-peel strength could remain almost constant or a slight decrease, which is in accordance to the results described earlier regarding shear strength values.

The effects of the exposure time to UV radiation during the photopolymerization process of AA are also evident from the observation of SEM microphotographs of fractured surfaces of PP–PP adhesion joints from the T-peel tests (Fig. 6). Figure 6(a,b) shows SEM microphotographs of fractured surfaces of PP–PP adhesion joints with a photopolymerization pretreatment for 60 and 120 s. We can see smooth surfaces and this is related to poor interaction between polypropylene substrate and the polyurethane adhesive. As we have described earlier, the photopolymerization process promotes grafting of AA monomers into polypropylene surface. These grafted monomers are characterized by high polarity so that these points act as a bridge for the establishment of interactions between the polypropylene surface (characterized by low polarity) and the adhesive to form strong adhesion joints. In a similar way to shear tests of adhesion joints, the fractured surfaces for short UV exposure times are highly smooth (adhesive fracture), and it is representative for poor adhesion between the adhesive and the polypropylene substrate. As the UV exposure time increases [Fig. 6(c,d)], we observe a remarkable increase in surface roughness. This is due to the presence of high amount of grafted AA, which acts as a bridge for the establishment of strong interactions between polypropylene substrate and polyurethane adhesive. So that T-peel tests lead to adhesive breakage, and the cohesive fracture grows in a remarkable way.

## CONCLUSIONS

The photopolymerization process of AA on a polypropylene substrate is an efficient method to increase its wettability and subsequently to improve adhesion properties. This is mainly due to surface grafting of AA (highly polar) into polypropylene surface (characterized by low polarity). The action of UV radiation promotes different reactions during the photopolymerization process: scission of polypropylene chains, activation of AA monomer, activation of initiator, graft polymerization of AA on polypropylene chains, etc. The overall effect of all these simultaneous processes is a remarkable increase in surface free energy of polypropylene, which changes from 31.4  $\text{mJ m}^{-2}$  up to values close to 46.7  $\text{mJ m}^{-2}$  because of the interlock of AA on the topmost layers of polypropylene as revealed by FTIR analysis. It is

important to remark the increase in the polar component of the solid surface energy ( $\gamma_s^p$ ), which changes from 3.0 up to 25.3  $\text{mJ m}^{-2}$  for an exposure time of 210 s. So that optimum wetting properties are obtained for exposure times in the 180–210 s range. Long exposure times could lead to surface degradation. Hence, the use of these conditions is interesting from an industrial point of view as they lead to high wettability with relatively short exposure times.

Regarding mechanical properties of PP–PP adhesion joints, it is important to remark that similar tendency is observed for both shear and T-peel tests. The small layer of AA photopolymerized on polypropylene surface acts as a bridge for the establishment of strong interactions between the polyurethane adhesive and polypropylene substrates, thus obtaining good adhesion properties. For short UV exposure times, the adhesive is easily removed because of low interactions between adhesive and the photopolymerized layer of AA, and this fact results in adhesive fracture type as detected by SEM analysis. On the other hand, long exposure times in the 180–210 s lead to great amounts of AA photopolymerized on polypropylene surface, and this is responsible for the strength of adhesion joints as the polar groups of AA can intensively interact with polyurethane adhesive to form strong and stable adhesion joints. In this case, SEM analysis has revealed a combined adhesive–cohesive fracture type, thus indicating good adhesion properties.

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