Surface Modification of Polypropylene Sheets by UV-Radiation Grafting Polymerization

Jung-Dae Cho,[1] Soon-Gi Kim,[2] Jin-Who Hong[2]

[1]*Institute of Photonics & Surface Treatment, Q-Sys Co. Ltd., 971–14 Wolchul-Dong, Buk-Gu, Gwangju 500–460, South Korea*
[2]*Department of Polymer Science & Engineering, Chosun University, Gwangju 501–759, South Korea*

ABSTRACT: 1,6-Hexanediol diacrylate (HDDA) was grafted onto polypropylene (PP) substrates in the presence of benzophenone (BP) and isopropylthioxanthone (ITX) photoinitiators, and then polyurethane acrylate formulations were coated onto the HDDA-*g*-PP substrates, using UV radiation. The amount grafted and the grafting efficiency of the polymerizations were determined gravimetrically. The effects of the photoinitiator concentration and the UV radiation intensity on the physicochemical surface properties and the grafting efficiency of the UV-radiation grafting polymerizations were characterized in detail using contact-angle measurements, Fourier transform infrared spectroscopy with attenuated total internal reflection, and scanning electron microscopy. The results showed that the amount grafted and the surface polarity of the HDDA-*g*-PP substrates both increased linearly with increasing BP photoinitiator concentration and UV radiation intensity, and that the addition of a small amount of ITX markedly enhanced both parameters, probably due to photosensitization. The adhesion of the UV-cured coating onto the HDDA-*g*-PP substrates was evaluated using the crosshatch adhesion test. The results indicated that the amount of HDDA grafted onto the PP substrates should exceed about 1 mmol/cm^2 for satisfactory adhesion with the UV-cured coating. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1446–1461, 2006

Key words: radiation; grafting polymerization; polypropylene; FTIR; surface polarity

INTRODUCTION

Most polymer materials are chemically inert and essentially hydrophobic, i.e., they have an inert surface of low surface energy and high contact angle with water and other polar liquids; therefore, they require surface treatment to enhance their low adsorption of dyes and inks and low adhesion to coatings and other polymers, achieve biocompatibility, and decrease electrostatic charge effects. Various surface-modification techniques have been widely used to alter surface properties, including chemical reactions, corona discharge, flame and plasma treatments, and high-energy irradiation.[1–5]

Ultraviolet (UV) irradiation is one such surface-modification technique, which is based on photografting polymerization at the surface of polymeric materials, using a hydrogen abstraction-type photoinitiator (e.g., Norrish type II), and has been also applied to modify the physicochemical surface properties of polymers because of its simplicity and economics. This approach for surface modification has been recently employed in various industrial fields, such as poly- meric reagents, polymeric catalysts, polymer film gels, and temperature-responsive polymer films.[6]

In recent years, several research groups have reported surface modification using this UV-radiation technique. Decker et al. grafted acrylate onto polyvinylchloride and polypropylene (PP) films, and reported that surface photografting is an efficient method of protecting the surface of polymer-formed materials against photodegradation and weathering, since it greatly improves the adhesion of the coating which, in addition, acts as an effective UV screen.[7,8] Rånby and Yang proposed the kinetics and mechanism of bulk surface photografting of an interlayer between polymer films.[3,9,10] Garnett et al. reported on the effects of additives such as photoinitiator, monomer, and solvent on the photografting efficiency, and on the UV grafting of complex charge-transfer systems for photoinitiator-free UV curing.[11–13] However, to our knowledge, there are no reports of surface modification by UV-radiation grafting polymerization initiated by a blend of photoinitiators having different UV absorption regions for the improvement of photografting efficiency and of the adhesion to coatings.

The present study was divided into three parts:[1] designing UV-radiation-initiated grafting and coating processes for acrylates systems,[2] investigating the effects of a blend of photoinitiators (benzophenone (BP) and isopropylthioxanthone (ITX)) and UV-radiation

TABLE I
Grafting Systems of the HDDA With Varying Amounts of BP, With and Without ITX Photoinitiator[a]

Component	A	B	C	D	AI	BI	CI	DI
HDDA (acrylate monomer)	100	100	100	100	100	100	100	100
BP (photoinitiator)	1	3	5	7	1	3	5	7
ITX (photoinitiator)	0	0	0	0	0.3	0.3	0.3	0.3

[a] Data are shown as weight percentages

intensity on the physicochemical surface properties of the UV-radiation grafting polymerizations, and[3] determining simple and effective techniques for evaluating the surface radiation grafting polymerization systems and the coatings onto grafted polymer substrates.
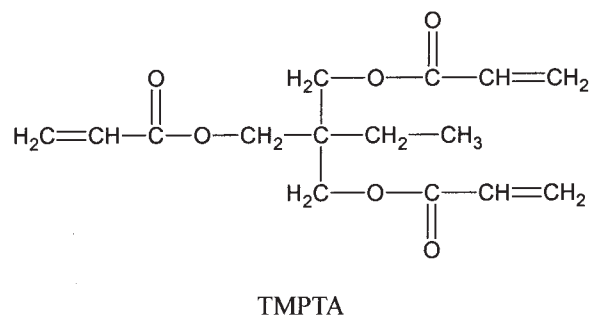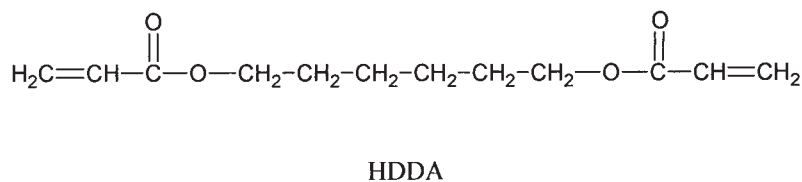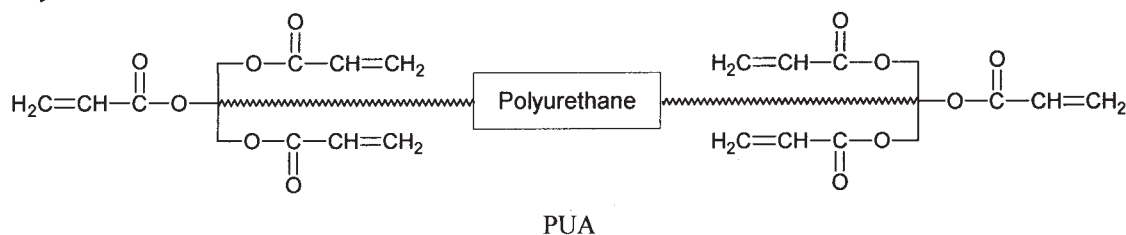
EXPERIMENTAL

Materials

Substrate

Commercial-grade PP sheet (Polypenco, Korea) with a thickness of 3 mm was used as a substrate. It was cut
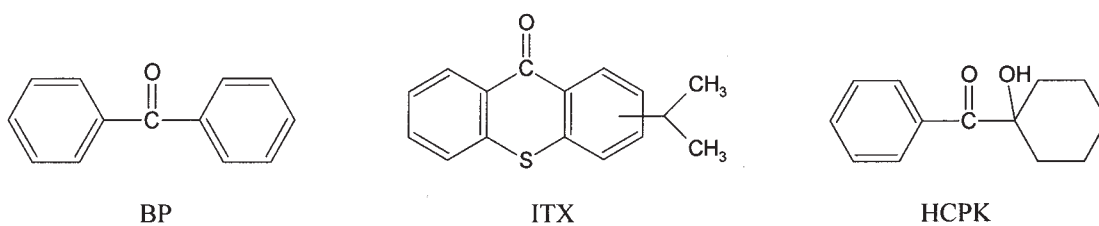

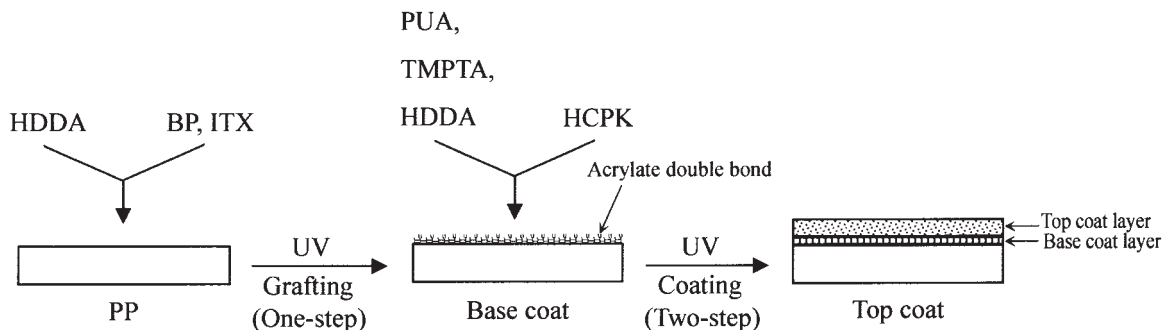Figure 1 Chemical structures of the various acrylates and photoinitiators used.

Figure 2 Radiation-initiated grafting and coating processes of the UV-curable acrylates systems.

into rectangular samples with an area of 100×70 mm^2, rinsed clean with isopropyl alcohol, and then immersed in methyl ethyl ketone for 72 h to remove impurities from the sheet surface. Afterward, the sheets were dried to a constant weight at 50°C in a vacuum oven for 72 h.

Grafting solutions

The grafting systems containing 1,6-Hexanediol diacrylate (HDDA) and different amounts of photoinitiators are specified in Table I. HDDA from UCB Chemicals was used as the monomer for grafting to PP

substrate, and BP from Aldrich and ITX from First Chemical were used as photoinitiators.

Coating formulation

Aliphatic polyurethane hexa-acrylate (PUA, Ebecryl 9970, UCB Chemicals) was used as the resin. Trimethylolpropane triacrylate (TMPTA, Sartomer) and HDDA (UCB Chemicals) were used as a reactive diluent. 1-Hydroxy-cyclohexyl-phenyl ketone (HCPK, Irgacure 184, Ciba-Geigy) was used as a free-radical photoinitiator. The formulation comprised a blend of 60 wt % PUA, 20 wt % TMPTA, and 20 wt % HDDA,
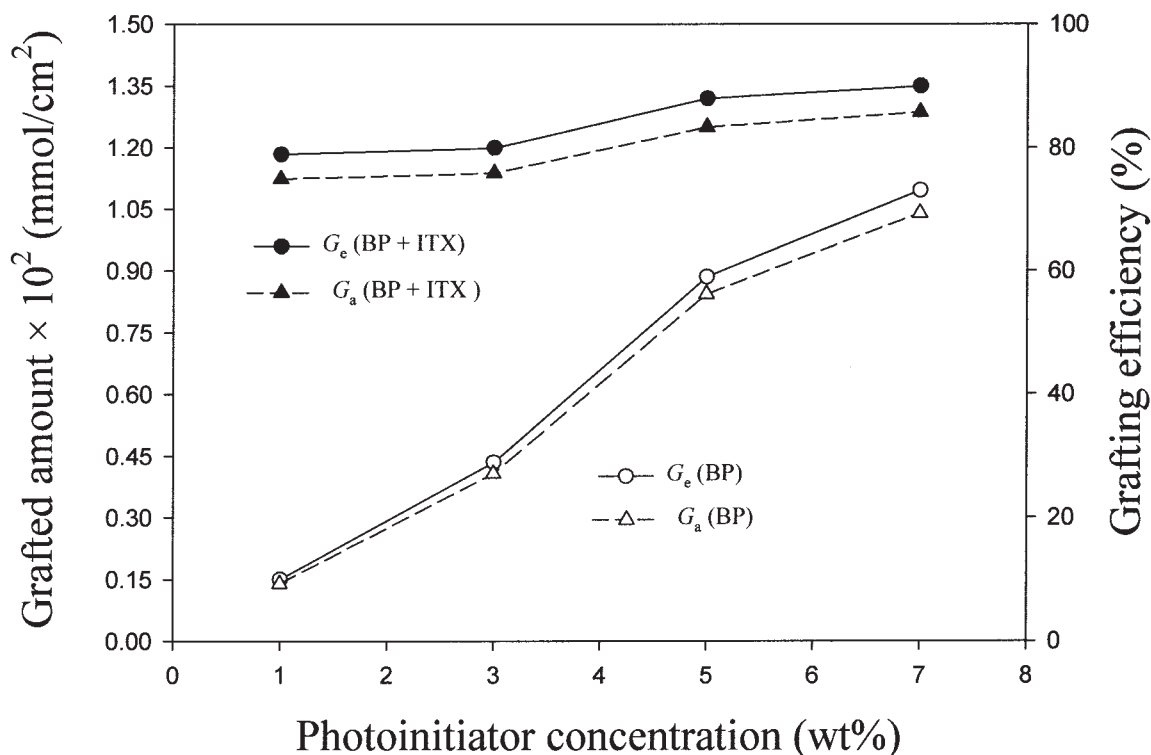

Figure 3 Superimposition of the amount grafted (G_a) and the grafting efficiency (G_e) for PP substrates in systems without and with ITX (A–D and AI–DI, respectively) as a function of BP photoinitiator concentration. UV radiation intensity: 5.2 J/cm^2.
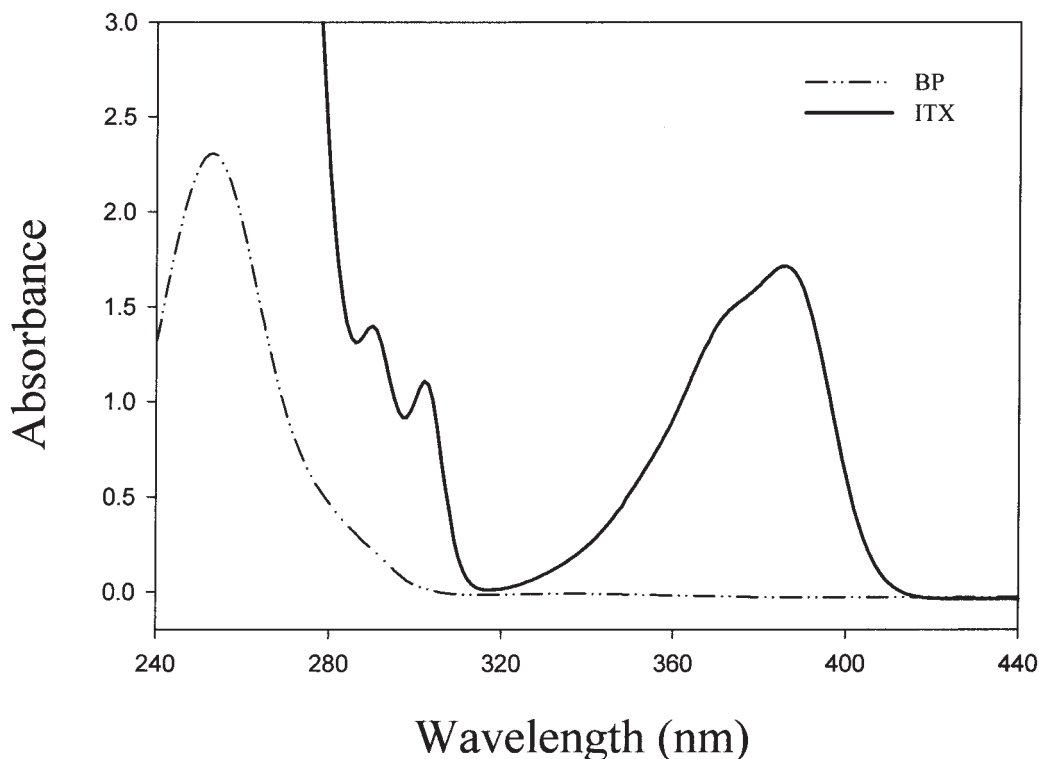
Figure 4 Absorption spectra for the photoinitiators BP and ITX.

to which HCPK was added at 3 wt %. All the materials were used as received. The structures of the materials are illustrated in Figure 1.

Surface radiation grafting procedure

The UV-radiation grafting polymerization of HDDA onto the PP sheet was performed as follows. HDDA was applied to the PP sheet substrate, using a wire-wound rod, and the sheet was exposed to UV radiation at 120 W/cm, using conventional UV equipment with a medium-pressure mercury lamp. The range of UV wavelengths was 200–445 nm, and the intensities of UV radiation—-varied by adjusting the conveyor speed—-were 2.2, 3.1, 4.0, and 5.2 J/cm^2, respectively, as measured with a UV radiometer (UV POWER PUCK, EIT). While conveyor speed was used to control UV exposure, the approximate exposure times for the samples were 10.2, 14.5, 18.4, and 24.1 s, respectively. After grafting, the sheet samples were sufficiently washed with isopropyl alcohol to remove residual HDDA, and dipped in methyl ethyl ketone for 72 h, brushed for 5 min in hot water to remove any homopolymer formed, and then dried to a constant weight at 50°C in a vacuum oven for 72 h. The amount grafted (G_a) and the grafting efficiency (G_e) were calculated gravimetrically and defined according to the following equations:

$$G_a(\text{mmol/cm}^2) = \left(\frac{\text{grafted PP(g)} - \text{ungrafted PP(g)}}{\text{surface area (cm}^2) \times M}\right) \times 1000 \quad (1)$$

$$G_e(\%) = \frac{W_g}{W_p} \times 100 \quad (2)$$

where M is the molecular weight of the monomer used for grafting, W_p is the weight of polymer formed as

TABLE II
Contact Angles, Surface Energies, and Polarity Onto the Surface of the Pure PP and the HDDA-g-PP Substrates Grafted by the Systems (A–D) Without ITX and the Systems (AI–DI) With ITX As a Function of the BP Photoinitiator Concentration[a]

Grafting system	Contact angle (θ)		γ_s (mJ/m^2)	γ_s^d (mJ/m^2)	γ_s^P (mJ/m^2)	X^P
	Water	TCP				
Pure PP	84.6	58.3	26.7	19.7	7.0	0.26
A	81.2	53.7	29.3	21.2	8.1	0.28
B	72.8	46.5	34.9	23.0	11.9	0.34
C	56.7	33.4	46.4	25.4	21.0	0.45
D	53.1	29.2	49.2	26.2	23.0	0.47
AI	53.2	29.4	49.1	26.1	23.0	0.47
BI	52.8	28.5	49.4	26.3	23.1	0.47
CI	52.1	27.9	50.0	26.5	23.5	0.47
DI	51.6	27.4	50.3	26.5	23.8	0.47

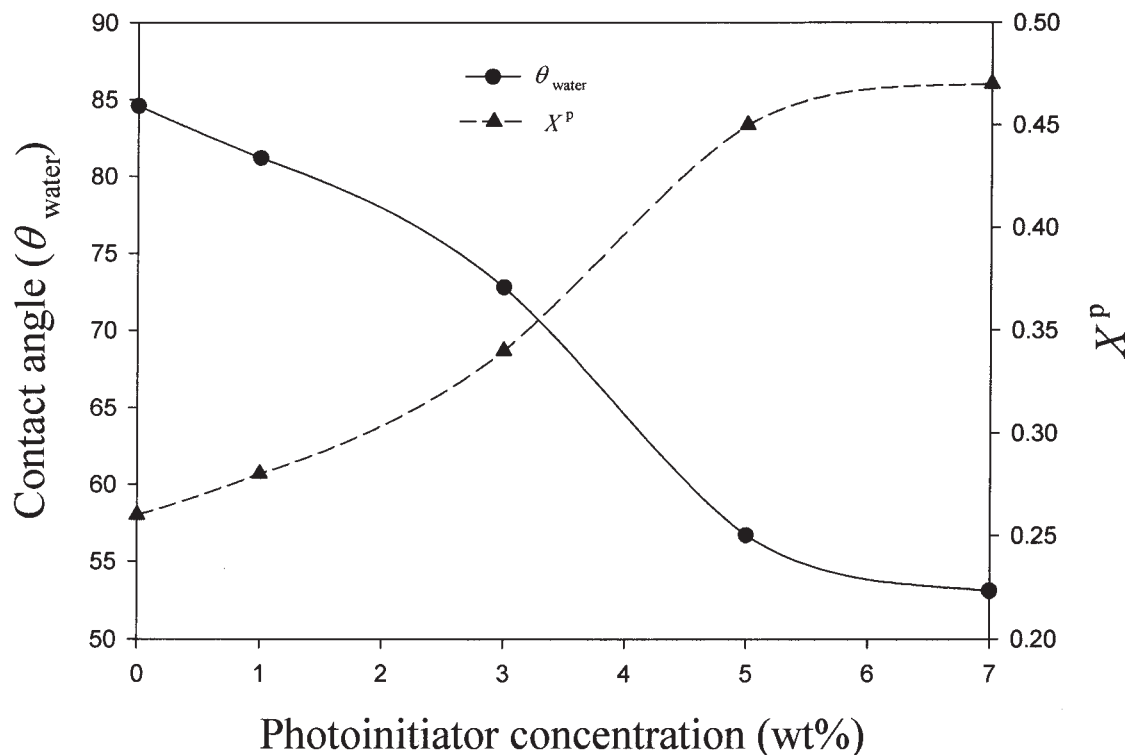[a] UV radiation intensity: 5.2 J/cm^2

Figure 5 Superimposition of the contact angle of water and the surface polarity of the pure PP and the HDDA-g-PP substrates grafted in systems A–D as a function of the photoinitiator concentration. UV radiation intensity: 5.2 J/cm^2.

obtained by weighing after removal of the residual monomer, and W_g is the weight of the grafted polymer as obtained by weighing after extraction of the homopolymer with appropriate solvents.

UV–visible spectroscopy

The absorption spectra of the photoinitiators (BP and ITX) were obtained using a Cary 3 Bio UV–visible spectrophotometer. Dilutions of 0.02 g/L in methylene chloride were prepared, and quart cells with a 1-cm path length were used in the analysis.

Contact-angle measurements

The contact-angle measurements were carried out using a contact-angle goniometer (SEO 300 A) by a sessile drop method at about 20°C. Liquid droplets were laid onto the PP sheet substrates, with a microsyringe. To verify the reproducibility, the measurements were repeated five times, and the average value was obtained for each sample.

Surface energy is a direct expression of intermolecular forces. The surface of a solid possesses additional free energy like that of a liquid; however, owing to the reduced molecular mobility, this free energy is not directly observable and hence must be measured by indirect methods.

When a liquid drop is in contact with an ideally smooth, homogeneous, insoluble, and rigid solid, it shows an equilibrium contact-angle given by Young's equation:[14]

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos\theta \qquad (3)$$

where γ_{sv} is the surface energy of a solid; γ_{sl} and γ_{lv} are the interfacial surface tension between the liquid and the solid, and the surface tension of the liquid against saturated vapor, respectively; and θ is the equilibrium contact-angle. It should be noted that γ_{sv} is not the surface energy of the solid (γ_s in vacuum)—the difference is referred as the spreading pressure π_e ($\pi_e = \gamma_{sv} - \gamma_s$). The vapor adsorption of the polymers (which are low-surface-energy solids) was assumed to be negligible, so that $\gamma_s = \gamma_{sv}$.

According to the Owens–Wendt–Kaelble equation,[15,16] the surface energy ((γ_s)) of a solid is equal to the sum of dispersion (γ_s^d) and polar (γ_s^p) components:

$$\gamma_s = \gamma_s^d + \gamma_s^p \qquad (4)$$

and the following relation has been used:

$$\gamma_{sv} = \gamma_s + \gamma_{lv} - 2(\sqrt{\gamma_s^d \gamma_{lv}^d} + \sqrt{\gamma_s^p \gamma_{lv}^p}) \qquad (5)$$

where γ_{lv}^d and γ_{lv}^p are the dispersion and polar components of the surface energy of the liquid, respectively. Combining eqs. (4) and (5) with eq. (3) yields the following equation:

$$(1 + \cos\theta) = 2\left(\frac{\sqrt{\gamma_s^d \gamma_{lv}^d}}{\gamma_{lv}} + \frac{\sqrt{\gamma_s^p \gamma_{lv}^p}}{\gamma_{1v}}\right) \qquad (6)$$

By measuring the contact angles of two different liquids with known values of γ_{lv}, γ_{lv}^d and γ_{lv}^p against a solid surface, the two unknown components of a solid surface, γ_s^d and γ_s^p, occurring in eq. (6) can be determined, and the polarity of a solid surface, X^p, is calculated using the following equation:

$$X^P = \frac{\gamma_s^P}{\gamma_s} \qquad (7)$$

The Owens–Wendt–Kaelble method is commonly used in the measurement of the surface energy of a polymer surface. In this study, the dispersive (γ_s^d) and polar ((γ_s^p)) components of the surface energy of the grafted and ungrafted PP sheets were evaluated from the contact angles of distilled water ($\gamma = 72.8$ mJ/m^2 with $\gamma^p = 50.3$ mJ/m^2, $\gamma^d = 22.5$ mJ/m^2, and a polarity ($X^P = \gamma^p / \gamma$) of 0.69) and tricresylphosphate (purchased from Aldrich; $\gamma = 40.9$ mJ/m^2 with $\gamma^p = 1.7$ mJ/m^2, $\gamma^d = 39.2$ mJ/m^2, and $X^P = 0.04$).

FTIR-ATR spectroscopy

FTIR-ATR (Fourier transform infrared spectroscopy with attenuated total internal reflection) spectra of the grafted PP sheet samples were recorded on a Perkin–Elmer Spectrum GX, using a horizontal ATR accessory for FTIR spectroscopy (PIKE Technologies), which was continuously purged with purified air that was free of carbon dioxide and water (desiccant air dryer from New Techniques). To increase the signal-to-noise ratio, each set of reference and sample spectra shown here represents the average of 128 scans recorded at a resolution of 8 cm^{-1}. A ZnSe crystal was used as the internal reflection element, and the incident angle was 45°. Pure PP sheet was also measured as a reference sample, under the same conditions. The depth of penetration (D_p), which depends upon the wavelength considered (λ), can be calculated from the following equation:[17]

$$D_p = \frac{\lambda}{2\pi(n_1^2\sin^2\theta - n_2^2)^{1/2}} \qquad (8)$$

where θ is the angle of incidence, and n_1 and n_2 are the refractive indices of the reflection element and the sample, respectively.

Scanning electron microscopy

The surface morphology of the UV-cured films was observed using scanning electron microscopy (SEM; Hitachi S-4700) at an accelerating voltage of 1 kV.

Coating procedure and tests of coating properties

The UV-curable acrylates coating formulations were applied to the ungrafted and grafted PP substrates, using a wire-wound rod, and the wet films were exposed to UV radiation at 120 W/cm, using conventional UV equipment with a medium-pressure mercury lamp. The range of UV wavelengths was 200–445
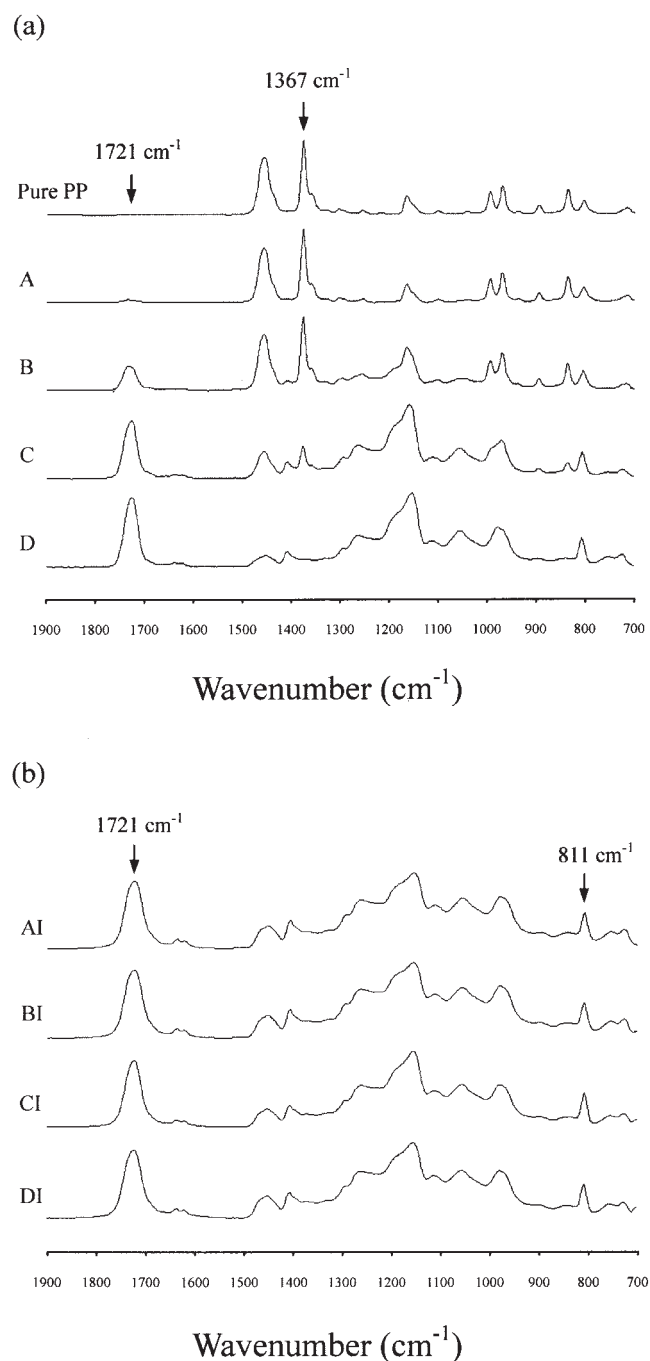

Figure 6 FTIR-ATR spectra of the pure PP and the HDDA-g-PP substrates grafted in systems A–D ((a) without ITX) and systems AI–DI ((b) with ITX) as a function of the BP photoinitiator concentration. UV radiation intensity: 5.2 J/cm^2.

nm, and the intensity of UV radiation was 3.1 J/cm^2. To evaluate the adhesion of the UV-cured coating onto the HDDA-g-PP substrates, a crosshatch adhesion test was conducted according to the standard ASTM method D4541. This test method of crosshatch adhesion involves sticking pressure-sensitive tape to an area on the film upon which an 11 × 11 grid of cuts has been made. The tape is pulled off, and the percentage remaining is then quoted. The film properties were measured 24 h after UV exposure.

RESULTS AND DISCUSSION
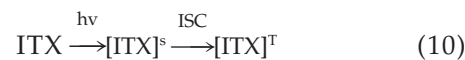
UV-radiation grafting and coating processes

The adhesion between coatings and polymeric substrates that are chemically inert and essentially hydrophobic remains one of important issues in UV-curing technology, especially in coatings and adhesives applications due to the significant shrinkage that occurs during the rapid liquid-to-solid phase change, and to the absence of a solvent in the formulation that would swell the organic substrate and help to achieve good adhesion. Consequently, adhesion failure is commonly observed at the interfacial area between coatings and polymeric substrates.

As one of the methods to improve the adhesion characteristics of coatings to organic materials with a hydrophobic surface, the UV-radiation grafting process has been used in UV-curing technology. The basic idea was to promote a photoinitiated grafting polymerization at the surface of polymeric materials by using hydrogen abstraction-type photoinitiator (Norrish type II), and has been also applied to modify the physicochemical surface properties of various polymer materials, in particular, polyolefins.[3–13] Indeed, the creation of chemical bonds between the grafted polymer network and the organic substrate was shown to markedly enhance the adhesion and surface properties. In the present work, surface modification by UV-radiation-initiated grafting polymerization onto PP substrates was performed by using a blend of photoinitiators having different UV absorption regions in a two-step radiation grafting and coating process, which improved photografting efficiency and adhesion characteristics to acrylate coatings, as presented in Figure 2.
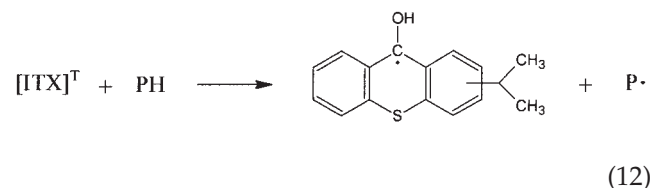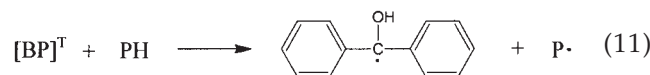
To make the PP substrate more receptive to photografting by the UV-curable coating, it was photo-

chemically treated to generate acrylate groups bonded to its surface. In the first step of the radiation grafting process, grafting solutions of HDDA containing different amounts of BP and ITX photoinitiators were coated with a thin layer and then exposed to UV radiation. The excited triplet states formed upon UV exposure of BP or ITX are known to interact with organic compounds by electron transfer followed by proton transfer.[18] In the present case, because of the significant difference in bond energy between the tertiary C—H bond (93 kcal/mol) on the surface of the substrate and the ethylenic C—H bond (106 kcal/mol) in HDDA, the labile tertiary atoms of the PP substrate are the most likely to be abstracted by the excited BP or ITX molecules.[3] The alkyl radicals formed onto the PP backbone will initiate the grafting polymerization by reacting with the surrounding HDDA monomers and will thus generate polymer chains grafted at the surface of the substrate and then form a grafted polymer network containing acrylate double bonds at its surface. The reaction mechanism is summarized below:

Excitation

$$BP \xrightarrow{h\nu} [BP]^S \xrightarrow{ISC} [BP]^T \tag{9}$$

$$ITX \xrightarrow{h\nu} [ITX]^S \xrightarrow{ISC} [ITX]^T \tag{10}$$

Photoreduction

$$[BP]^T + PH \longrightarrow \quad + \quad P\cdot \tag{11}$$

$$[ITX]^T + PH \longrightarrow \quad + \quad P\cdot \tag{12}$$

Initiation

$$P\cdot + HDDA \longrightarrow \tag{13}$$

Propagation

$$+ nHDDA \longrightarrow \text{Primary Grafting Polymerization} \tag{14}$$

$$[BT]^T \quad or \quad [ITX]^T \quad + \quad P\text{-}CH\text{-}CH\text{-}COO(CH_2)_6OOC\text{-}CH=CH_2 \quad \longrightarrow \tag{15}$$

$$P\text{-}CH\text{-}\overset{\bullet}{C}\text{-}COO(CH_2)_6OOC\text{-}CH=CH_2 \quad + \quad nHDDA \quad \longrightarrow \quad \text{Secondary Grafting Polymerization}$$

$$\text{(benzophenone ketyl)} \quad or \quad \text{(ITX ketyl)} \quad + \quad nHDDA \quad \longrightarrow \quad \text{Homopolymer} \tag{16}$$

Termination

$$P\text{-}CH\text{-}\overset{\bullet}{C}\text{-}COO(CH_2)_6OOC\text{-}CH=CH_2 \quad + \quad \text{(benzophenone ketyl)} \quad or \quad \text{(ITX ketyl)}$$

$$\longrightarrow \quad P\text{-}CH_2\text{-}C\text{-}COO(CH_2)_6OOC\text{-}CH=CH_2 \quad or \quad P\text{-}CH_2\text{-}C\text{-}COO(CH_2)_6OOC\text{-}CH=CH_2 \tag{17}$$

$$P\text{-}CH\text{-}\overset{\bullet}{C}\text{-}COO(CH_2)_6OOC\text{-}CH=CH_2 \quad + \quad P\text{-}CH\text{-}\overset{\bullet}{C}\text{-}COO(CH_2)_6OOC\text{-}CH=CH_2$$

$$\longrightarrow \quad P\text{-}CH_2\text{-}C\text{-}COO(CH_2)_6OOC\text{-}CH=CH_2 \\ P\text{-}CH_2\text{-}C\text{-}COO(CH_2)_6OOC\text{-}CH=CH_2 \qquad \text{(Crosslinking)} \tag{18}$$
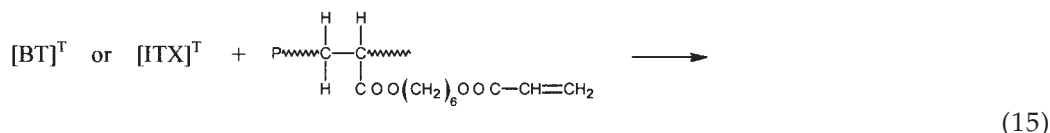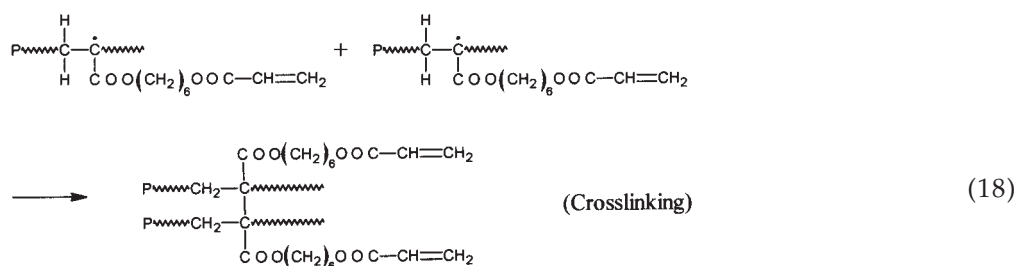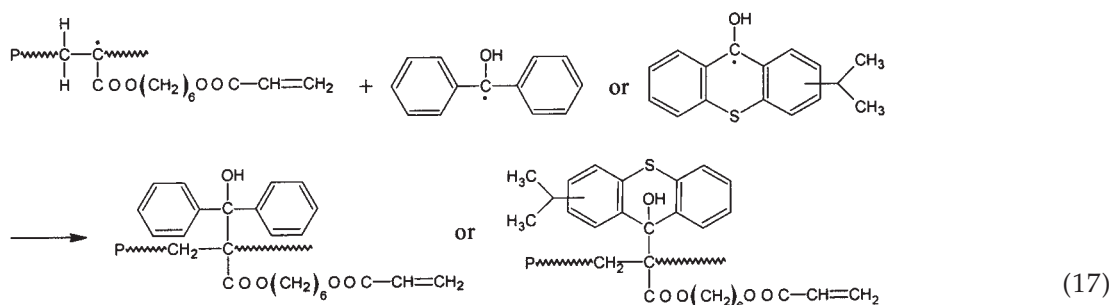
where *P* stands for the PP substrate. The molecular mechanism of surface radiation grafting involves primary and secondary grafting reactions, as shown above in eqs. (14) and (15). The primary grafting includes initiation and propagation of linear chains, which are terminated by the addition of ketyl radicals. Therefore, BP and ITX act both as initiator and terminator (eq. (17)). In the presence of sufficient amounts of photoinitiators (BP and ITX) and monomer (HDDA), continued UV irradiation produces subsequent branching of the primary grafted linear chains by a secondary grafting reaction. The mechanism is abstraction of tertiary-bonded hydrogen on the chains, and thereby the primary grafted linear chains grow to branched chains from the PP substrate surface and give the crosslinked polymer network formed by the reaction between radicals on the linear or branched chains and acrylate double bonds. In addition, during the propagation reaction process homopolymer can be formed by ketyl radicals; however, only small amounts of homopolymer are formed because the active species produced by the reaction of eqs. (14) and (15) have a much higher reactivity than do the ketyl radicals.[10] Some crosslinking may occur by radical combination of two growing chain ends, which leads to the termination reaction (eq. (18)).

In the second step of the radiation coating process represented in Figure 2, the UV-curable PUA formulation containing TMPTA and HDDA as a reactive diluent and a photocleavable-type initiator (HCPK, Norrish type I) was coated on the top of the HDDA-grafted PP substrate as a ~45-μm-thick film and exposed to UV radiation at 3.1 J/cm². The few initiating radicals produced at the interface will generate PUA radicals which will, in turn, react with the pendant acrylate double bonds of the grafted HDDA chains. The polymerization reaction can also begin by reaction of the initiating radicals of HCPK with the acrylate
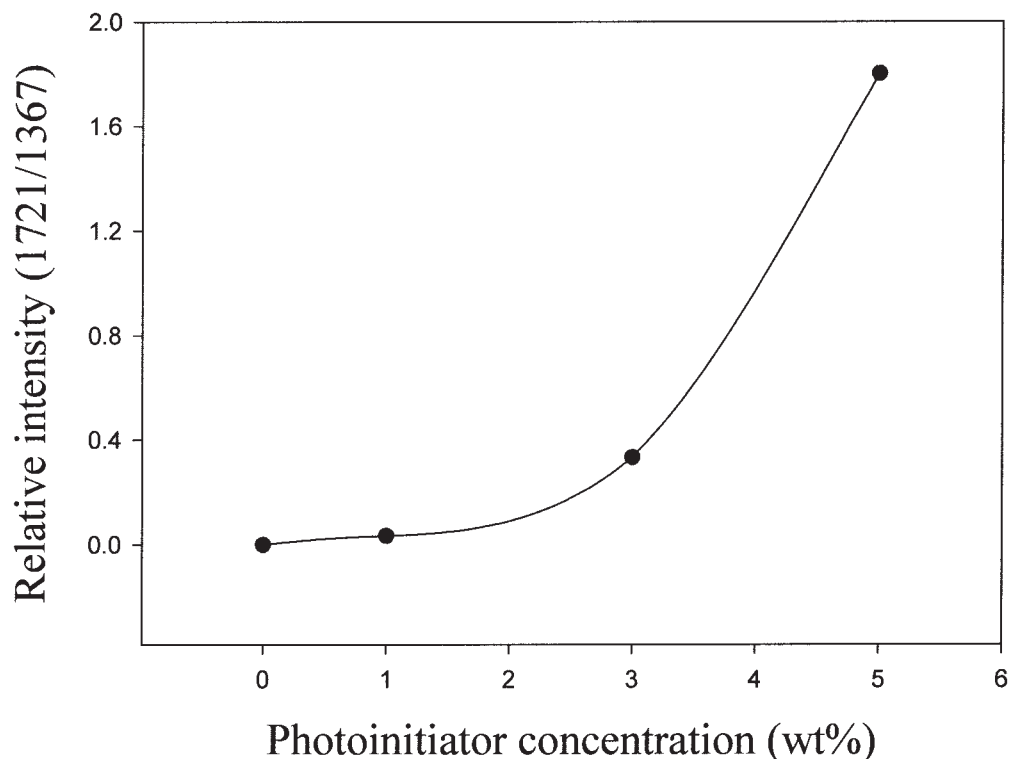
Figure 7 Plots of FTIR-ATR intensity ratio ($1721\ cm^{-1}/1367\ cm^{-1}$) versus photoinitiator concentration.

double bonds of the grafted HDDA chains, and propagate by further reaction with the PUA double bonds. In both cases, a chemical bond will form between the UV-cured coating and the PP substrate through the grafted base coat, which thus will increase the adhesion between the coating and substrate.

Effects of photoinitiators

The effects of the BP photoinitiator concentration (1–7 wt %) and the addition of ITX photoinitiator on the UV-radiation grafting polymerization are presented in Figure 3, from which it is clear that the photoinitiator concentration greatly influences the amount grafted and the grafting efficiency onto the surface of the PP substrate. It is not surprising that both G_a and G_e of the grafting polymerization systems (A–D) without ITX increased linearly with increasing BP concentration. However, it is noteworthy that the addition of a small amount of ITX markedly enhanced both G_a and G_e, especially even at the lower concentrations of BP. For example, system AI containing 1 wt % BP and a small amount of ITX (0.3 wt %) exhibit higher G_a and G_e values than those obtained for system D containing 7 wt % BP. This result may be due to ITX photoinitiator also acting as a photosensitizer that transfers electrons or energy to other photoinitiators by forming the excited-state complex (exciplex) in UV-curable formulation systems, thereby improving the efficiency of the photoinitiator to produce more active species. This phenomenon is called the photosensitization effect.[19–22]

Further experiments using a UV–visible spectrophotometer were designed to elucidate the mechanisms underlying the above observation. Figure 4 shows absorption spectra for the photoinitiators. The BP photoinitiator exhibits an absorption that is maximal at 250 nm and then decreases rapidly to near zero at 300 nm. In contrast, the ITX photoinitiator exhibits not only absorption below 300 nm but also a secondary absorption in the 320–400 nm range. Because of this strong absorption by the ITX, the initiating wavelength for the UV-radiation grafting polymerization may be enlarged to these regions by including ITX photoinitiator, and the excited ITX exhibits a synergistic interaction with BP photoinitiator by forming the exciplex, by which the efficiency of the photoinitiator was significantly improved to produce more active species.

For the grafting polymerization systems with ITX (AI–DI) shown in Figure 3, although the BP photoinitiator concentration increased steadily, G_a and G_e did not increase dramatically compared with the grafting polymerization systems (A–D) without ITX. This is probably due to the production of many ketyl radicals by the photoreduction and photosensitization reactions of BP and ITX, which greatly increases the opportunity for ketyl radicals to participate in the ho-
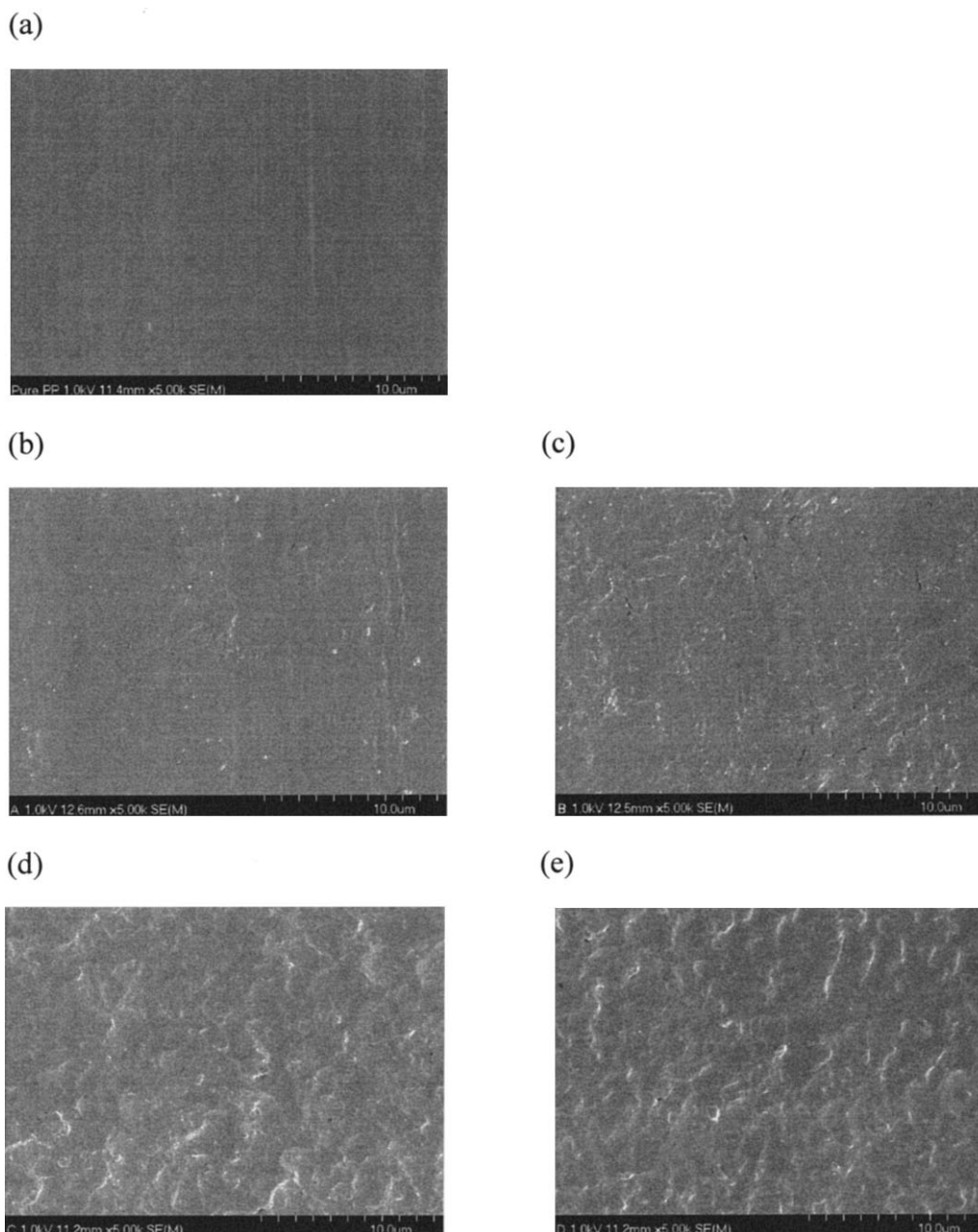
Figure 8 Scanning electron micrographs of the surface of HDDA-g-PP substrates: (a) pure PP; (b) system A, $G_a = 0.140 \times 10^{-2}$ mmol/cm^2; (c) system B, $G_a = 0.407 \times 10^{-2}$ mmol/cm^2; (d) system C, $G_a = 0.843 \times 10^{-2}$ mmol/cm^2; and (e) system D, $G_a = 1.039 \times 10^{-2}$ mmol/cm^2.

mopolymerization and termination reactions (eqs. (16) and (17)).

Changes in the hydrophilicity of the PP substrates after the UV-radiation grafting treatment were quantified by measuring the contact angles of a drop of water and of tricresylphosphate. The data obtained are collected in Table II, and Figure 5 depicts a superimposition of the contact angle and the surface polarity of the pure PP and the HDDA-g-PP substrates grafted in systems A–D as a function of BP photoinitiator concentration presented in Table II.

From Table II and Figure 5, it is obvious that the wettability of the PP substrate grafted in systems A–D (without ITX) improves continuously with increasing BP photoinitiator concentration. The decrease in contact angles and the increase in surface energies confirm indirectly the formation of HDDA-g-PP. In addition, the polarity (X^P) of the PP substrate grafted in system D was approximately 80% higher than that obtained for the ungrafted one. For the PP substrate grafted in systems AI–DI (with ITX), the wettability is improved drastically, which demonstrates the effectiveness of adding a small
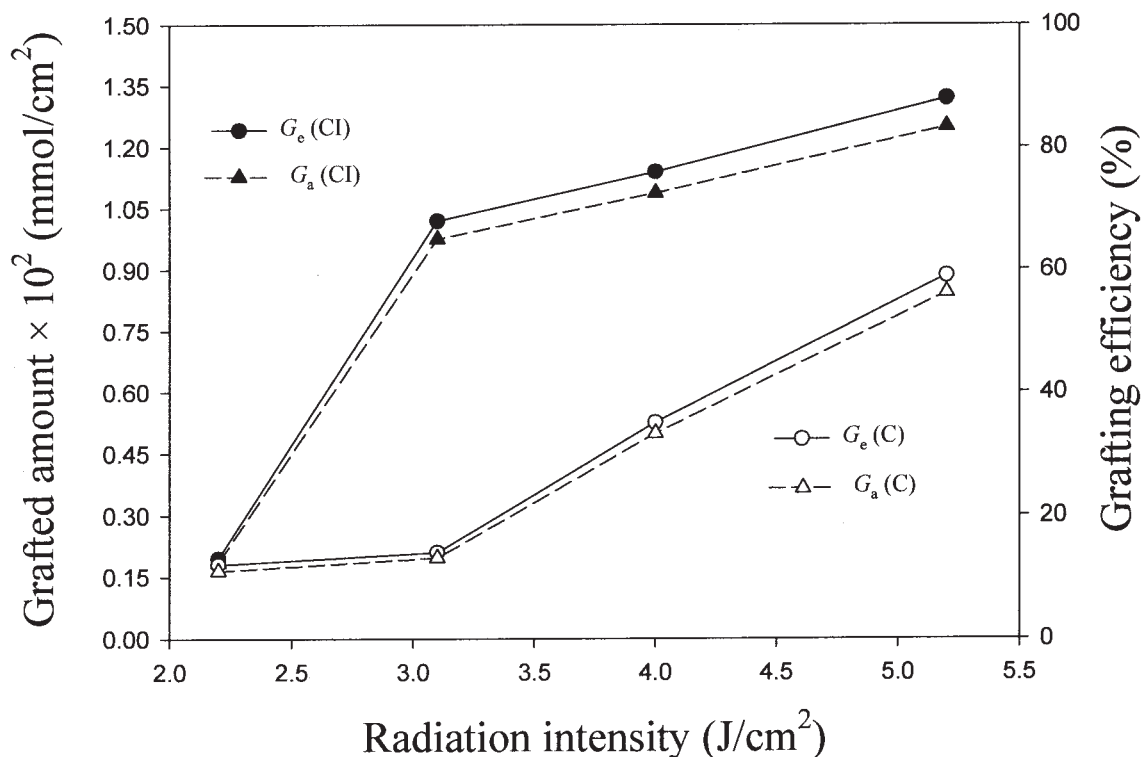
Figure 9 Superimposition of G_a and G_e values for the PP surfaces grafted in system C (without ITX) and system CI (with ITX) as a function of the UV radiation intensity.

amount of ITX. These results are consistent with those obtained from the above experiments on G_a and G_e.

For a more detailed interpretation of these observations, the FTIR-ATR spectra of the pure PP and the PP substrates grafted in the systems without and with ITX (A–D and AI–DI, respectively) as a function of the BP photoinitiator concentration were measured, and are shown in Figure 6.

Compared with the FTIR-ATR spectrum of pure PP substrate (Fig. 6(a)), the new characteristic absorption peak at 1721 cm^{-1} corresponding to the acrylate carbonyl group indicates that the grafted PP sheet samples contain HDDA chains. It is notable that FTIR-ATR measurements of the PP substrates grafted in systems A–C exhibited the spectrum of HDDA chains superimposed on the PP spectrum bearing the characteristic absorption peak at 1367 cm^{-1} of the symmetric bending of a methyl group. In contrast, the PP substrates grafted in system D containing 7 wt % BP did not exhibit a peak at 1367 cm^{-1} in the PP spectrum, indicating that the PP surface was fully covered with grafted HDDA chains. In the same way, Figure 6(b) indicates the surface of the PP substrates grafted in systems AI–CI (with ITX) was fully covered with grafted HDDA chains bearing pendant acrylate double bonds characterized by an absorption peak at 811 cm^{-1} associated with the wagging of the $=CH_2$ group. Thus, the FTIR-ATR analysis results support the above interpretations of the experiments on G_a, G_e, and contact-angle measurements.

In addition, the FTIR-ATR analysis can be used for surface analysis measuring the relative intensity of acrylate carbonyl group and $=CH_2$ bands at 1721 and 1367 cm^{-1}, respectively, in these grafting polymerization systems. As illustrated in Figure 7, the relative intensity ratio (1721 cm^{-1}/1367 cm^{-1}) for the surface analysis of the PP substrates grafted in systems A–C increased exponentially with increasing BP concentration, which represents evidence that both G_a and G_e values onto the surface of PP substrate increased significantly as the BP concentration was increased. However, in the case of the PP substrates grafted in systems D and AI–DI, we could not measure the relative intensity ratio due to the absence of the peak at 1367 cm^{-1} in the PP spectrum due to the full covering of grafted HDDA chains.

We used SEM to observe the surface morphology of the PP substrates grafted in systems A–D. Figure 8 shows that pure PP has a nearly flat surface, whereas the surfaces of the HDDA-g-PP substrates (systems A–D) exhibit a more grained structure with increasing amounts of grafted HDDA. These results verify that a higher BP photoinitiator concentration is associated with higher amounts of grafted HDDA.

Effects of UV radiation intensities

The effects of UV radiation intensity on the grafting polymerizations of HDDA with and without ITX were investigated with the grafting polymerization contain-
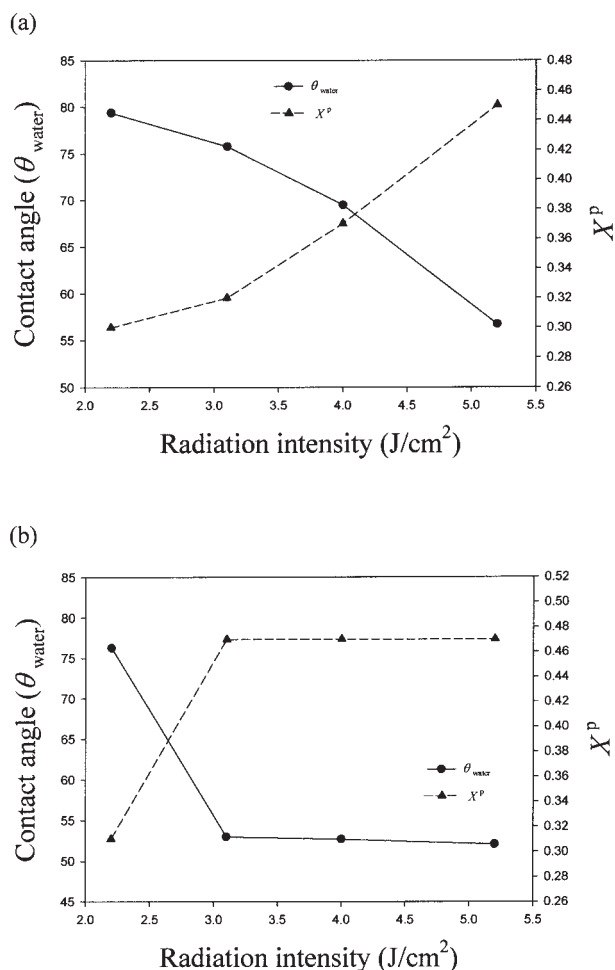
(a)

(b)

Figure 10 Superimposition of the contact angle of water and the surface polarity of the HDDA-g-PP substrates grafted in system C ((a) without ITX) and system CI ((b) with ITX) as a function of the UV radiation intensity.

ing 5 wt % BP (system C) and that containing 5 wt % BP and 0.3 wt % ITX (system CI) at UV radiation intensities in the range 2.2–5.2 J/cm^2.

Figure 9 shows that increasing the intensity of UV radiation improves the HDDA grafting polymerization of both systems C and CI. From Figure 9, it is

notable that both higher G_a and G_e were higher in system CI (with ITX) exposed to UV radiation at 3.1 J/cm^2 than in system C (without ITX) exposed to 5.2 J/cm^2, which is also probably attributable to the aforementioned photosensitization effect produced by adding ITX. These results are very important because the related UV-radiation grafting polymerization system of HDDA is greatly enhanced when a small amount of ITX is added, which makes this technology more practicable and economicable.

Changes in the hydrophilicity were determined by making contact-angle measurements on the surface of the HDDA-g-PP substrates grafted in systems C and CI. The data obtained are collected in Table II, and Figure 10 depicts a superimposition of the contact angle and the surface polarity of the PP substrates grafted in systems C and CI as a function of the UV radiation intensity presented in Table III.

It is seen from Table III and Figure 10(a) that as the UV radiation intensity was increased, contact angles decreased and surface energies and polarity increased steadily, which indicates that the wettability of the HDDA-g-PP substrate grafted in system C (without ITX) is improved with increasing UV radiation intensity. For the PP substrate grafted in system CI (with ITX; Fig. 10(b)), an impressive phenomenon occurred for intensities between 2.1 and 3.1 J/cm^2: the contact angle of water decreased drastically and the polarity (X^P) increased dramatically, and then leveled off for higher intensities. This result is similar to that from the experiments on G_a and G_e, and shows that a higher grafting efficiency was obtainable with lower UV radiation intensity by adding a small amount of ITX to grafting polymerization systems of HDDA.

The FTIR-ATR spectra of the HDDA-g-PP substrates grafted in systems C and CI were measured as a function of the UV radiation intensity, and are shown in Figure 11. Figure 11(a) shows that as the UV radiation intensity was increased for system C, the characteristic absorption peak at 1721 cm^{-1} of

TABLE III
Contact Angles, Surface Energies, and Polarity Onto the Surface of the HDDA-g-PP Substrates Grafted by the System C Without ITX and the System CI With ITX As a Function of the UV Radiation Intensity

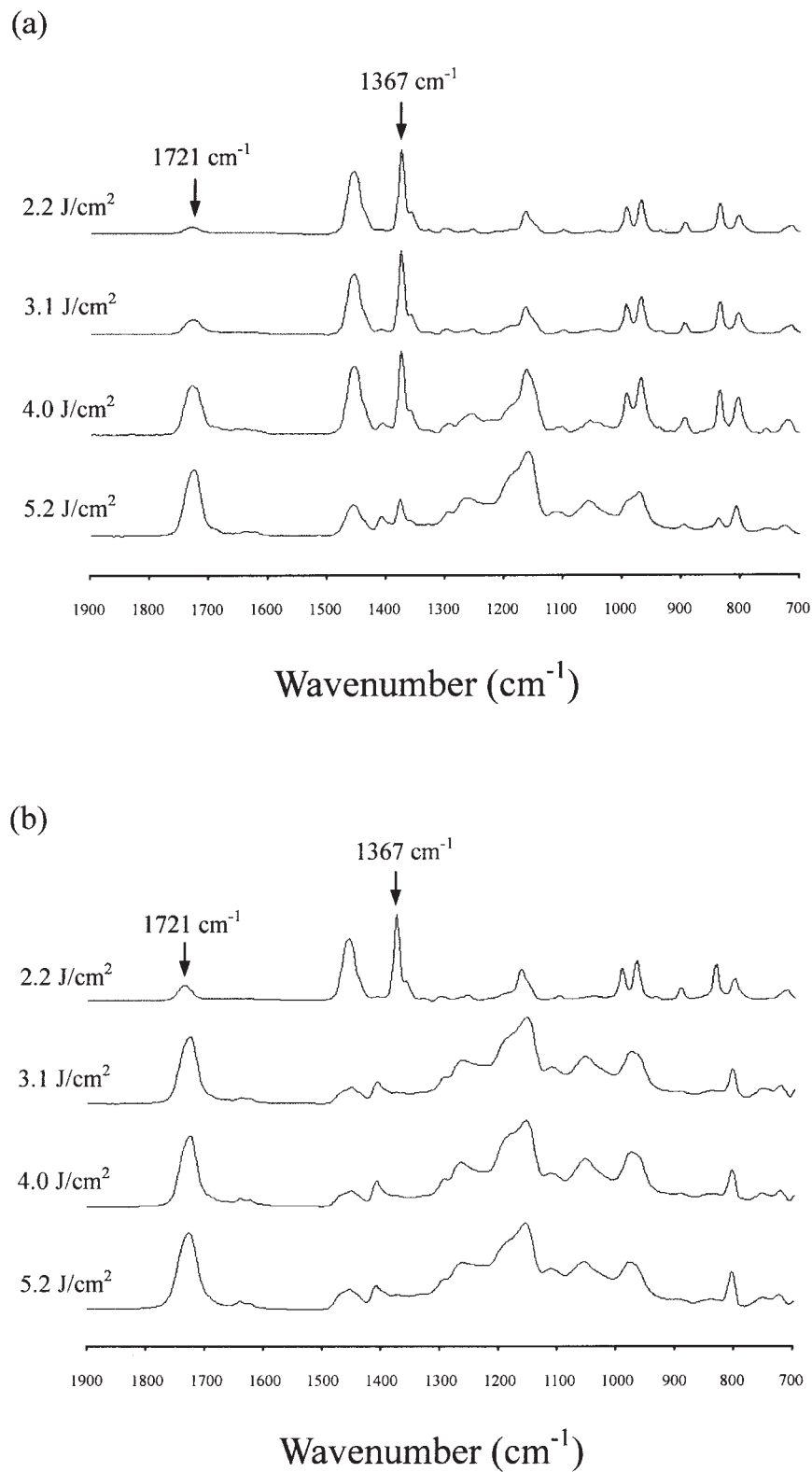| Grafting system	Intensity (J/cm^2)	Contact angle (θ)		γ_s (mJ/m^2)	γ_s^d (mJ/m^2)	γ_s^p (mJ/m^2)	X^P
		Water	TCP				
C	2.2	79.4	52.8	30.3	21.3	9.0	0.30
	3.1	75.8	49.2	32.8	22.4	10.4	0.32
	4.0	69.5	44.5	37.0	23.3	13.7	0.37
	5.2	56.7	33.4	46.4	25.4	21.0	0.45
CI	2.2	76.3	49.7	32.4	22.3	10.1	0.31
	3.1	53.0	26.9	49.3	26.3	23.0	0.47
	4.0	52.7	28.3	49.5	26.4	23.1	0.47
	5.2	52.1	27.9	50.0	26.5	23.5	0.47

(a)

(b)

Figure 11 FTIR-ATR spectra of the HDDA-g-PP substrates grafted in system C ((a) without ITX) and system CI ((b) with ITX) as a function of the UV radiation intensity.

the acrylate carbonyl group increased and the absorption peak at 1367 cm^{-1} in the PP spectrum decreased, indicating that the amount of HDDA

grafted onto the PP substrate increases with increasing UV radiation intensity. Moreover, the relative intensity ratio (1721 cm^{-1}/1367 cm^{-1}) for the sur-
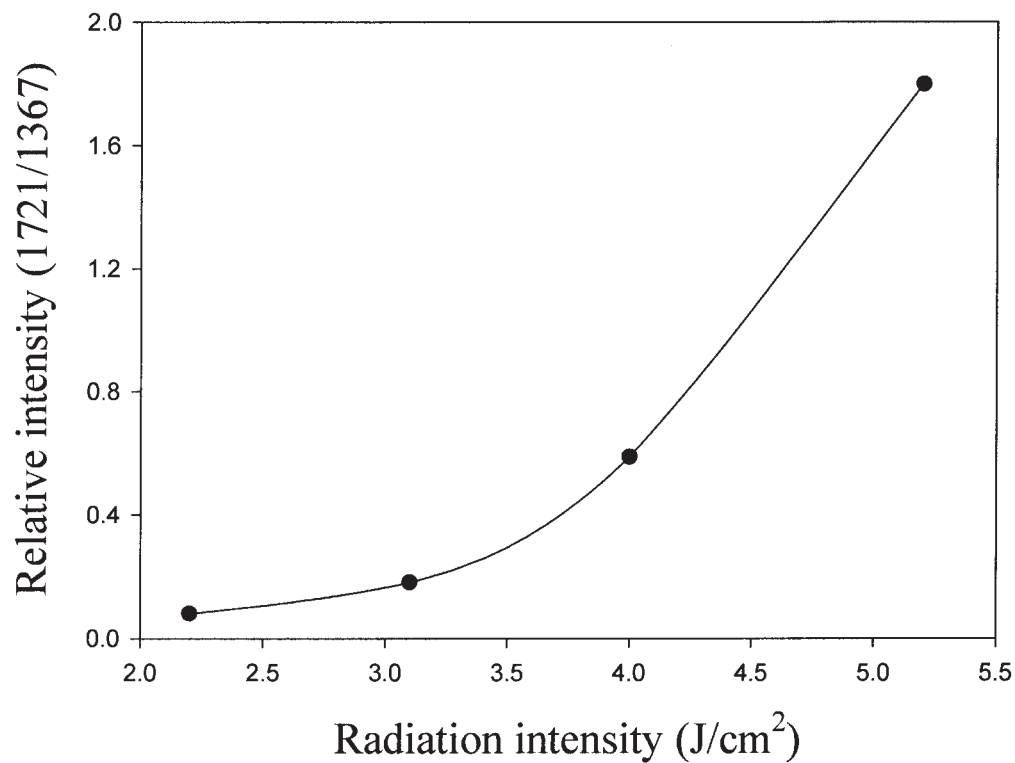
Figure 12   Plots of FTIR-ATR intensity ratio (1721 cm^{-1}/1367 cm^{-1}) versus UV radiation intensity.
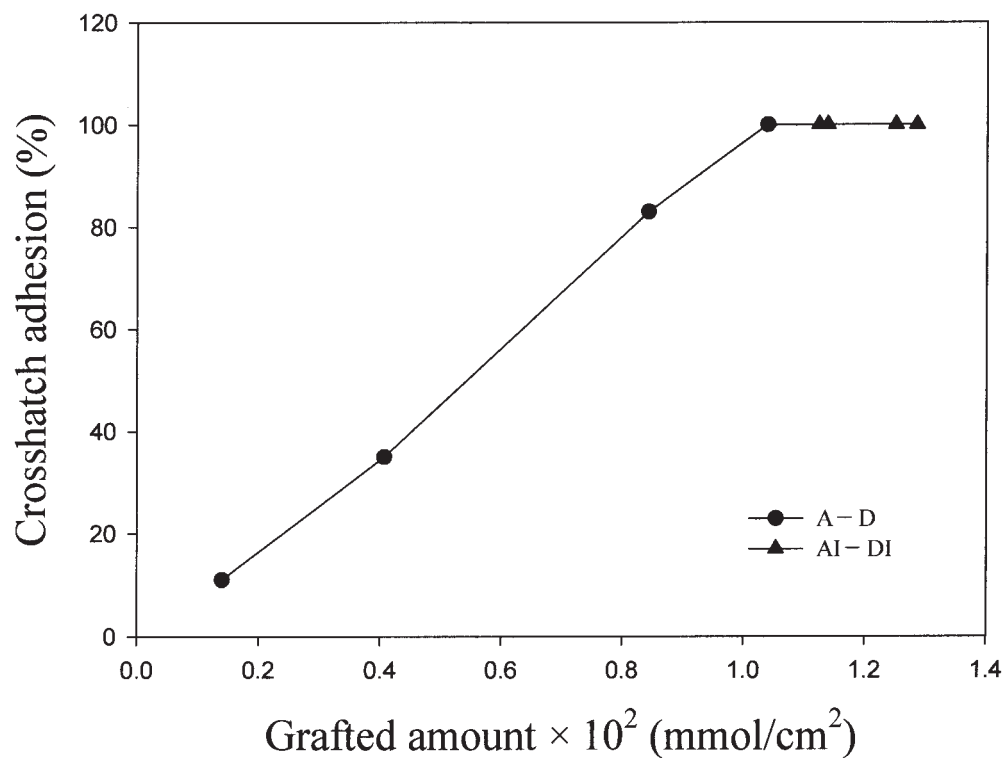

Figure 13   Percentage crosshatch adhesion of the UV-cured coatings onto the HDDA-g-PP substrates grafted in systems A–D (without ITX, ●) and systems AI–DI (with ITX, ▲) as a function of the amount of grafted HDDA.

face analysis of the PP substrates grafted in system C increased exponentially with increasing UV radiation intensity, which also represents evidence that the values of both G_a and G_e for HDDA grafted onto the PP substrate increased significantly as the UV radiation intensity was increased (Fig. 12).

In the case of the PP substrates grafted in system CI (Fig. 11(b)), the peak at 1367 cm^{-1} in the PP spectrum was not evident in the FTIR-ATR spectra for UV radiation above 3.1 J/cm^2, which demonstrates that the PP surface grafted in system CI was fully covered with grafted HDDA chains at these radiation intensities. This tendency is similar to the results of the experiments on G_a, G_e, and contact-angle measurements.

Adhesion of coating onto the HDDA-*g*-PP substrates

The UV-curable acrylate formulation containing PUA as a resin, TMPTA and HDDA as a reactive diluent, and HCPK as a photoinitiator was coated on the top of the HDDA-*g*-PP substrates as a ~45-μm-thick film, using a wire-wound drawdown rod, and exposed to UV radiation at 3.1 J/cm^2 under general curing conditions (22–25°C and 25–30% relative humidity). The crosshatch adhesion test was used to evaluate the adhesion of the UV-cured coatings onto the HDDA-*g*-PP substrates. The data were obtained at room temperature, 24 h after the UV curing.

The percentage crosshatch adhesion of the UV-cured coatings onto the HDDA-*g*-PP substrates grafted in systems without and with ITX (A–D and AI–DI, respectively) is shown in Figure 13 as a function of the amount of HDDA grafted. Note that the ungrafted pure PP exhibited a crosshatch adhesion of 0% with the UV-cured coating. From Figure 13, it is obvious that the amount of HDDA grafted greatly influences the adhesion of the UV-cured coatings onto the HDDA-*g*-PP substrates. As expected, the adhesion of the UV-cured coatings onto the HDDA-*g*-PP substrates grafted in systems A–D (without ITX) increased with increasing amounts of grafted HDDA. This result can be attributed to more HDDA-bearing acrylate double bonds being grafted onto the surface of PP substrate resulting in more chemical bonding being formed between the UV-cured coating and the PP substrate by the two routes discussed above, which thus will reinforce the adhesion between coatings and substrates when more HDDA is grafted.

On the other hand, when a small amount of ITX was added to the UV-radiation grafting polymerizarion systems, the adhesion between the UV-cured coating and the HDDA-*g*-PP substrate was markedly enhanced to a high level irrespective of the added BP photoinitiator concentration, which verifies that the presence of a small amount of ITX markedly improved the UV-radiation grafting polymerization of HDDA due to a photosensitization effect as mentioned earlier, by which the adhesion between the UV-cured coatings and the HDDA-*g*-PP substrates was significantly reinforced. Figure 13 indicates that the amount of HDDA grafted onto the PP substrates should exceed about 1 mmol/cm^2 for satisfactory adhesion with the UV-cured coating.

CONCLUSIONS

We have designed UV-radiation-initiated grafting and coating processes for acrylates systems, investigated the effects of blends of photoinitiators (BP and ITX) and UV radiation intensity on the physicochemical surface properties of the HDDA-*g*-PP substrates, using the UV-radiation grafting polymerization, and evaluated the adhesion of the UV-cured acrylates coating onto the HDDA-*g*-PP substrates, using the crosshatch adhesion test method. The HDDA-*g*-PP substrates were characterized gravimetrically and by contact-angle measurements, UV–visible spectroscopy, FTIR-ATR, and SEM. The results showed that the amount grafted and the surface polarity of the HDDA-*g*-PP substrates increased linearly with increasing BP photoinitiator concentration and UV radiation intensity, and that the addition of a small amount of ITX markedly enhanced both the amount grafted and the surface polarity of the HDDA-*g*-PP substrates, probably due to a photosensitization effect.

The crosshatch adhesion test demonstrated that the amount of HDDA grafted onto the PP substrates should exceed about 1 mmol/cm^2 for satisfactory adhesion in the UV-cured acrylates coating. Finally, our results demonstrate that the various test methods used in this study allow the simple and effective evaluation of the physicochemical surface properties of UV-radiation grafting polymerization systems and of the coatings grafted onto polymer substrates, and that they can be applied to a large variety of grafted polymeric substrates and to their cured coatings.

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