

Development and Physicochemical Characterization of Modified Polymeric Surfaces for Bacterial Adhesion

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Received 16 September 2008; accepted 13 July 2009

DOI 10.1002/app.32838

Published online 18 August 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Radiation-induced graft polymerization was used to modify the surfaces of polypropylene (PP) sheets for bacterial adhesion. For the experiments, two monomers were mixed: the quaternary ammonium salt (QAS) [2-(methacryloyloxy)ethyl]trimethylammonium chloride and acrylic acid (AAc). The PP sheets were activated by electron-beam radiation before the grafting reaction. Different AAc/QAS comonomer mixture ratios (50 : 10, 40 : 20, 30 : 30, 20 : 40, and 10 : 50) were used to determine the degree of grafting and to make the PP surfaces hydrophilic. The graft level increased with an increase in the percentage of AAc in the comonomer mixtures. Synergism was investigated during graft polymerization to quantify the poly(acrylic acid) and poly[[2-(methacryloyloxy)ethyl]trimethylammonium chloride] graft fractions in the resulting graft copolymers.

An approximation of the graft fractions was made with an analytical technique based on acid–base volumetric titration. The wettability of the modified surfaces was determined by the measurement of the water contact angles. The surfaces prepared with higher percentages of QAS in the comonomer mixtures had lower contact angles than those prepared with lower percentages of QAS. The presence of oxygen and nitrogen on the modified PP surfaces was investigated with X-ray photoelectron spectroscopy. Structural changes in unmodified and modified PP were characterized with differential scanning calorimetry. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1307–1315, 2011

Key words: electron; beam irradiation; poly(propylene) (PP); ESR/EPR

INTRODUCTION

The microbiological quality of food represents a major public health and economic challenge. In fact, the contamination of food by pathogenic microorganisms can be the cause of food poisoning likely to result in rather severe illnesses. In recent years, new infections have appeared, others have experienced a resurgence, and cases of resistance have developed; moreover, there are new modes of transmission related to the use of novel processes. Current trends in consumption (i.e., more fresh products and more ready-to-eat meals), new technologies, the globalization of markets, and the adaptability of microorganisms are all factors that today require improvements in food safety control. New techniques are being developed to reduce the risks of contamination in finished products and thus ensure their hygienic quality. They will ensure that food-contact surfaces (i.e., cutting tables, conveyors, containers, kitchen utensils, and food packaging) do not serve as vehicles for the transmission of pathogens. To

reduce contamination risks in finished products and thus ensure their hygienic quality, companies currently have recourse to curative actions (optimization of cleaning–disinfection procedures) used alone or in combination with preventive actions (bacterial adherence surveillance and reduction systems). Up to now, curative actions have relied mainly on the use of disinfectants.¹ Although these compounds are effective, they can be responsible for toxicity or the appearance of bacterial resistance. As for preventive approaches, they have usually been based solely on the choice of the material to be used (the nature and finish of the surface or even the topography). Recent works,^{2–5} nevertheless, have led us to envisage new strategies based on the development of new bacteriostatic, bactericidal, and generally nonfouling materials. A number of surface modification techniques have been used to develop surfaces with such antimicrobial properties; they include silver coating, surface immobilization of poly(ethylene oxide), surface thiocyanation, surface modification by various gas plasmas (e.g., oxygen and argon), and plasma immersion ion implantation.^{6–12} Radiation-induced graft polymerization has also been proved to be efficient at introducing different functionalities onto polymer surfaces and into the bulk.¹³ The modification of polypropylene (PP) structures by radiation grafting has been projected to be one of the most

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convenient routes for achieving a desired chemical functionality. In our previous investigation,¹⁴ the surface modification of PP sheets was carried out via radiation-induced graft polymerization of pure acrylic acid (AAc). We obtained very hydrophilic surfaces with higher degrees of grafting, and high degrees of grafting are well known to affect the physical structure of PP (notably its crystallinity).¹⁵ The objective of this study was to decrease the degree of grafting and to achieve hydrophilicity on the surface with a mixture of two monomers: the quaternary ammonium salt (QAS) [2-(methacryloyloxy)ethyl]trimethylammonium chloride and AAc. We observed the effect of the comonomer mixture ratio on the degree of grafting and on the hydrophilicity of the grafted PP. The physicochemical changes in the PP structure due to radiation grafting were also studied. These modified PP surfaces were checked for bacterial adhesion.¹⁶

EXPERIMENTAL

Materials

PP sheets (1 mm thick) were received from Goodfellow Cambridge, Ltd. (United Kingdom). AAc, QAS, and Mohr's salt were supplied by Aldrich (Germany). AAc and QAS were used without any purification. RBS-35 was supplied by Chemical Products (Belgium). Distilled water was used for all the experiments.

Irradiation

An electron beam from a Circe II linear electron accelerator was used for the irradiation of the PP sheets (Ionisos Laboratory, Orsay, France). The electron-beam energy was 10 MeV with a beam current of 1 A and a speed of 0.44 m/min. The irradiation was carried out in air to a dose of 100 kGy. Samples were exposed twice (50 kGy each time) for irradiation.

Grafting reaction

A monomer solution was prepared via the mixing of the two monomers (AAc and QAS) in distilled water (different ratios of the monomers were used).¹⁶ The required amount of the monomer solution was added to a glass reactor along with Mohr's salt as a homopolymer inhibitor. The reactor was regulated at 70°C in an oven for 10 min to heat the solution.¹⁴ Argon was continuously pumped into the reaction mixture to create an inert atmosphere. An electron-beam-irradiated PP sheet (100 kGy) was then introduced into the reactor. After the desired period, the grafted PP sample was taken out and washed with distilled water in an ultrasonic water bath at 40°C for 15 min to remove any traces of the homopolymer. Grafted PP samples were

dried overnight in an air oven at 40°C. The degree of grafting was calculated with the following equation:

$$\text{Degree of grafting (\%)} = \frac{W_g - W_o}{W_o} \times 100 \quad (1)$$

where W_o and W_g are the weights of the ungrafted and grafted PP sheets, respectively.

Contact angles

Contact angles were measured with a Kruss G40 (Krüss, France) goniometer. Samples were mounted onto a platform, and a drop of water was placed on the surface. The contact angle was measured within 30 s of the drop being placed on the sheet surface, and an average of seven measurements was reported.

Titration

The grafted PP samples were placed into a 0.5M KCl solution for 6 h at the ambient temperature. The solution was titrated against a 0.05M sodium hydroxide solution with phenolphthalein as the indicator. The carboxyl and QAS contents were calculated and are presented as millimoles per gram of the dry samples.¹⁷

X-ray photoelectron spectroscopy (XPS)

XPS measurements were made with an Escalab 250 (Thermo, France) equipped with a nonchromatized Al K_{α} X-ray source from Electron Corp. The pass energy was 100 eV for the general spectrum and 20 eV for the elementary spectrum. The analysis was carried out under an ultrahigh vacuum of 6×10^{-9} mbar, and for erosion, an ultrahigh vacuum of 8×10^{-8} mbar was used. An argon flow was added in the ion gun. During analysis, X-rays arrived on the sample surface at an angle of 45°. The angle of the detection column to the surface of the sample was, however, 90°. The spectra of C_{1s} , O_{1s} , and N_{1s} were calibrated for binding energies of 285, 531, and 401 eV.

Differential scanning calorimetry (DSC)

DSC studies of different samples were carried out with a PerkinElmer DSC-7 system (France). Vacuum-dried samples were loaded into the DSC apparatus, and the thermograms were run in the temperature range of 20–200°C under a nitrogen atmosphere at the heating rate of 10°C/min. The heat of fusion (ΔH_f) was obtained from the area under the melting thermograms. The crystallinity of the PP was obtained with the following expression:

$$\text{Crystallinity (\%)} = \frac{\Delta H_f}{\Delta H_{f(\text{crys})}} \times 100 \quad (2)$$

where $\Delta H_{f(\text{crys})}$ is the heat of fusion of 100% crystalline PP (163 J/g).¹⁸

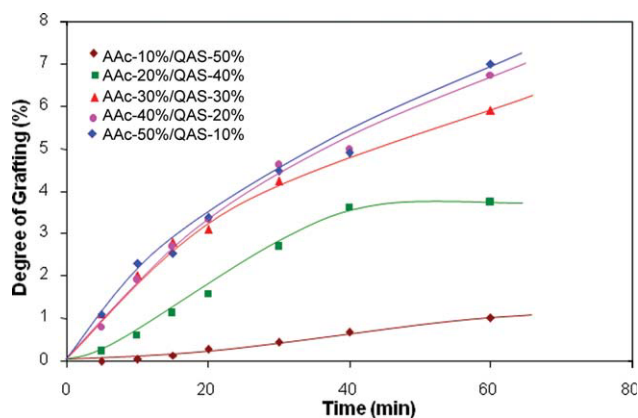


Figure 1 Variation of the degree of grafting with the reaction time for comonomer mixtures with different ratios (preirradiation dose = 100 kGy, temperature = 70°C, Mohr's salt concentration = 0.25%). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

Graft copolymerization is an easy process in the presence of a single monomer. When a mixture of two monomers is used, however, it becomes complex because of the synergistic effect caused by the different reactivity ratios of the two monomers. Moreover, the formation of the homopolymer is higher in the presence of two monomers. Here, graft copolymerization was carried out in the presence of Mohr's salt as a homopolymer inhibitor. The effect on the degree of grafting of each monomer in the comonomer mixture is shown with time in Figure 1. Different percentage ratios of the AAc/QAS comonomer mixtures [50 : 10, 40 : 20, 30 : 30, 20 : 40, 10 : 50] were used to determine the degree of grafting. The degree of grafting increased with time along with increases in the AAc percentage in the comonomer mixtures. However, a decreasing trend in the degree of grafting was observed with increases in the QAS percentage in the comonomer mixtures. This trend could be clearly seen, especially with the AAc/QAS comonomer ratios of 20 : 40 and 10 : 50. This decrease in the degree of grafting may have been due to the fact that when the percentage of QAS in the comonomer mixtures increased, the viscosity of the reaction medium increased as well because the viscosity of QAS was higher than that of AAc. It can be assumed that when the viscosity of a monomer solution is higher, the monomer chains will be less mobile, so less monomer will be available at the grafting sites for the grafting reaction. Hence, the degree of grafting decreases. Another reason could be swelling of the grafted layers. In our earlier investigation¹⁴ we observed that during the grafting reaction, one crucial factor was the swelling of the first grafted layer in the reaction medium, which allowed more monomer to diffuse within the

polymer bulk. Likewise, here the degree of grafting also increased with an increase in the monomer percentage because of the enhanced availability of the monomer to the grafting sites. This scenario is, however, limited to the grafting process in which the monomer is diluted with water. In this investigation, the monomer solution was viscous in the presence of QAS, and the swelling of grafted layers and subsequent monomer diffusion were thus inhibited; as a result, the degree of grafting was decreased. Maximum grafting was achieved at an AAc/QAS comonomer ratio of 50 : 10.

The surface hydrophilicity of ungrafted and grafted PP was determined via the measurement of contact angles. The contact angles of the virgin, exposed, and grafted PP are presented in Table I and Figure 2. The contact angles of the virgin and exposed PP were 90 and 89.5°, respectively. All grafted PP, however, showed a decreasing trend with an increase in the degree of grafting whatever the monomer ratio was in

TABLE I
Contact Angles with Water for Virgin PP, Exposed PP, and PP Grafted with Comonomer Mixtures of AAc and QAS

Sample	Degree of grafting (%)	Contact angle (°)
Virgin PP	0.0	90.0 ± 3.4
Exposed PP	0.0	89.5 ± 5.6
Grafted PP 50 : 10	1.0	59.4 ± 1.9
	2.3	54.7 ± 0.0
	2.5	53.3 ± 2.2
	3.4	54.6 ± 3.8
	4.5	52.5 ± 1.7
40 : 20	4.9	50.6 ± 0.7
	7.0	50.5 ± 0.3
	0.8	57.6 ± 2.8
	1.9	55.0 ± 0.8
	2.7	55.0 ± 0.8
30 : 30	3.3	54.4 ± 0.0
	4.6	54.5 ± 0.9
	5.0	49.2 ± 0.1
	6.7	47.9 ± 1.0
	1.1	49.2 ± 3.2
20 : 40	2.0	32.0 ± 0.2
	4.2	25.6 ± 2.3
	5.0	23.1 ± 0.4
	5.9	23.3 ± 2.3
	0.2	60.1 ± 1.4
10 : 50	0.6	34.0 ± 0.7
	1.1	34.9 ± 4.0
	1.6	25.1 ± 1.0
	2.7	22.0 ± 0.7
	3.6	23.9 ± 0.7
	3.7	20.4 ± 1.1
	0.04	70.0 ± 5.5
	0.1	51.5 ± 4.9
	0.3	43.4 ± 0.6
	0.4	43.0 ± 2.2
	0.7	34.2 ± 3.9
	1.0	26.0 ± 2.6

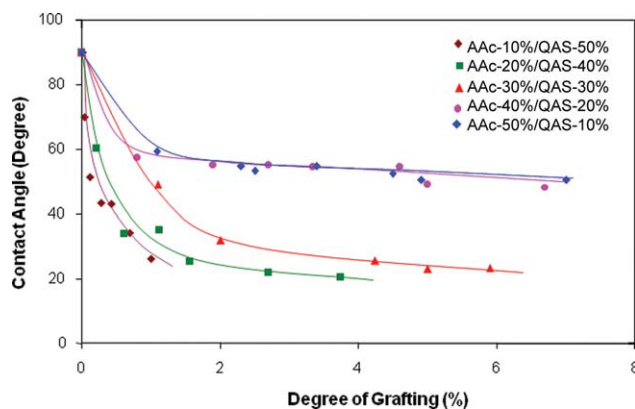


Figure 2 Variation of the contact angle with the degree of grafting for comonomer mixtures with different ratios (preirradiation dose = 100 kGy, temperature = 70°C, Mohr's salt concentration = 0.25%). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

the reaction medium. Surfaces prepared with higher percentages of QAS in the comonomer mixtures had lower contact angles than those prepared with lower percentages of QAS. In our earlier investigation,¹⁴ we observed that in the presence of the pure monomer, the grafted chains remained confined to the surface, but in the case of the diluted monomer (80% monomer), water acted as a vehicle for monomer diffusion within the surface layers. Most grafts, therefore, tended to move inside, and only small grafts were left on the surface. We observed the same behavior in this study. Considering the hydrophilic nature of AAc, we expected the contact angle to decrease significantly when we increased its percentage in the comonomer mixtures. This, however, was not the case. The contact angle increased as we increased the ratio of AAc in the comonomer mixtures. This situation may have been due to the dilution of the monomer. Moreover, when the percentage of QAS was lower, the viscosity of the monomer solution was also less, so the monomer

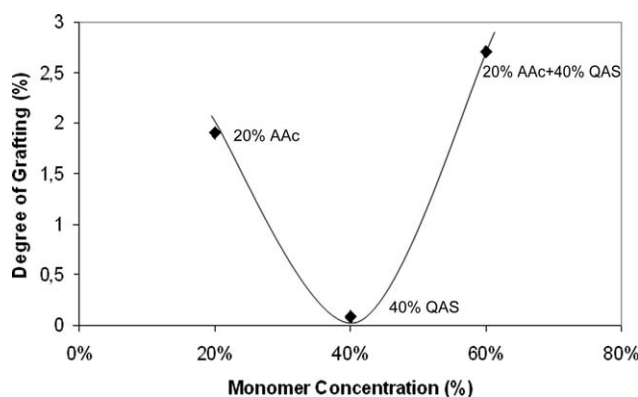


Figure 3 Comparison of the degrees of grafting with 20% AAc, 40% QAS, and a mixture of 20% AAc and 40% QAS (preirradiation dose = 100 kGy, temperature = 70°C, Mohr's salt concentration = 0.25%, reaction time = 30 min).

diffused within the surface layers more easily than when the percentage of QAS was higher. A higher QAS percentage resulted in increased viscosity, which slowed the diffusion of the monomer inside the surface layers and ensured grafts on the surface of PP. Hence, a decrease in the value of the contact angle was observed because of the presence of hydrophilic QAS.

According to the values of the contact angle, we chose one AAc/QAS comonomer mixture ratio, that is, 20 : 40, for further investigations. Samples grafted with this ratio showed contact angles as low as 22°, and we found appropriate amounts of both monomers. In addition, we observed the individual effect of each monomer on the degree of grafting. Figure 3 compares the degrees of grafting with 20% AAc in distilled water, with 40% QAS in distilled water, and with a mixture of 20% AAc and 40% QAS in distilled water. Grafting with 20% AAc alone followed the regular trend of grafting.¹⁹ The first surface layer swelled in the reaction medium because of a very dilute monomer solution, and further grafting took place because of the diffusion of the monomer inside the bulk. The grafting of 40% QAS was quite difficult because of the viscosity of the monomer solution. Surface layers of the polymer did not swell in the grafting medium, and the diffusion of the monomer was inhibited through these surface layers; this resulted in a very low degree of grafting. When the grafting was carried out in a comonomer mixture (20% AAc and 40% QAS), interesting results were observed. In the presence of the monomer mixture, the degree of grafting was higher than the degree of grafting with either monomer individually. It seems that the presence of AAc in the comonomer mixture facilitated the grafting of QAS. In the presence of diluted AAc, the surface layers swelled, and monomer diffusion took place through these swollen layers because of the enhanced availability of the monomers at the grafting sites.

The contact angles also support our previous results,^{14,16} as shown in Table II. The contact angle of PP grafted with diluted AAc (20%) was 59° at the

TABLE II
Contact Angles with Water for Virgin PP, Exposed PP, and PP Grafted with 20% AAc, 40% QAS, or a Comonomer Mixture (20% AAc and 40% QAS)

Sample	Degree of grafting (%)	Contact angle (°)
Virgin PP	0.0	90.0 ± 3.4
Exposed PP	0.0	89.5 ± 5.6
PP grafted with 20% AAc	1.9	59.0 ± 6.6
PP grafted with 40% QAS	0.09	28.0 ± 0.09
PP grafted with 20% AAc and 40% QAS	2.7	22.0 ± 0.7

TABLE III
Contents of AAc and QAS in Comonomer
Mixtures With Different Ratios

Comonomer mixture (%)	Grafting (%)	AAc (mmol/g)	QAS (mmol/g)
40% AAc and 20% QAS	2.71	0.048	0.147
30% AAc and 30% QAS	2.34	0.026	0.101
20% AAc and 40% QAS	3.23	0.017	0.144
10% AAc and 50% QAS	1.19	0.007	0.053

grafting level of 1.9%. For the samples grafted with only QAS (40%), the measured contact angle was 28° at 0.09% grafting. As discussed before, the contact angle of PP grafted with an AAc/QAS comonomer mixture (20 : 40) at the graft level of 2.7% was 22° . It may be assumed that in the grafted sample, QAS was present at the interface of the sample, and AAc was in the sublayers of the surface; this may account for the lower value of the contact angle for PP grafted with the comonomer mixture.

The carboxyl and QAS contents are shown in Table III. The carboxyl content increased as the percentage of AAc increased in the comonomer

mixtures. However, the QAS content decreased when we increased the percentage of QAS in the reaction medium. This may have been due to the fact that as the percentage of QAS increased in the reaction medium, the degree of grafting decreased, and this resulted in a decrease in the QAS content. Interestingly, the carboxyl content was always lower than the QAS content, despite the higher concentration of AAc in the comonomer mixtures. This situation may have been due to the lower accessibility of the carboxyl group in the titration. Moreover, because the content of QAS was inversely proportional to the carboxyl content, we obtained a higher QAS content when the carboxyl content was lower. These results are in contrast to the AAc content calculated on the basis of grafting by the difference in the weight increase. According to the level of grafting (increased weight), we observed a difference of 10^1 versus the AAc content calculated by titration. This difference was found in all the samples grafted with pure AAc at different degrees of grafting.

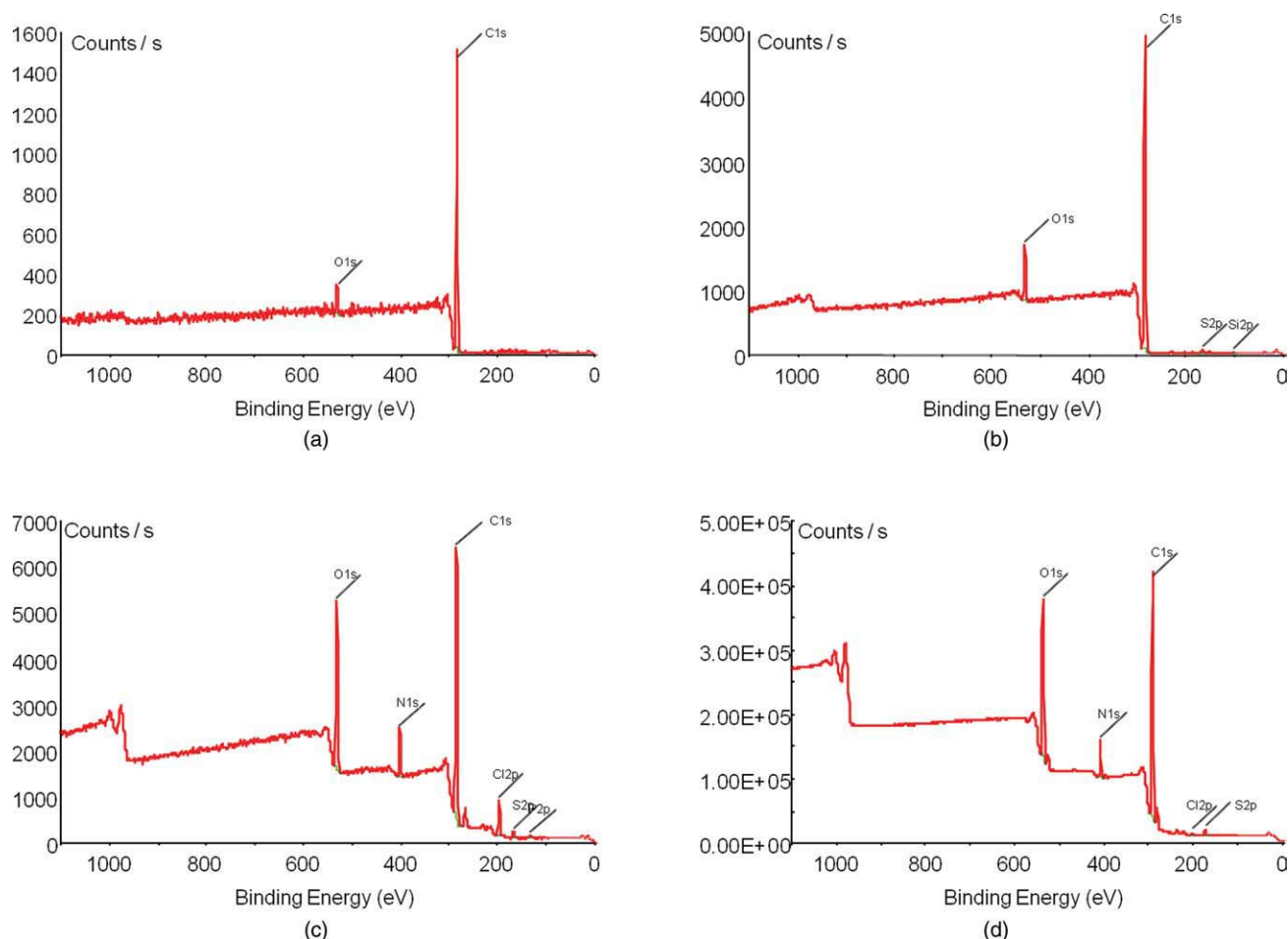


Figure 4 XPS spectra of (a) virgin PP, (b) exposed PP, (c) PP grafted with 40% QAS, and (d) PP grafted with a comonomer mixture (20% AAc and 40% QAS). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

TABLE IV
XPS Elemental Composition

Sample	Grafting (%)	C ^{1s} (%)	O ^{1s} (%)	N ^{1s} (%)	Cl _{2p} (%)	O ^{1s} /C ^{1s}	N ^{1s} /C ^{1s}
Virgin PP	—	95.2 (100) ^a	4.8	—	—	0.05	—
Exposed PP	—	92.7 (100) ^a	6.4	—	—	0.06	—
PP grafted with 40% QAS	0.03	72.8 ± 1.2 (66.6) ^a	17.6 ± 0.9 (16.8) ^a	5.9 ± 0.6 (8.3) ^a	3.8 ± 0.7 (8.3) ^a	0.23 (0.25) ^a	0.08 (0.12) ^a
PP grafted with 20% AAc and 40% QAS	2.7	75.9 ± 1.6 (65.6) ^a	18.3 ± 1.4 (20.6) ^a	4.8 ± 0.2 (6.8) ^a	0.3 ± 0.06 (6.8) ^a	0.24 (0.31) ^a	0.06 (0.10) ^a

^a Calculated value.

The XPS spectra of virgin, exposed, and grafted PP are shown in Figure 4. XPS is a surface-selective tool that provides information about the elemental composition of the molecule in approximately the top 5 nm of the polymer material. The percentages of the elemental composition are presented in Table IV. The spectrum of virgin PP [Fig. 4(a)] revealed the presence of a carbon signal. Moreover, despite the paraffin nature of PP, an oxygen signal was also observed. The presence of oxygen may have been due to thermooxidative degradation and partially to surface oxidation of PP during storage, as previously suggested.¹⁵ It may also have been due to environmental contamination on the silicon wafer, as observed by coworkers.²⁰ The C_{1s} content was 95.2%, and the O_{1s} content was just 4.7%, as shown in Table IV. The electron-beam irradiation [Fig. 4(b)] of PP to 100 kGy increased the O_{1s} content to 6.4%. Figure 4(c) shows the spectra of PP grafted with 40% QAS. Grafting led to an additional peak of nitrogen (5.9%), which showed the presence of QAS on the surface. In addition, the O_{1s} content increased from 6.4 to 17.6%. We also detected an additional peak of Cl_{2p} (3.8%) due to the grafting of QAS onto PP. Cl was present as a counterion in QAS. When the grafting was performed in a comonomer mixture of 20% AAc and 40% QAS, the spectrum [Fig. 4(d)] showed the same peaks found in Figure 4(c), but the O_{1s} content increased (18.3%), and the N_{1s} content (4.8%) decreased. However, the difference was not significant in either of the spectra, as shown by the insignificant difference in the calculated values of O_{1s} and N_{1s} [Fig. 4(c,d)]. Moreover, the Cl_{2p} content in the latter spectrum dropped significantly from 3.8 to 0.3%. The O_{1s}/C_{1s} ratio, derived from XPS analysis, was 0.06 for exposed PP. It increased in grafted samples to 0.24. The N_{1s}/C_{1s} ratios were 0.06 and 0.08 in the comonomer mixture and QAS-grafted samples. In all the grafted samples, the intensity of the carbon peak decreased, whereas the intensity of the oxygen peak significantly increased; this reflected the surface grafting in our experimental setup.

The core-level spectra of C_{1s}, O_{1s}, and N_{1s} provided detailed information about the chemical analy-

sis of the PP surface modified by radiation grafting of a comonomer mixture of 20% AAc and 40% QAS, as shown in Figure 5. The deconvoluted XPS C_{1s} spectrum in Figure 5(a) shows three major peaks, which may be assigned to the C—C, C—O/C—N, and O—C=O species at binding energies of 288.2, 289.8, and 292.3 eV with an increased chemical shift of approximately 3 eV in the binding energy. The chemical shift was related to the part of the electron density contributed by the valence electrons.²¹ In the case of C=O, the carbon atom had two neighboring electronegative oxygen atoms, which led to the depletion of the electron density on the carbon atom and resulted in a higher chemical shift. The O_{1s} core spectra [Fig. 5(b)] could be fitted by three components corresponding to O—C, O=C—O, and O—C=O at binding energies of 533.9, 535.6, and 537 eV with a chemical shift in the range of 2–3 eV. The higher binding energy of O_{1s} was due to the higher nuclear charge on oxygen, which caused it to hold its 1s electron more strongly. The core spectra of N_{1s} [Fig. 5(c)] could be curve-fitted with two components. The first may be assigned to the sp³ N—C bonding at 402.8, and the second may be assigned to the sp² N—C bonding at 406 eV; both were chemically shifted to approximately 2–3 eV in an increasing trend.

XPS imaging enables mapping of the distribution of particular elements or functional groups on a surface. Conventional XPS provides the average composition over the analyzed area. However, many sample surfaces are not homogeneous, and an element present at apparently low concentrations in the spectrum may be concentrated in one region of the area of interest; this could possibly lead to a completely erroneous interpretation of the data. We therefore carried out XPS imaging of grafted PP samples to map the elemental distribution of nitrogen, as shown in Figure 6. Each resulting image pixel represents the peak height of the imaged nitrogen species at that spatial position. A set of images can thus be quantified pixel by pixel in a manner analogous to the quantification of the spectra; this means that for the grafted sample (Fig. 6), we obtained a surface with an almost

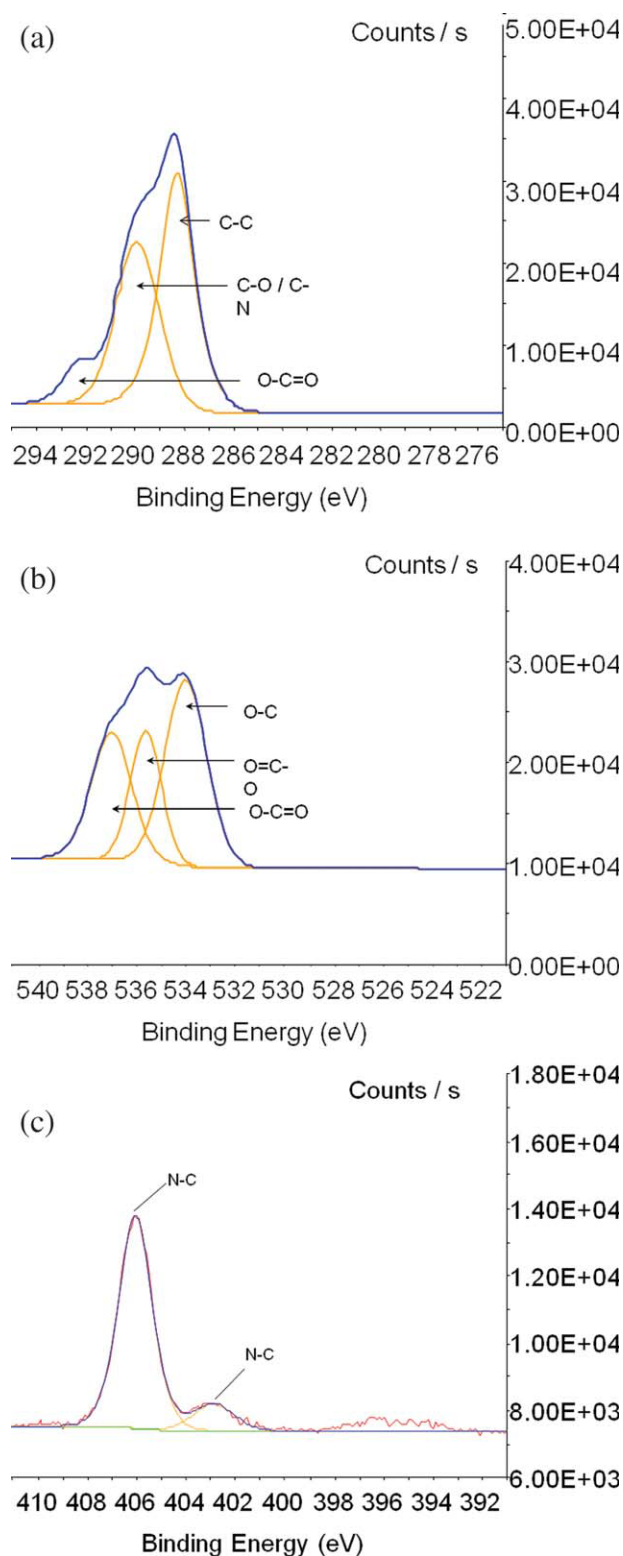


Figure 5 XPS core-level spectra of (a) C1s, (b) O1s, and (c) N1s for PP grafted with a comonomer mixture (20% AAC and 40% QAS). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

homogeneous finish of nitrogen. This result indicates that in our experimental system, grafting took place in a homogeneous manner.

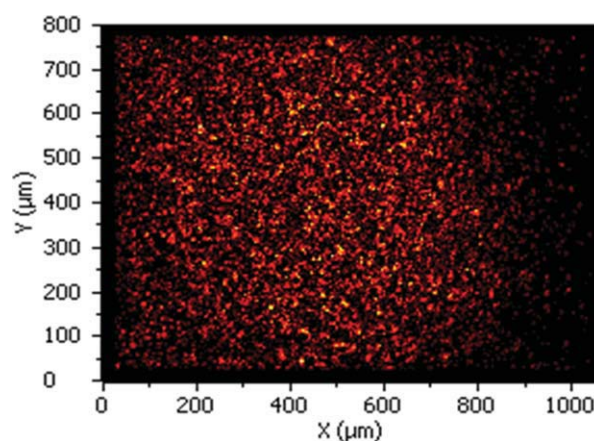


Figure 6 XPS map of nitrogen. Size of PP sample X.Y μm². [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

DSC thermograms of virgin PP, exposed PP, and PP grafted with 20% AAC, 40% QAS, or a comonomer mixture (20% AAC and 40% QAS) after the first heating and second heating are presented in Figure 7(a,b). In both cases, the areas under the

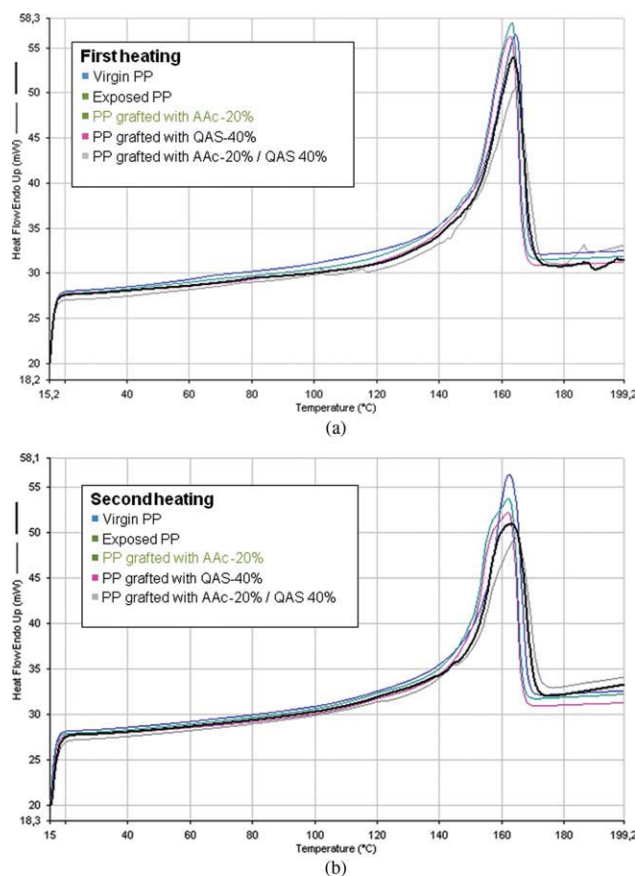


Figure 7 DSC thermograms of virgin PP, exposed PP, and PP grafted with 20% AAC, 40% QAS, or a comonomer mixture (20% AAC and 40% QAS): (a) first heating and (b) second heating. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE V
Heat of Fusion, Melting Temperature, and Crystallinity of Virgin PP, Exposed PP, and PP Grafted with 40% QAS, 20% AAc, and a Comonomer Mixture (20% AAc and 40% QAS) After the Second Heating

Sample	Grafting (%)	Melting point (°C)	Heat of fusion (J/g)	Crystallinity (%)
Virgin PP	—	162.5	89.2	54.7
Exposed PP	—	161.8	89.8	55.1
PP grafted with 20% AAc	2.0	162.9	84.0	51.5
PP grafted with 40% QAS	0.03	161.7	87.5	53.7
PP grafted with 20% AAc and 40% QAS	2.7	164.6	73.6	45.1

thermograms and the intensity of the melting peak decreased with an increase in the degree of grafting. There was, however, no change in the thermograms of virgin PP after the first heating and second heating, except for a broadening of the melting peak in the second heating. Virgin PP showed a single melting peak, which suggested that PP is characterized by one crystalline form.²² The exposure of PP to a dose of 100 kGy by an electron beam caused some changes in the thermograms, especially in the second heating. The melting peak became broad, and the origin of another peak, which was displaced toward a lower temperature, was observed. The changes in the peak of the exposed PP sample could be due to the crystalline reorganization during irradiation to 100 kGy. The thermograms of the grafted PP samples also showed some changes in the melting peaks in the first heating and second heating. The dual mode of the melting peaks may be attributed to structural changes. In a wide variety of semi-crystalline polymers, multiple endotherms can be observed. This situation can arise from the segrega-

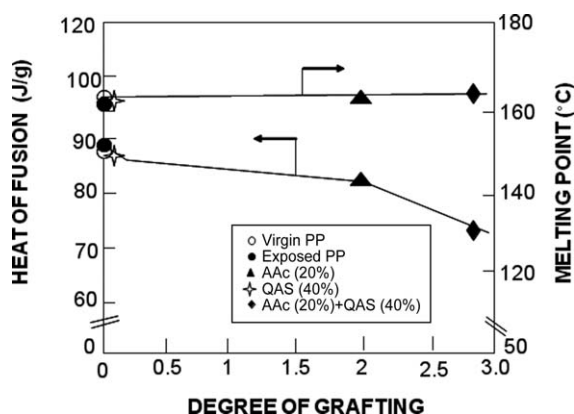


Figure 8 Variation of the heat of fusion and melting temperature of virgin PP, exposed PP, and PP grafted with 20% AAc, 40% QAS, or a comonomer mixture (20% AAc and 40% QAS).

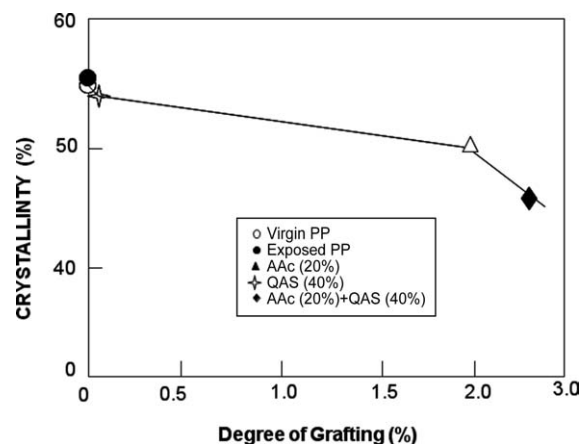


Figure 9 Crystallinity of virgin PP, exposed PP, and PP grafted with 20% AAc, 40% QAS, or a comonomer mixture (20% AAc and 40% QAS).

tion effects brought about by the molecular weight, among other parameters.²³

The variations of the heat of fusion, melting temperature, and crystallinity after the second heating are presented in Table V and Figure 8. The melting temperature did not change as a result of the grafting process and remained almost identical for unmodified and modified PP. These results support our previous investigation¹⁵ and suggest that the identical melting temperature was due to the perfection of crystallites, which was not impeded by the grafting process. No change was observed in the heat of fusion of virgin or exposed PP. Significant changes were, however, found in the shape of the melting peak of exposed PP, as discussed in the previous section. Subsequent grafting on this exposed PP led to a loss in the heat of fusion. A decrease in the heat of fusion of the samples was caused by the addition of poly(acrylic acid) chains within the non-crystalline region of PP, which interfered with crystallinity.²⁴ The crystallinity of PP (Fig. 9 and Table V), calculated with eq. (2), decreased with an increase in the degree of grafting. The loss of crystallinity may have been due to the addition of amorphous poly(acrylic acid) chains within the PP matrix. Another possible reason for the decrease in the crystallinity of the grafted samples could be the decrease in the macromolecular chains, crosslinking, and other modifications. This degradation behavior was accentuated by the presence of oxygen, which simultaneously led to oxidation.²²

CONCLUSIONS

The aim of these studies was to modify the PP surface at a low graft level and to introduce hydrophilicity with a mixture of two monomers (QAS and AAc) so that these surfaces could be analyzed for

bacterial adhesion. We used AAc/QAS comonomer mixtures with different ratios (50 : 10, 40 : 20, 30 : 30, 20 : 40, and 10 : 50) to determine the degree of grafting, and we observed that the graft level increased with an increase in the AAc concentration. Acid–base volumetric titration was carried out to determine the graft fractions. Titration revealed that the carboxyl content was always lower than the QAS content, despite the higher concentration of AAc in the comonomer mixtures. Measurements of the contact angle showed hydrophilicity on the grafted PP surface. The contact angle decreased more significantly on the sample surfaces prepared with higher percentages of QAS in the comonomer mixtures versus those prepared with lower percentages of QAS. These results indicated that we could change the surface hydrophilicity by changing the monomer ratio in the comonomer mixtures and could modify the PP surface as required. These modified PP surfaces were further analyzed by XPS to investigate the chemical composition (carbon, oxygen, and nitrogen). The intensity of the carbon peak decreased for all grafted samples, whereas the oxygen peak intensity increased significantly. An additional nitrogen peak appeared and showed the presence of QAS on the grafted PP surface. The core-level spectra of C_{1s} , O_{1s} , and N_{1s} showed an increasing chemical shift due to the electronegativities of neighboring atoms. XPS imaging was used to map the distribution of particular elements on the grafted surface, and we obtained a surface with an almost homogeneous nitrogen finish. This result suggested the efficiency of our experimental system, which resulted in homogeneous grafting. Grafting, however, led to significant changes in the physical structure of PP. DSC revealed changes in the melting peak of PP, and the crystallinity decreased with an increase in the degree of grafting.

PP surfaces prepared with a specific AAc/QAS comonomer mixture ratio (20 : 40) were used for the analysis of bacterial adhesion.¹⁶

The authors are deeply indebted to Alain Guinault for his help with the DSC experiments.

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