Surface Designing of Polypropylene by Critical Monitoring of the Grafting Conditions

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ABSTRACT: The grafting of acrylic acid onto electron beam-irradiated polypropylene was carried out using preirradiation method. The stability of peroxy radicals was investigated by electron spin resonance. It was found that the decay of peroxy radicals is much faster at 70°C than at 40°C and ambient temperature. The grafting has been observed to be strongly dependent on the monomer dilution in the reaction medium. The grafting was ascertained by attenuated total reflectance (ATR). The distribution of grafts across the samples was monitored by infrared microscopy. It was found that the graft management is considerably influenced by composition of the grafting medium. The grafting involving pure monomer leads to the surface enrichment with the polyacrylic acid chains. The samples grafted in pure monomer led to much lower contact angles as compared to the diluted monomer solution. The swelling of the grafted samples also showed a trend that was governed by the graft management. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 546–553, 2006

Key words: radiation grafting; polypropylene; acrylic acid; ESR; ATR; IR microscopy; contact angle

INTRODUCTION

Polymeric materials have acquired enormous potential in the packaging industry, where food materials are needed to be preserved for a long duration without altering their inherent physical characteristics.[1] One such requirement is the development of a proper packaging so that the food stays fresh and remains protected against any microbial infection during the storage span. Researches have been directed towards the development of the proper polymer packaging where the material surface exerts antimicrobial nature and provides enhanced self life of food without any risk of pathogen contamination.[2–5] These studies involve the modification of the polymer composition by chemically altering the macromolecular structure, immobilization of an antimicrobial agent onto the surface, and by blending the polymer with an antimicrobial agent. As a result, a wide range of antimicrobial compositions have been projected as the appropriate alternatives for food packaging. However, one has to keep in mind not only the tiresome processing of the blended composition with respect to the stability of the additive at processing temperature but also the changes in the physical properties of the finished materials due to the incompatibility of the two components. This opens up considerable activity in the development of polymeric materials in such a way that the antimicrobial nature is achieved but physicochemical properties, such as mechanical, thermal, optical behavior, and permeability, are still retained.

The modification of polymers by radiation grafting is the state-of-the-art to produce materials with required architecture. The attractive feature of the grafting is that the desired properties may be incorporated onto a polymer without any significant alteration of its inherent characteristics. Radiations, such as gamma radiation, and electron beam by virtue of their high energy may be used to activate and create free radical sites in polymers so that the graft polymerization of a monomer may be initiated.[6] The major advantage of the radiation grafting is that it provides an unique way to combine properties of two incompatible polymers. Moreover, modification may be carried out on the polymer already existing in a film form of the polymer, which eliminates the difficult processing of the graft copolymer into a thin foil. The radiation-induced graft modification of polymers has been investigated by a number of workers keeping in view a wide range of applications of the modified materials.[7–16] These studies suggest that the grafting is significantly influenced by the irradiation as well as the reaction conditions and a proper designing of the polymer structure may be accomplished by careful variation of these grafting conditions. It has been observed that the nature of the grafting medium and the additives influence the surface characteristics of the acrylamide-grafted polyethylene films.[17] The addition of inorganic salts (such as ferrous sulfate) and the

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organic additives (such as acetone and methanol) lead to a homopolymer free grafting reaction, but subsequently render the surface hydrophobic in nature in spite of the hydrophilic nature of the grafted polyacrylamide chains. In one of the studies of Chapiro and Bozzi[18] methylene blue has been found to exert homopolymer inhibition in the grafting of acrylic acid into Teflon-FEP films. These investigations show that the additives tend to inhibit graft propagation on the surface, as the surface remains directly in contact with the reaction medium, and whatever the grafts are generated on the surface, they undergo surface reorganization due to the interfacial tension between the hydrophilic surface layer and hydrophobic bulk. Similar behavior has been observed for the acrylic acid grafting onto polyester films.[19] These studies are in contrast to the observations on the grafting of acrylic acid on FEP where a significant decrease in contact angle was observed.[20] It seems that the surface hydrophilicity is dependent on the nature of the polymer–monomer combination and is essentially a function of the reaction conditions.

The tailoring of the polypropylene (PP) structure by radiation grafting has been projected as one of the most convenient routes to achieve desired chemical functionality. A wide range of monomers have been grafted onto PP and interesting materials for medical, antimicrobial, textile, and membranes have been developed.[21–31] The approach behind modification for biomedical domain is to functionalize the polymer surface in such a way that it becomes receptive to bioactive molecules by hydrogen bonding or by ionic interaction. These molecules are subsequently released once the polymer surface comes in contact with the proper environment. This development may well be extended to the food packaging industry where the antimicrobial nature of the polymer becomes primary requirement. As it is the surface of the polymer that remains in contact with the food, the polymer modification route must allow selective functionalization of the surface so that the bulk matrix remains almost unaltered with its inherent physicochemical characteristics. These observations led us to extend our investigations to the surface construction vis-a-vis the reaction conditions during the grafting of acrylic acid onto PP. In the present investigation, the PP was modified by the grafting of acrylic acid using preirradiation method. The polymer sheets were activated by electron beam irradiation in air under ambient conditions so that radicals are generated in the polymer matrix, which are subsequently transformed into peroxides and initiate the grafting process. The surface behavior of the grafted sheets prepared under different grafting conditions is also investigated.

EXPERIMENTAL

Material

Polypropylene (PP) of 1 mm thickness was received from Goodfellow Ltd. Cambridge, UK. Acrylic acid and Mohr's salt were supplied by Aldrich (Steinheim, Germany). Acrylic acid was used without any purification. RBS-35 was supplied by Chemical Products (Brussels, Belgium). Distilled water was used for all the experiments.

Irradiation

Electron beam (Linear electron accelerator CIRCE II) was used for the irradiation of PP sheets. The energy of electron beam was 10 MeV and the power was 20 kW, with the speed of 0.44 m/min (IONISOS laboratory, Orsay, France). The irradiation was carried out in air for a dose of 100 kGy. Samples were exposed twice for the irradiation (dose of 50 kGy each). After the irradiation, PP sheets were kept at −80°C prior to the grafting reaction.

Electron spin resonance

Electron spin resonance (ESR) spectra were measured with a Bruker ESP 300 (9.6 GHz) spectrometer (Wissembourg, France) in the temperature range 0–70°C, using a variable temperature unit (Bruker ER 4111 VT). The conditions of ESR measurement were as follows: magnetic field, 3415 gauss; microwave power, 20 mW; modulation, 2.29 gauss; sweep width, 200 gauss; and receiver gain, 10. The weighed samples (2 × 3 × 30 mm^3 slices) were placed in an ESR tube (diameter, 5 mm; height, 18 cm) and analyzed directly in the spectrometer cavity.[32] Radical density was accessed from the area (double integration) of the signal per mass unit, using a computer-controlled software system.

Contact angle measurement

Contact angle measurements were carried out on KRUSS G 40 goniometer. Samples were mounted on platform and a drop of water was placed on the surface. The contact angle was measured within 30 s of placing the drop on the sheet surface and an average of seven measurements were reported.

Attenuated total reflectance

Attenuated total reflectance (ATR) measurements were carried out on Magna 560 from Nicolet. Sixty-four scans were made for each spectrum and the background was refreshed before each analysis.
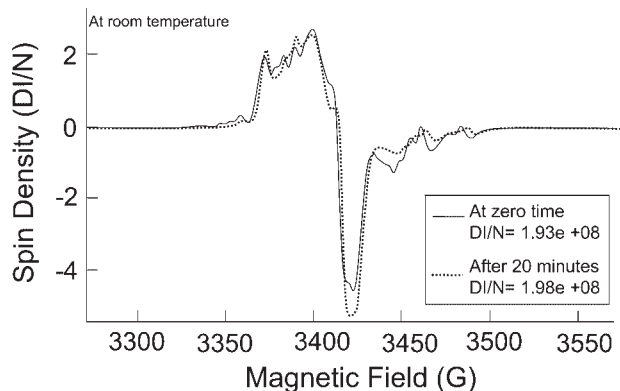
Figure 1 ESR spectra of exposed samples. Preirradiation dose, 100 kGy.

Infrared microscopy

Infrared microcopy measurements were carried out on Michelson MB 100 microscope from BOMEN. Slices of grafted PP were cut into 10 μm thickness with a Microtome. The slices of the sample were placed perpendicular on a sodium chloride plate. The samples were analyzed on a microscope (Spectra Tech), which is connected to an FTIR spectrometer. We used a mask of 20×40 μm^2 for analysis and a step of 20 μm between two analyses. For each spectrum, 16 scans were made.

Grafting procedure

Grafting reaction was carried out in a closed reactor. PP sheet was cut into 5×2.5 cm^2 pieces and washed with 2% RBS-35 solution in water for 10 min at 40°C, followed by five times each in tap water at 40°C and distilled water at room temperature. Washed samples were dried at 40°C overnight. The required amount of monomer solution in water (v : v) was added to the reactor. Mohr's salt was added to the monomer solution as homopolymer inhibitor. The reactor was placed in an oven at 70°C. Electron beam-irradiated PP sheet (100 kGy) was placed in monomer solution in a closed reactor. Argon was continuously purged into the reaction mixture to create inert atmosphere. After desired period, grafted PP sample was taken out and washed with distilled water in ultrasonic water bath at 40°C. Grafted PP samples were dried overnight in an air oven at 40°C. The degree of grafting was calculated from the following equation.

$$\text{Degree of grafting (\%)} = \frac{W_g - W_0}{W_0} \times 100$$

Where, W_0 and W_g are the weights of ungrafted and grafted PP, respectively.

Swelling measurements

Swelling measurements on predried samples were conducted by placing the sheets of known weight into deionized water a solution for overnight at ambient temperature. The samples were subsequently wiped with a paper and the weight was measured. The percent swelling was obtained from the following equation.

$$\text{Swelling(\%)} = \frac{W_s - W_0}{W_0} \times 100$$

Where, W_0 and W_s are the weights of dried and swollen PP, respectively.

RESULTS AND DISCUSSION

The electron beam irradiation of PP sheets and its subsequent grafting with acrylic acid has been observed to be significantly influenced by the grafting conditions. These studies reflect that proper control over the grafting conditions may be utilized to achieve modification of the PP surface. The ESR spectra of PP exposed to 100 kGy are presented in Figures 1 and 2. As the irradiation was carried out in the air, the spectra are typical of the peroxy radicals as per eqs. (1) and (2). These results are well in agreement with our previous studies on irradiation, where we could not see any residual peak for P$^{\bullet}$ radicals.[33] These observations suggest that a very fast transformation of P$^{\bullet}$ radicals to POO$^{\bullet}$radicals proceeds in the polymer.

Interestingly, the spin density (DI/N) of radicals remains almost identical for the sample stored at room temperature. In fact, we noticed slight increase in the spin density of radicals after the storage. This indicates that some of the trapped primary radicals are still reacting with the oxygen that diffuses slowly inside the polymer matrix and lead to peroxide radicals. However, the area of the spectra decreased consider-
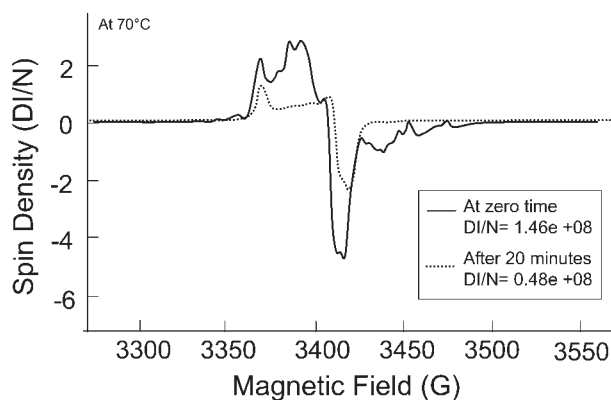

Figure 2 ESR spectra of exposed samples. Preirradiation dose, 100 kGy.

TABLE I
Spin Density of Peroxy Radicals at Different Storage Periods for Different Doses

Storage time (months) at −80°C	Spin density (DI/N)		
	30 kGy	50 kGy	100 kGy
0	87	107	178
1	51	45	182
2	64	58	161

ably when the storage is carried out at 70°C. This indicates the quick transformation of POO˙ radicals to POOH. Even if the trapped primary radicals are reacting with the oxygen during storage, this is superimposed by the fast deactivation of the radicals at an elevated temperature of 70°C.

The irradiated samples were stored at −80°C for different periods. The spin density of peroxy radicals for different doses is shown in Table I. The spin density tends to be higher at 100 kGy as compared to 30 and 50 kGy. However, the spin density of peroxy radicals for 100 kGy has almost identical values after one and two months of storage. Interestingly, when samples exposed for 30 and 50 kGy were stored for one and two months, a decrease in spin density was observed.

The decay of peroxy radicals with time for the sample exposed to 100 kGy at different temperatures is presented in Figure 3. The radical decay was found to be much faster at 70°C than at room temperature and 40°C. This may be due to the fact that at 70°C, the process of recombination and termination of radicals is enhanced and most of the radicals decayed within 20 min. The irradiation of PP under oxygen leads to the formation of alkyl radicals (P˙), which subsequently undergo reaction with oxygen to produce peroxide radicals (POO˙) [eqs[i]. (1) and (2)].[6,34,35] It is the

Figure 4 Variation of the degree of grafting with the reaction time at different monomer concentrations. Preirradiation dose, 100 kGy; temperature, 70°C; and Mohr's salt, 0.25%.

peroxy radicals that subsequently undergo stabilization by H-abstraction from the polymer main chain or by combining with primary radicals to produce hydroperoxides and diperoxides, respectively, as per eqs. (3) and (4). It seems that at 70°C most of the radicals are stabilized within 20 min and then rest of the radicals follow only a slow transformation.

$$\text{Irradiation: } P \rightarrow P^{\bullet} \qquad (1)$$

$$\text{Propogation: } P^{\bullet} + O_2 \rightarrow POO^{\bullet} \qquad (2)$$

$$\text{H-abstraction: } POO^{\bullet} + PH \rightarrow POOH + P^{\bullet}$$
$$(3)$$

$$\text{Termination: } POO^{\bullet} + P^{\bullet} \rightarrow POOP \qquad (4)$$

The graft polymerization was carried out in the presence of Mohr's salt as the homopolymer inhibitor. Mohr's salt deactivates the hydroxyl radical into a hydroxyl ion so that this radical is unable to initiate the homopolymerization during the grafting process.[12] Figure 4 shows the variation of degree of grafting with time at different monomer concentrations. Degree of grafting increases with time up to 20 min for 10 and 40% monomer concentrations and then tends to reach equilibrium. In case of 80 and 100% monomer concentrations, the grafting increases even after 30 min. The interesting observation in these results is that the grafting increases with the monomer concentration up to 80%, beyond which it tends to decrease significantly (Fig. 5).

It may be assumed that the grafting process proceeds under the cumulative influence of the two factors, viz, monomer availability to the grafting sites, and monomer permeability into polymer bulk. Earlier
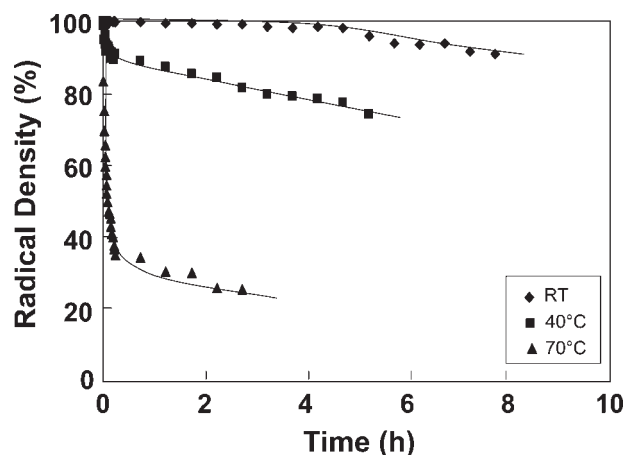

Figure 3 Radical decay with the time at different temperatures. Preirradiation dose, 100 kGy.

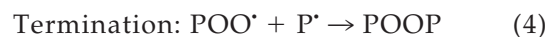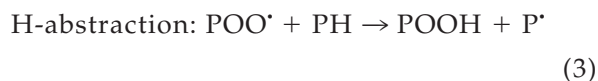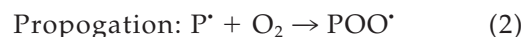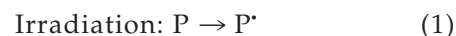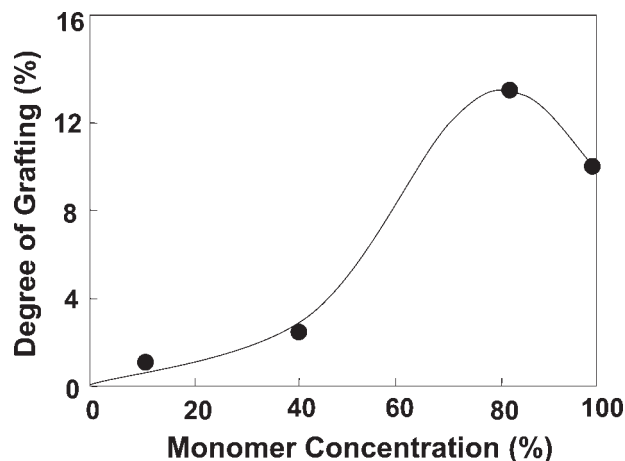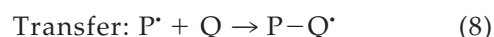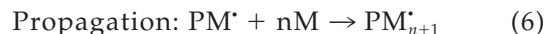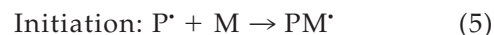**Figure 5** Variation of the degree of grafting with the monomer concentration. Preirradiation dose, 100 kGy; temperature, 70°C; Mohr's salt, 0.25%, and reaction time, 20 min.

investigations involving grafting on different polymers has established that the process follows "grafting front mechanism" where the initial grafting takes place only on the film surface and leads to the formation of a front, which moves farther deep into the polymer matrix by progressive diffusion of monomer into the polymer bulk.[36–40] Here, one crucial factor is the swelling of the very first grafted layer in the reaction medium so that the more monomer could diffuse within the polymer bulk. This is where the degree of grafting would also increase with the increasing monomer concentration because of the enhanced availability of the monomer to the grafting sites. However, this scenario is limited to the grafting process where monomer is diluted with water, which is a solvent for the polyacrylic acid (PAA) chains. As soon as the very first grafting takes place, owing to the solubility of PAA grafts in water, the grafted zone swells in the grafting medium and allows more monomer to diffuse in so that the propagation proceeds smoothly [eqs[i]. (5) and (6)]. This is subsequently reflected in the higher graft levels with the increasing monomer concentration up to 80%. Once the monomer concentration reaches 100% (pure monomer), the swelling of the grafted layers in the reaction medium is no more there (acrylic acid acts as the nonsolvent for the PAA grafted chains) and this inhibits the graft penetration within the polymer bulk. As a result, the monomer accessibility to the primary radicals (P·) within the polymer bulk is markedly lowered. The ultimate fate of these primary radicals is therefore to deactivate by mutual recombination [eq[i]. (7)] or by transfer to some impurity (Q) present in the medium [eq[i]. (8)]. The degree of grafting therefore tends to diminish. The importance of the swelling of the grafted layers in the grafting medium is supported by the studies of Plessier et al.[41] on the grafting of acry-

lonitrile into PP filament. It was found that the grafting diminished once the pure monomer is utilized for the grafting reaction probably because of the precipitating action of the monomer on the grafted layers. Moreover, the samples that are grafted with pure monomer are opaque and white, while samples grafted under aqueous monomer solutions, such as 10, 40, and 80%, are transparent almost like virgin PP.

$$\text{Initiation: } P^\bullet + M \rightarrow PM^\bullet \qquad (5)$$

$$\text{Propagation: } PM^\bullet + nM \rightarrow PM^\bullet_{n+1} \qquad (6)$$

$$\text{Termination: } P^\bullet + P^\bullet \rightarrow P{-}P \qquad (7)$$

$$\text{Transfer: } P^\bullet + Q \rightarrow P{-}Q^\bullet \qquad (8)$$

The presence of PAA grafts in PP was ascertained by ATR and IR microscopy measurements on the samples. The differential ATR of the samples grafted with PAA is presented in Figure 6. The two spectra show peak at 1705 and 1710 cm^{-1} characteristics of the carboxyl group (the two measurements were taken on the same sample). Interestingly, the peak for the sample grafted with pure monomer was more pronounced than the one grafted under dilute monomer concentration. As ATR can monitor in submicron range on the surface, it may be deduced that the grafts are located in the surface layers in both samples. The IR microscopy results on the grafted samples are presented in Figure 7. The distribution of the PAA grafts was monitored by the carboxyl peak across the sample thickness. This figure shows the origin of this peak at the surface layers and the middle of the sample does not have PAA chains. These observations support the grafting front mechanism (as discussed in the preceding section) where initial grafts remain confined only to the surface and move to the middle as the grafting progresses. With pure monomer, the grafting is re-
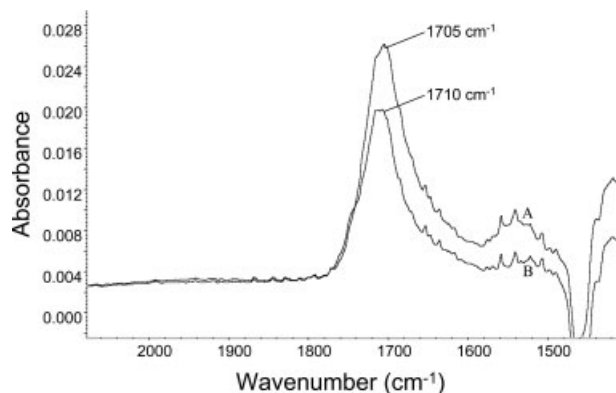

Figure 6 ATR spectra of (A) degree of grafting, 10% (prepared in pure monomer) and (B) degree of grafting, 11% (prepared in 80% monomer).
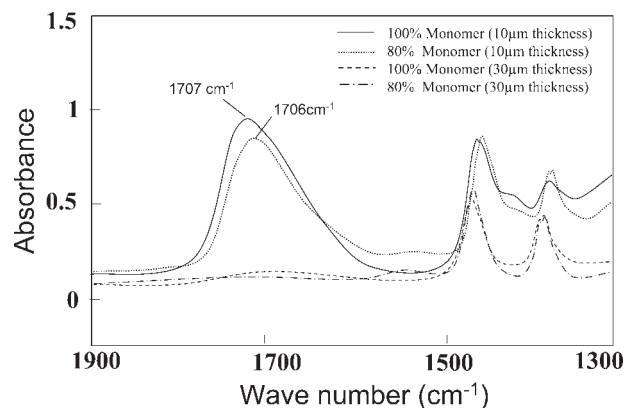
Figure 7 Infrared microscopy of samples at different thicknesses. Degree of grafting, 4% (prepared in pure monomer) and degree of grafting, 7% (prepared in 80% monomer).

Figure 8 Variation of the contact angle with the degree of grafting at different monomer concentrations. Preirradiation dose, 100 kGy; temperature, 70°C; and Mohr's salt, 0.25%.

stricted more towards the surface but penetrates relatively deeper for the 80% monomer concentration. A comparison of these results with the contact angle measurements would offer exact nature of the graft movements in and on the sample surfaces.

The contact angle measurements on the original and the grafted samples are shown in Table II and Figure 8. Contact angle of virgin PP was observed to be 90° and decreases for all samples irrespective of the grafting conditions. However, the grafting with pure monomer ensures much lower contact angles as compared to samples prepared under dilute monomer conditions (10, 40, and 80% monomer). These results indicate that the graft management is truly a function

TABLE II
Contact Angle of Polypropylene-*g*-polyacrylic Acid Copolymers

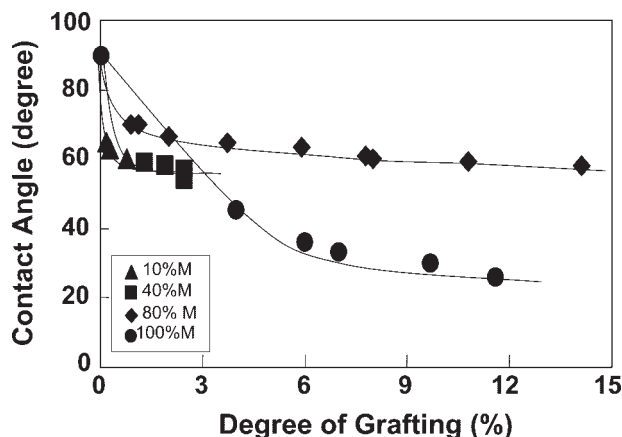| Monomer concentration (%)	Degree of grafting (%)	Contact angle (degree)
10	0.19	65 ± 2.0
	0.3	63 ± 2.0
	0.54	61 ± 1.4
	0.74	61 ± 1.5
40	1.3	59 ± 1.2
	1.9	58 ± 1.0
	2.47	58 ± 1.0
	2.48	57 ± 1.2
	2.49	54 ± 0.7
80	5.9	65.0 ± 1.2
	7.8	61.0 ± 1.0
	8.0	59.9 ± 1.3
	10.8	59.4 ± 0.6
	14.1	58.0 ± 0.9
100	4.0	45 ± 1.3
	6.0	36 ± 1.5
	7.0	33 ± 0.8
	9.7	30 ± 0.5
	11.6	26 ± 0.9

of the monomer concentration. Although ATR and IR microscopy show the presence of grafts on the polymer surface (Figs. 6 and 7), it is evident that the grafted chains are not localized only at the interface. Instead, a significant fraction of these chains is confined to the subsequent surface layers to an extent, which seems to be governed by the monomer concentration. In the presence of pure monomer, the grafted chains remain confined more to the surface. This surface enrichment by grafts tends to increase the surface energy and the contact angle as a result decreases. The effect of the surface enrichment by grafted PAA chains is so intense that the contact angle decreases to 26° for a graft level of 11%. In case of dilute monomer conditions, water acts as the vehicle for the monomer permeation within the surface layers. Therefore, most of the grafts tend to move inside and little grafts remain on the surface. This renders the PP surface still significantly hydrophobic in nature and contributes to the higher contact angles (>58°) as compared to the one obtained at pure monomer conditions. Our results are supported by the studies of other workers where the grafting of acrylic acid (~2%) led to a minor decrease in contact angle up to 80°.[34] Authors have attributed this behavior to the heterogeneous distribution of the grafting at the film surface. However, if we look at their grafting conditions, the reaction was performed at 50% monomer concentration and most of the grafts truly would have migrated within the surface layers and needs to be considered. These results are extremely attractive and provide unique concept in the grafting process where one single consideration of monomer concentration may lead to the surface designing and construction of the PP matrix without any significant alteration of the bulk structure.

It is interesting to mention that the ferrous salt is also used as the additive in the grafting medium. This is known as the inhibitor to the growing PAA-grafted
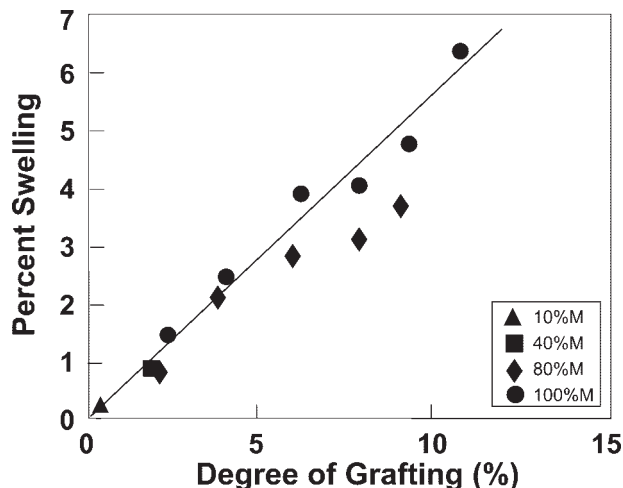
Figure 9 Variation of the percent swelling with the degree of grafting at different monomer concentrations. Preirradiation dose, 100 kGy; temperature, 70°C; and Mohr's salt, 0.25%.

or homopolymer chains.[11,18] In one of the studies on polyethylene–acrylamide system, it is found that the Mohr's salt (0.2–0.6%) hinders the growth of grafted chains and introduces hydrophobicity on the surface in spite of the high graft levels (high contact angles were observed for the grafted surfaces).[17] It seems that the Mohr's salt concentration in our system is too low (0.25%) and does not cause any appreciable impact on the graft inhibition on the surface. A significant grafting still remains on the surface and influences the surface contact angle.

The swelling behavior of these grafted samples in deionized water is shown in Figure 9. An increase in the water up take with the increase in the degree of grafting was observed. This is because of the fact that as the grafting increases, the amount of carboxyl groups also increases, which leads to the increase in the hydrophilicity of the sample and is reflected in the higher water up take. However, the most innovative aspect of these results is that the swelling is significantly influenced by the monomer composition in the grafting medium. The swelling of the samples prepared in pure monomer was higher than the one prepared under aqueous monomer conditions. This indicates that it is the graft localization within the samples that controls the swelling behavior. On the basis of our contact angle measurements, we assume that under pure monomer conditions, the grafts are more inclined to the surface due to limitation of the monomer diffusion into the polymer bulk as observed in the IR microscopy. Once the monomer is diluted (irrespective of the concentration), it facilitates the graft penetration inside. This leads to a situation where a major fraction of the PAA grafts is confined within the PP matrix. During the water absorption by

PAA chains, these PP chains impose some restrictions on the grafts displacement and influence the swelling process. In pure monomer, the grafts are confined more on the surface and the restrictions from PP chains are not much pronounced and hence higher swelling is observed for the identical graft level.

CONCLUSIONS

The surface designing of PP may be achieved by radiation-induced graft polymerization of acrylic acid under proper variation of the grafting conditions. One controlling factor for the graft management on the surface is the behavior of the grafted surface towards the grafting medium. If the grafted zone does not swell in the reaction medium, it tends to restrict the monomer diffusion towards the bulk. The grafted chains, as a result, remain confined to the surface and that is what we have observed in the grafting process involving pure acrylic acid monomer. Once the monomer is diluted with water, the grafted layers on PP surface swell and the monomer penetrates into the matrix and further grafting proceeds. This is where the grafting front mechanism operates in the system.

The surface grafting is subsequently reflected in the contact angle, which decreases significantly in the samples that are grafted with pure monomer. Here, we need to make a distinctive approach towards the surface and surface layers. The surface describes the very first molecular layer to which the grafts interact with. However, the surface layer involves the region comprising of subsequent molecular layers towards the PP bulk. Although ATR is the surface selective technique, it still takes into account a few microns inside the surface. The IR microscopy also shows that grafts are localized within the surface layers and their localization is governed by the monomer concentration. The carboxyl peak intensity was higher for the system involving pure monomer as compared to diluted monomer. These observations are in line with an assumption that the grafting with pure monomer leads to accumulation of grafts on the surface. The swelling of grafted samples in water also follows a trend, which is dependent on the monomer concentration in the grafting medium. Grafting under pure monomer leads to the higher swelling of the samples.

References

1. Appendini, P.; Hotchkiss, J. H. Innov Food Sci Emerg Technol 2002, 3, 113.
2. Han, J. Food Technol 2000, 54, 56.
3. Paik, J.; Dhanasekharan, M.; Kelley, M. J. Packag Technol Sci 1998, 11, 179.
4. Weng, Y.; Chen, M.; Chen, W. Inter J Food Sci Technol 1997, 32, 191.
5. Appendini, P.; Hotchkiss, J. J Appl Polym Sci 2001, 81, 609.

6. Chapiro, A. Radiation Chemistry of Polymeric Systems; Wiley Interscience: New York, 1962.
7. Wirson, A.; Albertsson, A. C. J Polym Sci Polym Chem Ed 2039 1995, 33.
8. Chen, J.; Yang, L.; Wu, M.; Xi, Q.; Le, S.; Li, Y.; Nho, Y. C. Radiat Phys Chem 2000, 59, 331.
9. Åkerman, S.; Åkerman, K.; Karppi, J.; Koivu, P.; Sundell, A.; Paronen, P.; Järvinen, K. Eur J Pharm Sci 1999, 9, 137.
10. Patri, M.; Hande, V. R.; Phadnis, S.; Somaiah, B.; Roychoudhury, S.; Deb, P. C. Polym Adv Technol 2004, 15, 270.
11. Chapiro, A. Eur Polym Mater 1983, 19, 859.
12. Gupta, B.; Anjum, N.; Jain, R.; Revagade, N.; Singh, H. J Macromol Sci Part C 2004, C44, 275.
13. Ellinghorst, G.; Fuehrer, J.; Vierkotten D. Radiat Phys Chem 1981, 18, 889.
14. Cohn, D.; Hoffman, A. S.; Ratner, B. D. J Appl Polym Sci 1984, 29, 2645.
15. Hegazy, E. A. Polymer 1992, 33, 96.
16. Brack, H. P.; Wyler, M.; Peter G.; Scherer, G. G. J Membr Sci 2003, 214, 1.
17. Gupta, B.; Anjum, N. J Appl Polym Sci 2000, 70, 1401.
18. Chapiro, A.; Bozzi, A. Eur Polym Mater 1987, 23, 255.
19. Gupta, B.; Hilborn, J.; Bisson, I.; Frey, P. J Appl Polym Sci 2001, 81, 2993.
20. Gupta, B. Ind J Technol 1991, 29, 47.
21. Mao, C.; Zhang, C.; Qiu, Y.; Zhu, A.; Shen, J; Lin, S. Appl Surf Sci 2004, 228, 26.
22. Chen, J.; Nho, Y. C.; Kwon, O. H.; Hoffman, A. S. Radiat Phys Chem 1999, 55, 87.
23. Okamura, A.; Itayagoshi, M.; Hagiwara, T.; Yamaguchi, M.; Kanamori, T.; Shinbo, T.; Wang, P. C. Biomaterials 2005, 26, 1287.
24. Gupta, B.; Jain, R.; Anjum, N.; Singh, H. J Appl Polym Sci 2004, 94, 2509.
25. Tyagi, P. K.; Gupta, B.; Singh, H. J Macromol Sci 1993, 30, 303.
26. Yang, J. M.; Lin, H. T. J Membr Sci 2004, 243, 1.
27. Mukherjee, A. K.; Gupta B. J Appl Polym Sci 1985, 30, 4445.
28. Plessier, C.; Gupta, B. J Appl Polym Sci 1999, 73, 2293.
29. Yang, J. M.; Lin, H. T.; Wu, T. H.; Chen, C. C. J Appl Polym Sci 2003, 90, 1331.
30. Shim, J. K.; Na, H. S.; Lee, Y. M.; Huh, H.; Nho, Y.C. J Membr Sci 2001, 190, 215.
31. Xu, Z.; Wang, J.; Shen, L.; Men, D.; Xu, Y. J Membr Sci 2002, 196, 221.
32. Six, T.; Feigenbaum, A.; Riquet, A. M. J Appl Polym Sci 2002, 83, 2654.
33. Marque, D.; Feigenbaum, A.; Riquet, A. M. J Polym Eng 1995, 15, 101.
34. Louis Joseph Dogue, I.; Mermilliod, N.; Gandini, A. J Appl Polym Sci 1995, 56, 33.
35. Garton, A.; Carlsson, D. J; Wiles, D. M. Macromolecules 1979, 12, 1071.
36. Chapiro, A.; Gupta, B. Eur Polym Mater 1989, 25, 1137.
37. Gupta, B.; Büchi, F. N.; Scherer, G. G.; Chapiro, A. Polym Adv Technol 1994, 5, 493.
38. Hegazy, E. S. A.; Ishigaki, I.; Dessouki, A. M.; Okamoto, J. J Appl Polym Sci 1982, 27, 535.
39. Gupta, B.; Büchi, F. N.; Scherer, G. G. J Polym Sci Polym Chem Ed 1931 1993, 32.
40. Gupta, B.; Anjum, N. J Appl Polym Sci 2000, 70, 1331.
41. Plessier, C.; Gupta, B.; Chapiro, A. J Appl Polym Sci 1998, 69, 1343.