

Modification of Industrial Polypropylene Film by Grafting of Poly(acrylic acid)

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SYNOPSIS

Grafting of poly(acrylic acid) onto commercial polypropylene films following irradiation by γ -rays was carried out in order to improve their surface properties. The amount of grafting with the irradiation dose was found not to follow the expected linear dependence as it is normally observed for polypropylene films prepared in laboratory amounts. We therefore analyzed the influence of the industrial manufacture process in terms of orientation of the film and addition of antioxidants by determining the peroxide surface density and the extent of grafting therefrom. The unoriented polypropylene film presented the highest peroxide concentration and was thus the most adapted material for successful grafting. Whereas phenol antioxidants limit the peroxide formation and thus must be removed from the film for grafting, the thickness of the chemical modification can be controlled by means of phosphites. Atomic force microscopy and wettability measurements showed that the grafted poly(acrylic acid) was heterogeneously distributed on the surface of the film, explaining the observed low reproducibility of the grafting reaction. However, we observed that the polarity of the surface was increased by the grafting. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The modification of polymeric materials is an important field of research for various applications such as the dyeability of textiles,¹⁻³ the improvement of adhesion for packaging industry,⁴ and the elaboration of membranes with specific properties.⁵ Because of its growing commercial applications, polypropylene (PP) films have attracted particular attention.⁶ Our work was focused on the improvement of the adhesion properties of industrial PP films toward some polar films like polyester and polyamide. However, most of the published studies dealing with PP were performed on laboratory samples and not commercial ones. At least two features differentiate a laboratory film from an industrial one. First, to increase their mechanical properties industrial films

are often oriented, thus presenting well-crystallized zones, which is not the case for usual laboratory films. Second, industrial films contain various additives to prevent their thermal oxidation. Our purpose was to understand the influence of the morphology and of the additives on grafting mechanism.

We modified the surface of the films by grafting them with poly(acrylic acid). For this kind of polymerization, different techniques are available.⁶ We choose the one which consists in an activation of the material before the actual chemical step of grafting, namely preirradiation in oxygen with γ -rays. In this way, hydroperoxides and diperoxides are created, which will be the initiators of the grafting. Their thermal decomposition in the presence of monomer induces the grafting reaction. Different commercial PP films were tested in order to evaluate the influence of the surface morphology on the peroxide formation and to analyze the effect of the additives on the peroxide formation and the grafting reaction. We then studied the homogeneity of the grafting and characterized the modified surface in terms of surface tension.

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EXPERIMENTAL

Samples

Three industrial films were used in this study. Two were used to evaluate the influence of the orientation of the film during the industrial manufacturing process: (i) the unoriented PP (PPu) which was a homopolymer, PPA quality, isotacticity 95%, from Minigrip and (ii) a bioriented PP (PPo) film, from I.C.I (Propafilm). Both had approximately the same crystallinity of 50%, as determined by differential scanning calorimetry (DSC), and contain additives. PPu and PPo are produced by two different industrial processes. The PPu was extruded and then rapidly cooled to produce an unoriented film. Its crystalline phase is a smectic one, as determined by X-ray spectrometry. The PPo film is bioriented after extrusion. Its low speed of crystallization induces the formation of a well-defined crystalline phase identified by X-ray spectrometry as an α crystalline phase.

The third film was provided by Appryl (PPa). It was an unoriented PP film with a crystalline rate of 50% (DSC) in which no phenolic additives were introduced.

The last PP film (PPw) contained no additives and was an experimental sample kindly provided by the Institut Textile de France. Its crystallinity determined by differential thermal analysis (DTA) and X-ray diffraction was in the range of 50–60%.

Prior to irradiation the films were washed in acetone and dried at 50°C.

Products

The acrylic acid (AA) monomer 99% was from Aldrich. It was cryo-distilled to eliminate the stabilizers before use.

Mohr's salt, which prevents homopolymerization, was purchased from Aldrich and was used without further treatment.

Peroxide Determination

Preirradiated films were plunged in a degassed benzene solution of 1,1-diphenyl-2-picrylhydrazyl (DPPH) and kept 24 h at 70°C. The benzene is a bad solvent of polypropylene, and only the surface of the film was swollen. As a consequence, only the peroxides at or near the surface were determined.

The peroxides close to the surface are decomposed into radicals, and DPPH molecules react with those radicals. We measured the DPPH concentration of the solution by ultraviolet (UV) spectrometry at 520 nm, against a reference solution of DPPH in benzene. The difference of absorbance is proportional to the consumed DPPH and thus to the peroxides surface concentration. This method gives a value exceeding the real species initiating the grafting. In fact, the DPPH molecules react with all kind of radicals. In our case, the decomposition of peroxides induces the formation of RO' radicals which initiate the grafting and HO' radicals which are responsible for the AA homopolymerization.

Grafting Reaction

The preirradiated films were immersed in a degassed aqueous solution of 50% in weight of acrylic acid with 0.1% of Mohr's salt to prevent its homopolymerization. After degassing, the flasks were kept at 85°C for 2 h to promote grafting. The films were then rinsed in distilled water and rapidly washed with acetone. They were dried in an oven at 50°C or under vacuum at room temperature overnight. The percentage of grafting was determined as follows:

$$G\% = (W_g - W_i)/W_i$$

where W_i is the initial weight and W_g the weight of the grafted film.

Contact Angle Measurements

Static contact angles of water were measured on preirradiated and grafted films at 20°C with a Krüss instrument (GP40). Ten readings were averaged.

Irradiation

PP films were irradiated at room temperature with 60 Co γ -rays in an oxygen atmosphere. The dose rate was 1.25 kGy/h, and the irradiation doses ranged from 0.5 up to 20 kGy.

Atomic Force Microscopy (AFM)

The AFM analysis were carried out with a Park Instrument (SFM-BD2). The size of the pictures was $5 \times 5 \mu\text{m}$.

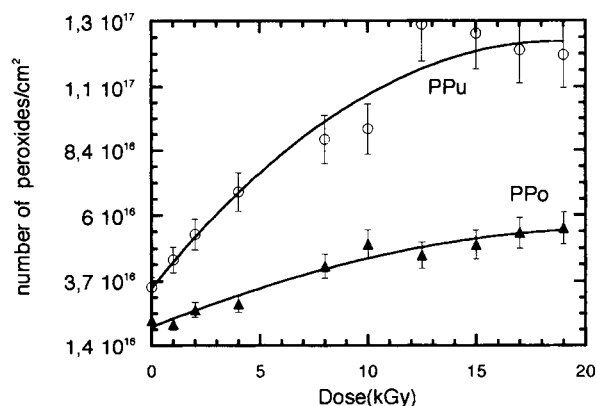


Figure 1 Influence of the morphology of the polypropylene film on the variation of the surface density of peroxides as a function of the irradiation dose. PPU and PPO are, respectively, the unoriented and the bioriented polypropylene film.

RESULTS AND DISCUSSION

Influence of the Morphology and of the Additives on the Formation of Peroxides

The irradiation in an oxygen atmosphere induces the formation of peroxides (hydroperoxides and diperoxides) into the PP film. The mechanism of peroxide formation can be described as follows⁷⁻¹⁰:

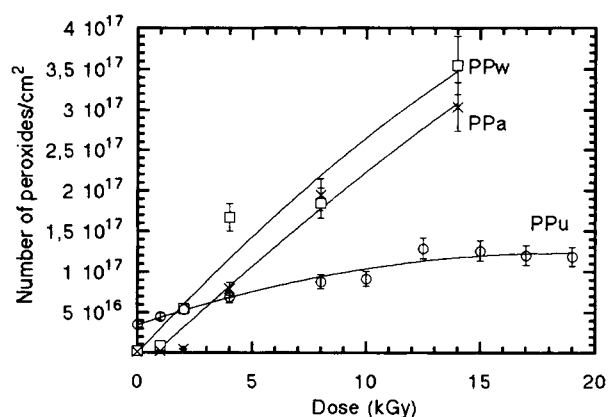
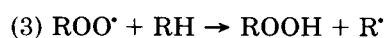
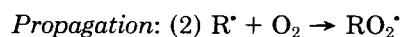
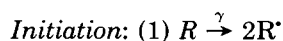


Figure 2 Influence of the additives on the variation of the surface density of peroxides vs. the irradiation dose: PPw (no additives), PPU (phosphite and phenol antioxidants), and PPa (only phosphite additives).

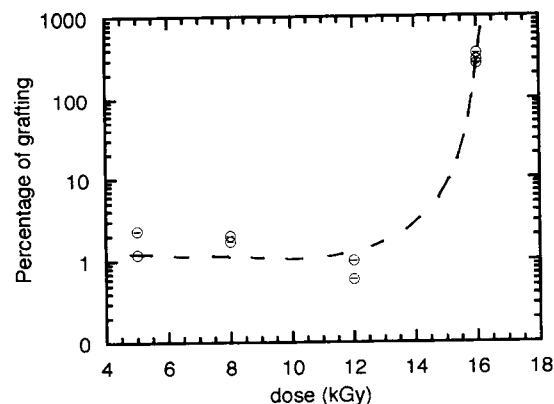


Figure 3 The percentage of grafting of poly(acrylic acid) on polypropylene film as a function of the preirradiation dose.



and other nonradical products



The formation of polymeric hydroperoxides is due to the chain reaction (3), whereas the diperoxides are issued from recombinations (4) and (5).

The film was subsequently grafted in the presence of AA, the grafting reaction being induced by the free radicals issued from the thermal decomposition of the peroxides. Consequently, it appears important to determine the amount of species able to initiate the grafting and particularly, in our case, the surface concentration of peroxides. These concentrations

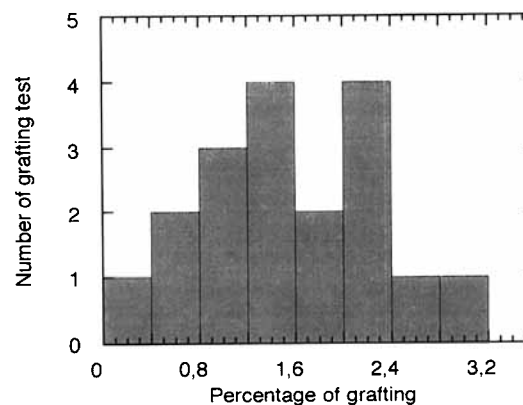


Figure 4 Reproducibility of the grafting reaction of poly(acrylic acid) on polypropylene film preirradiated at 5 kGy.

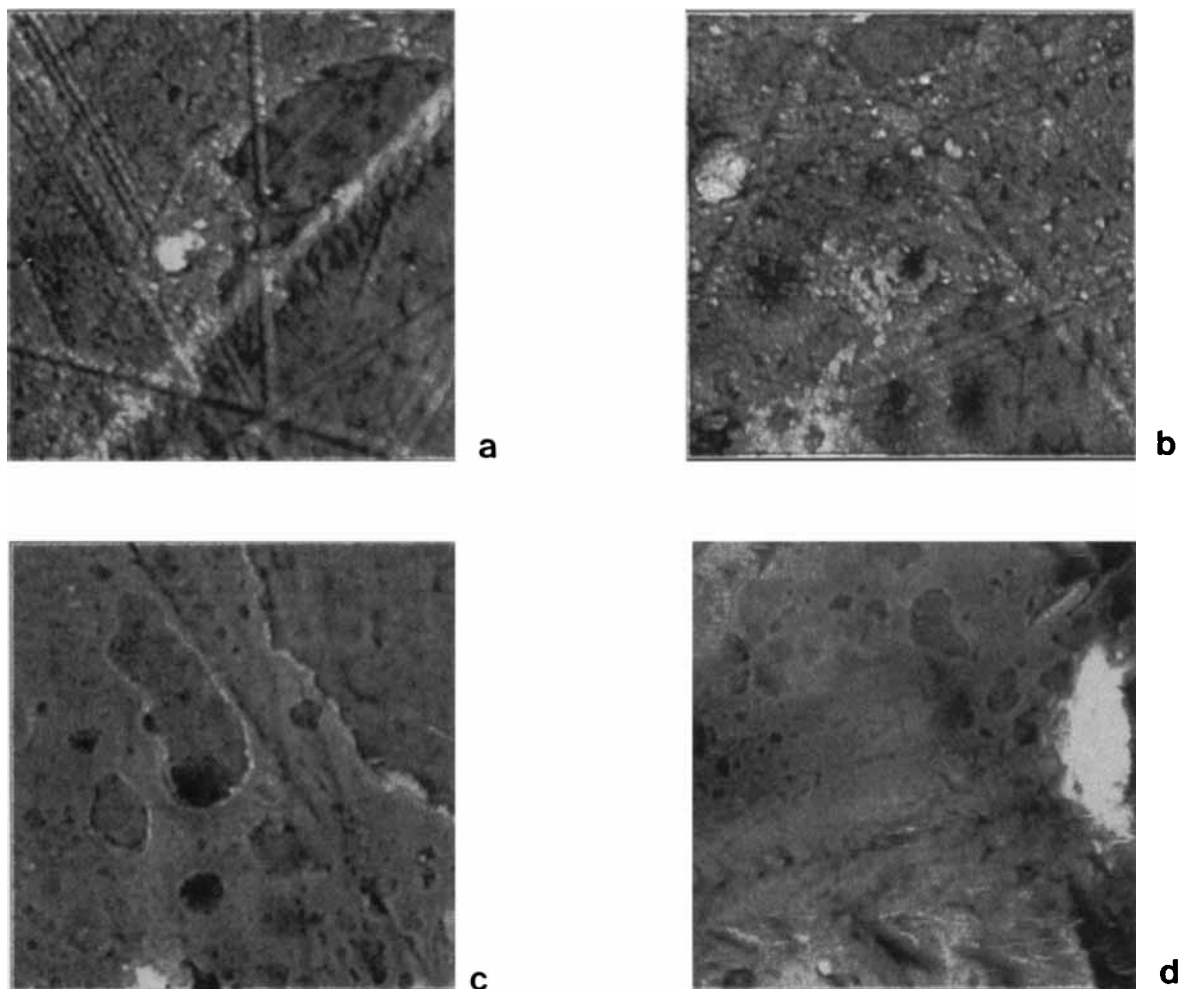


Figure 5 AFM images of a grafted polypropylene film with 2.3% of poly(acrylic acid) in weight.

measured by the DPPH method are presented on Figures 1 and 2.

Influence of the Morphology

Figure 1 shows that PPU forms more peroxides than PPO; in other words the peroxide concentration is dependent on the morphology of the film which is directly related to its manufacture process. These results confirm the conclusion of our previous study¹¹ in which it was found that at low irradiation doses, part of the PPO peroxy radicals were trapped in the crystalline zones and thus less susceptible to form peroxides than those raising for PPU. In fact, due to its poor structural order, the PPU macromolecular chains are rather mobile, and the PPU peroxy radicals can easily diffuse, react, and recombine to form peroxides. Because of this higher peroxide concentration, one can expect that PPU films

are more adapted to grafting than PPO. The remaining part of this work was exclusively carried out with unoriented films.

Influence of the Additives

One can see from Figure 2 that PPU, which contains different useful antioxidants (phenols and phosphites), also contained the lowest amount of peroxides. On the other hand, PPA, which contains only a phosphite additive, showed the same behavior as the PPw film synthesized without any additives.

The three films—PPU, PPA, and PPw—are unoriented and had practically the same crystallinity. Their difference of behavior must therefore be attributed to the presence of additives and one can easily conclude that the phosphite antioxidant (Irgafos 168) has a negligible influence on the peroxide formation. On the contrary, the presence of phenol

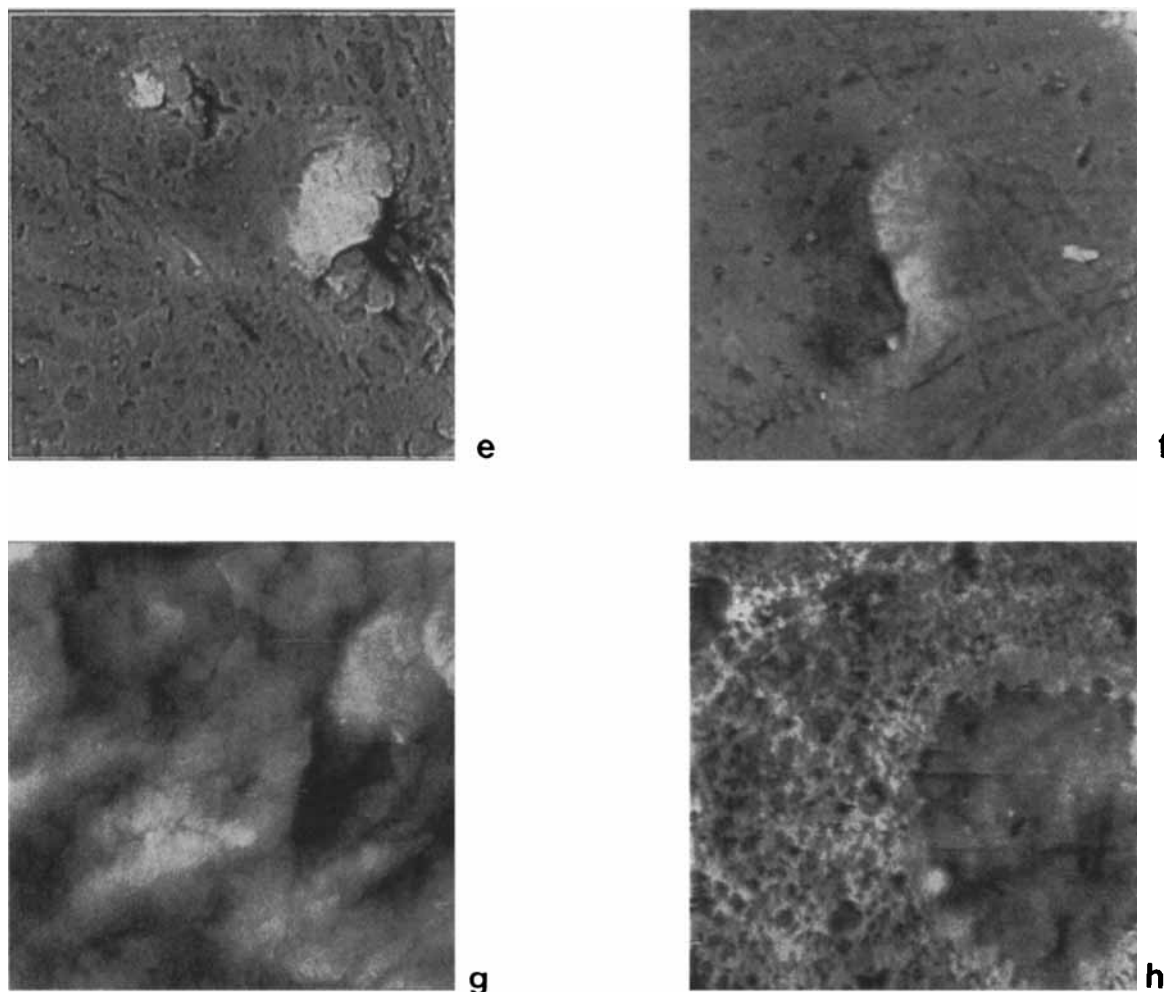


Figure 5 (Continued from the previous page)

compounds induces a loss of peroxides. In fact, phenols are usually considered as chain breaking antioxidants¹² and they are added to PP to prevent the formation of either the peroxy radicals (reaction 2) or the hydroperoxides (reaction 3) during its industrial processing. As a consequence, they induce a loss of initiating sites for grafting.

The unoriented film presents higher peroxide concentration than the bioriented one, and it is thus expected to be grafted more efficiently.

Grafting Experiments

The grafting tests were carried out on PPa films, which contained only phosphite additives. The grafted films were characterized by three different techniques: (i) the determination of the amount of grafting by weight measurements, (ii) the observation of the surface structure due to grafting at the

surface by AFM, and (iii) contact angle measurements to evaluate the surface polarity changes.

Amount of Grafting

Figure 3 gives the percentage of grafting as a function of the irradiation dose. The amount of grafting remained quite constant in the range of 0.4–2.5% up to 14 kGy and then suddenly increased to 300% at doses higher than 14 kGy. With less than 3% of grafting, the films seemed to be grafted only at the surface, whereas they became completely swollen by the grafted poly(AA) at 300%.

We would have expected that the evolution of the amount of grafting should be directly proportional to the surface concentration of peroxides as it was observed by Chevet,¹³ but that was not the case. In fact, Figure 3 is characteristic of a radical polymerization in the presence of inhibitors. The limitation

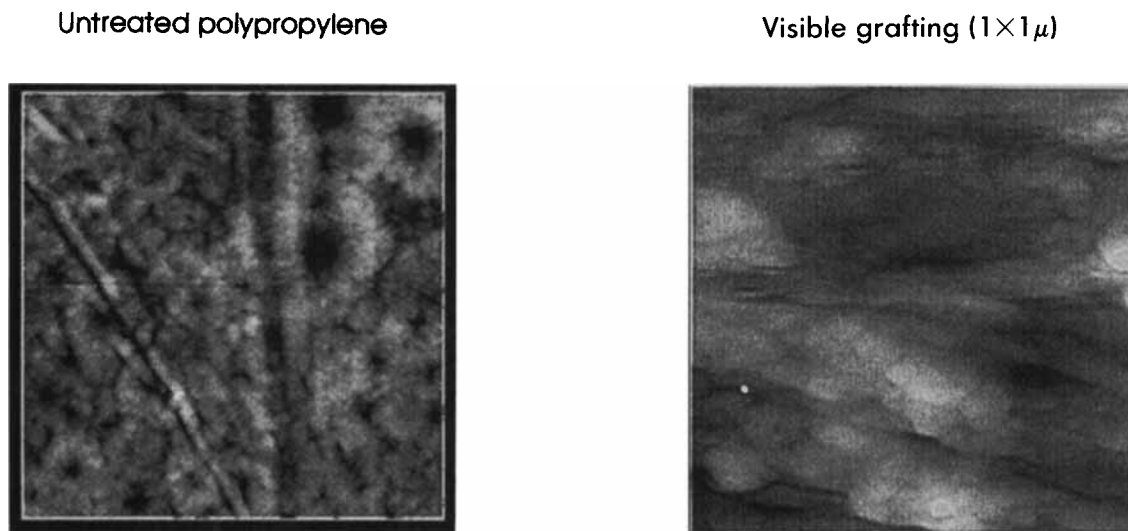


Figure 6 AFM images of a untreated polypropylene film and visible point of grafted polypropylene film.

of the grafting reaction for irradiation doses smaller than 14 kGy can be explained by the presence of the phosphite additive: this additive is a peroxidolytic antioxidant which reduces hydroperoxides to alcohols by a nonradical reaction, in order to prevent the degradation of PP during the manufacture, an operation which calls upon high temperatures. Consequently, the grafting is impossible until all the phosphite molecules are consumed, which in our case corresponds to a dose of about 14 kGy. It was also proved by electron spectroscopy for chemical analysis (ESCA) that those additives are not present in the first layers of the film (no traces of phosphorus compounds were found), and that can explain the fact that the reaction only occurs at the surface, leading to almost constant amounts of grafting.

Above 14 kGy, all the additives are consumed, and the grafting can have a normal evolution in the film as described by Uchida et al.¹⁴ who used ESCA techniques to follow the reaction: they proposed a mechanism initiating at the surface of the film and progressively propagating in its deeper layers. In fact, the grafting depends on the accessibility of AA monomer to the initiating sites: the AA molecules will reach the surface-active sites by molecular absorption. Then the grafting starts and the polarity of the film progressively changes, allowing the diffusion of the monomer in the deeper layers to reach some new active sites. As a consequence, when the additives are consumed, the grafting can rapidly progress in the bulk of the film giving a material completely swollen by the grafted polymer, as we can observe with 300% reaction.

The low values of the amount of grafting obtained for irradiation doses below 14 kGy suggest that the grafting only occurs at the surface of the film. This might be due to the distribution of the additives in the thickness of the film having an influence on the depth of the reaction and thus on the amount of grafting. As previously shown by Romero et al.,¹⁵ the depth of radiochemical grafting can be controlled by means of antioxidants. The mechanism of grafting is kinetically controlled by a progressive change in the balance between the hydrophilic (grafted PP) and the hydrophobic parts (virgin PP). In our case, we have shown that the presence of phosphite antioxidants inhibits the grafting in the bulk of the film. Thus, these antioxidants, which prevent the oxidation of the film, can help to control the depth of the grafted layer, which is preferably limited to the surface for applications to adhesion.

Homogeneity of the Grafting on the Surface

A first observation is that our results of grafting are not reproducible for a given irradiation dose: Figure 4 represents the statistical distribution of the amount of grafting for a 5-kGy irradiation dose. A hypothesis for this result was the inhomogeneity of the grafting.

This hypothesis was confirmed by the AFM observations. Eight different areas of a sample with 2.3% of grafting were characterized. The pictures are given on Figure 5.

By comparison with characteristic pictures of untreated film and visible point of grafting (Fig. 6),

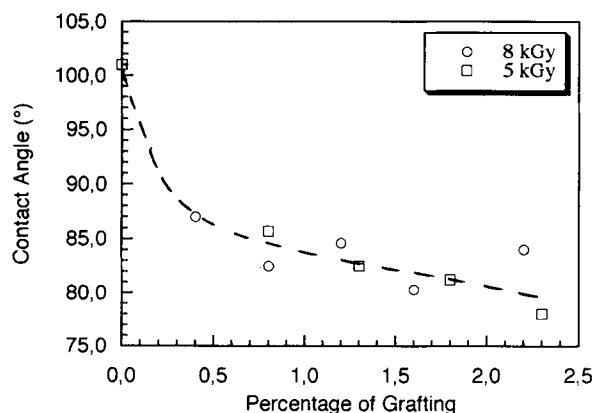


Figure 7 Variation of the water contact angle of grafted polypropylene film with the amount of grafting. The films were preirradiated either at 5 or 8 kGy.

each picture can be analyzed as a representation of a given local extent of grafting.

1. *a/b: low amount of grafting.* The defaults on the film can always be seen but the grafting seems to amplify the stripes due to the extrusion and other manipulations of the films.
2. *c/d: medium amount of grafting.* The structure of the film is progressively covered by the grafting.
3. *e/f: high amount of grafting.* Some areas are completely swollen by the grafted polymer.
4. *g/h: very high amount of grafting.* The structure of the film is completely lost (no stripes or holes) and the film is considerably swollen.

These pictures show that the distribution of the grafting on the surface of a given film is highly heterogeneous, and this also explains the low reproducibility of the extent of grafting.

The inhomogeneity of the grafting is also reflected by the large variation of the contact angle for the same samples: from place to place on the surface of a given sample, the contact angle can vary as much as from 65–100°.

To explain this heterogeneity, different hypotheses can be proposed:

1. As invoked earlier to explain the lack of reproducibility of the grafting, the presence of additives distributed heterogeneously in the thickness of the film can be also responsible for this problem.
2. The presence of defaults at the surface of the film and mainly the stripes due to the extrusion and other manipulations could be an-

other reason. Indeed, the stripes become thicker with increasing grafting as if grafting preferably occurred in those areas.

3. Following some authors,¹⁶ even if one degasses thoroughly before the grafting reaction, oxygen can be absorbed in some localized areas at the surface of the film and act as an inhibitor.
4. Another possible explanation to do with the presence of short grafted chains due to the local concentration of Mohr's salt, which is used to limit the homopolymerization but which is also well known to limit the length of the grafted chains.
5. One last reason could be the grafting mechanism: the grafting progresses from the surface into the film and when the grafting starts in one place, the wettability of the film increases and the acrylic acid molecules may diffuse in the first layers of the film. Thus, the grafting can progress from this place into the volume of the film with an irregular depth distribution.

The comparison between plasma-treated and gamma-irradiated samples may help to select between those hypotheses. Some experiments using plasma activation are in progress.

Evolution of the Surface Polarity

In spite of the large scatter of results, we were able to follow the evolution of the wettability as a function of the extent of grafting as shown in Figure 7. The contact angle decreases with the amount of grafting. However, it does not reach values as low as we might have expected. In fact, even with an amount of grafting lower than the values obtained here, the wettability of a surface grafted after a pretreatment by argon plasma is higher than with the present treatment: The contact angle of water decreases to 70°,¹⁶ whereas the lowest contact angle for our grafted films was only about 80°. This relatively weak improvement of the wettability might be due to the heterogeneous distribution of the grafting at the surface.

CONCLUSION

The surface of a commercial polypropylene film can be successfully modified by radiochemical grafting. The higher polarity of the resulting surface should provide better adhesion properties. We have shown

that a rapidly quenched polypropylene film produces more initiating sites for grafting than a bioriented stretched sample. Among all the usual compounds added to prevent the oxidation of polypropylene, phenols have a strong inhibiting effect on the peroxide formation and should be eliminated before any radical grafting, whereas phosphites allow a superficial grafting which is convenient for adhesion applications. The low reproducibility of the grafting reaction, the AFM, and the wettability measurements show a heterogeneous distribution of grafting at the surface of these materials.

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