Physicochemical characterization of polypropylene films grafted by poly(acrylic acid). 1

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I.r. spectroscopic analysis, in particular by means of the technique of attenuated total reflection, is used to characterize the grafting of polypropylene (PP) films by poly(acrylic acid). A method allowing us to separate the grafted part from that of unmodified PP is also used. Finally, we compare the results obtained when the film to be modified is initially treated or not to eliminate some of the additives present. We show that whatever the case, the grafting always starts from the interface between the PP and the polymerization solvent. Therefore, grafting in all the material can be easily obtained when the additives are extracted.

(Keywords: polypropylene; poly(acrylic acid); grafting; i.r. spectroscopy)

INTRODUCTION

Grafting of polyolefins allowing the modification of their physicochemical properties has been studied for several years[1-19]. Various fields of application are involved, including metalloplastic assemblies[1,2], textiles[3,10,11] and membranes[4,5]. Our work is focused on the grafting of polypropylene (PP) films by poly(acrylic acid) (PAA). Thus, we try to improve the surface properties of PP, the most important being adhesion on a metallic substrate (an aluminium sheet)[20].

If we consider the mechanisms involved in the assembly of a grafted polypropylene (PPg) film on an aluminium sheet, the two chemical structures present in the film, PP and PAA, clearly differ in their physicochemical and mechanical properties. Thus, the quality of the assembly will depend on the chemical composition of the superficial layers of the films. Therefore, it will be very important to know whether the grafting occurs at the film surface, in a given depth or in the bulk of the material.

For this kind of copolymerization, various chemical or physical initiations are possible. We chose electron beam irradiation which, in the presence of air, leads to the production of peroxides and/or hydroperoxides. Then, initiation takes place by heating the reaction medium which is the irradiated film fully immersed in a solution of monomers at a given concentration. This particular situation leads to grafting on both sides of the film.

In this work, our objective was to try to characterize the mode of grafting of PP by PAA. The main parameter involved was the grafting rate, and the various factors influencing it were studied. Thus, we showed the very important role played by the extraction of the additives introduced into the films during their processing.

EXPERIMENTAL

Materials

The PP sample was a 50 μm thick film processed by extrusion with ~1000 ppm of antioxidants. Acrylic acid was from Coatex and contained 200 ppm of stabilizer. All the other reactants and solvents were commercial products of reagent grade and aqueous solutions were prepared using deionized water.

Methods

Prior to treatment, the films were washed in methanol at ambient temperature for 40 min, then rinsed in methanol and dried *in vacuo* at ambient temperature. Two kinds of films were used: the first received no further treatment and the second underwent extraction of the additives. In the latter case, the PP films were introduced in glass tubes containing chloroform, and then rotated in an oven at 30°C for 15 h. After replacing the chloroform, another extraction was performed over 30 min. The films were finally dried *in vacuo* at 30°C.

The two types of films were irradiated by means of an electron beam accelerator (a prototype from Irelec, France). The first type of film was irradiated with a total dose of 2 Mrad and the second type with a dose of 2 and 4 Mrad.

The films were then introduced into glass tubes containing aqueous solutions of acrylic acid (AA) at

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various concentrations (10–30 w/w%). Nitrogen was bubbled into the tubes for 15 min. After closure by means of screw caps, the tubes were allowed to rotate in an oven thermostatically controlled at 99°C for 2 h. In order to remove the residual monomer and homopolymer, the grafted films were washed thoroughly in running water. Then, the free acidic form of the PPg films was prepared by soaking the films in 1.25×10^{-2} M HCl followed by washing in deionized water.

The separation of the various fractions of PPg was obtained as follows. A sample of known grafting rate was dispersed in *o*-dichlorobenzene (ODCB) at 140°C under stirring for 20 min–2 h depending on the grafting rate. This dispersion was filtered under vacuum on a no. 2 fritted glass, followed by several rinses with hot solvent. The insoluble fraction was collected and washed in ODCB at 140°C under stirring during 1 h. After a further filtration, the soluble part was evaporated to dryness at 100°C by means of a rotavapor and the insoluble fraction dried *in vacuo* at 100°C. To test its solubility, the insoluble fraction was placed in methanol under stirring at ambient temperature during 1 h. The filtrate and precipitate were then subjected to *FT*i.r. analysis: a drop of filtrate was evaporated on a KBr disc and the precipitate, which had swollen in the solvent, was pressed between two NaCl discs yielding a transparent system. A second solubility test was carried out in a 0.1 M NaOH aqueous solution. The first filtrate obtained on the no. 2 fritted glass was evaporated to dryness. A small amount of the powder obtained was used for *FT*i.r. analysis under a KBr disc and the remainder was solubilized in ODCB at 140°C under stirring for 30 min. After filtration on a no. 3 fritted glass, the same operation as above was repeated on a no. 4 fritted glass and finally on a 0.5 μm fritted metal (Waters-Millipore).

I.r. measurements were performed on a Perkin-Elmer 1760-X *FT*i.r. spectrophotometer. The transmittance measurements were carried out on the films without preliminary treatment. In the case of the analysis by attenuated total reflection (a.t.r.), a KRS-5 crystal was used with an angle of 45°. The incident beam was perpendicular to the bevelled surface and one sample was always placed on both sides of the crystal.

For the characterization of the grafting, i.r. analysis was preferred and an apparent grafting rate (G) was considered as the ratio $A_{1710\ \mathrm{cm}^{-1}}/A_{973\ \mathrm{cm}^{-1}}$. The first of these bands is characteristic of the C═O bond of the carboxylic acid and the second of the CH_3 bonds. The latter was chosen for its independence towards the crystallinity of PP. Thus, the corresponding absorbance was independent of the thermal treatments carried out. The base line was drawn by means of the tangent method obtained on both sides of the considered peak. The values of G measured by transmission and a.t.r. are denoted by $(A_{1710\ \mathrm{cm}^{-1}}/A_{973\ \mathrm{cm}^{-1}})_{\mathrm{T}}$ or G_{T} and $(A_{1710\ \mathrm{cm}^{-1}}/A_{973\ \mathrm{cm}^{-1}})_{\mathrm{a.t.r.}}$ or $G_{\mathrm{a.t.r.}}$, respectively.

RESULTS AND DISCUSSION

I.r. analysis of the grafted films

The grafting rate of the films can be characterized from i.r. measurements by means of two techniques: transmission, which gives a total value for the complete thickness of the sample, and a.t.r., which only allows the characterization of a superficial layer whose height is much smaller than that of the film.

It is important to note that the spectra obtained by these two techniques cannot be directly compared. The absorbances vary from one to the other according to a process which depends on the wavelength[21]. In a.t.r., the depth of penetration of the i.r. beam in the sample also depends on the wavelength. In addition, if we want to characterize the depth of the grafting of the films, it is necessary to consider the real penetration depth, d, which is equal to 3.6 and 6.3 μm for the absorption bands of interest at 1710 and 973 cm^{-1}, respectively.

For all the grafted films studied here, the a.t.r. analysis shows two bands at 1710 cm^{-1} ($\nu_{C=O}$) and 973 cm^{-1} (ν_{CH_3}) characteristic of the presence of acrylic acid and propylene residues, respectively. This means that for a depth within 3.6 and 6.3 μm both PP and PAA chain structures coexist for all the films. *Figure 1* shows the relationship between $G_{\mathrm{a.t.r.}}$ (on the same face of the films) and G_{T} for various grafting rates. All the PP films contain additives, with the antioxidants being the most important. If we consider the films modified without extraction of the additives, we notice an important enrichment of PAA grafts at the surface increasing with G value (curves A and B). This result is particularly well illustrated by the films irradiated at 4 Mrad. This enrichment can be the result of various situations, in particular, due to growth in the thickness of the superficial layer due to an increase of grafting only at this level or, of an increase of the total thickness due to grafting both at the surface and in the bulk. In the case of films irradiated at 4 Mrad, the very important enrichment in acrylic residues seems to correspond to the growth of the PPg layer located at the extreme surface of the film. In fact, as shown in

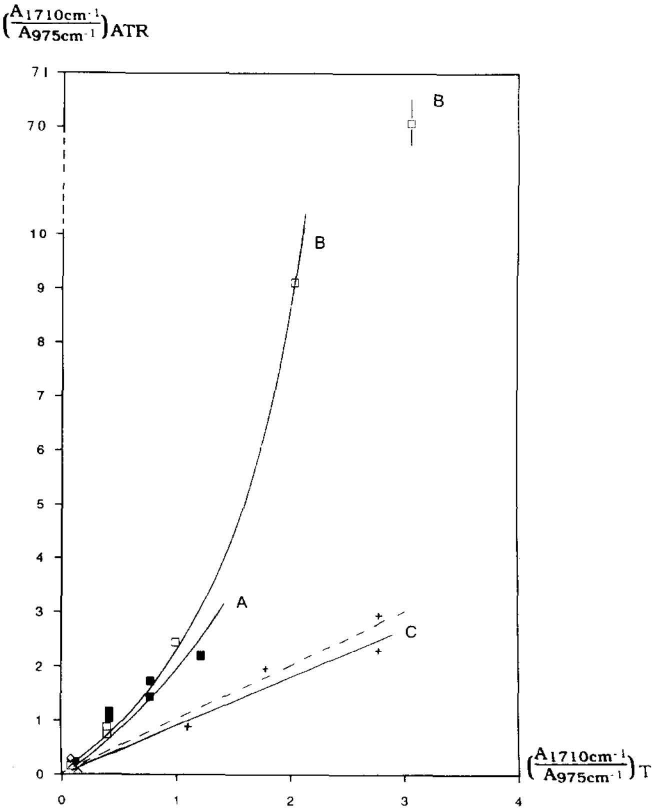

Figure 1 Relationship between the apparent grafting rate measured by a.t.r. (y) on the same face of the film and by transmission (x) for different kinds of films: films irradiated at 2 Mrad (A) and 4 Mrad (B) without extraction of the antioxidants, and films irradiated at 2 Mrad with prior extraction of the antioxidants (C). (– – –) $x = y$

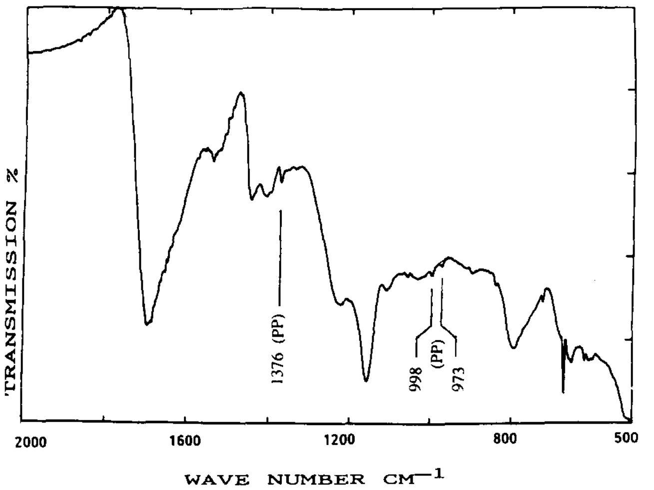

Figure 2 A.t.r. spectrum of a PPg film highly grafted (~20 w/w%), irradiated at 4 Mrad without prior extraction of the antioxidants

Figure 2, the a.t.r. spectrum obtained with a G value near 20 w/w% ($G_T = 3$) looks like that of the PAA homopolymer. Thus, we notice an almost complete disappearance of the bands characteristic of PP. In fact, the technique used only allowed analysis of the hypergrafted layer having a thickness approaching d.

It would seem interesting to compare curves A and B in *Figure 1* for high grafting rates, in particular for values of $G_T > 1.5$. In fact, for unextracted films irradiated at 2 Mrad, to obtain such values requires grafting with monomer concentrations of >30 w/w%. This leads rapidly to a medium of high viscosity in which the stirring crushes the film.

If we consider the films grafted after extraction of the antioxidants, we notice quite good agreement between the results obtained by a.t.r. and transmission (*Figure 1*). This means that G values measured at the surface or in the bulk of the sample are relatively similar. This behaviour is quite different from that described above and tends to show that in the latter case, there would be no particular enrichment in acrylic residues at the surface of the film. The experimental points are located a little below the bisector. This result can be interpreted if we assume that the depth of penetration of the i.r. beam in the sample is more important at 973 cm^{-1} (characteristic of PP) than at 1710 cm^{-1}. In these conditions, the values of $G_{\mathrm{a.t.r.}}$ lead to an overestimation of the proportion of PP to justify the experimental results.

This i.r. study allows us to show that the films grafted without extraction of the antioxidants show essentially a superficial grafting. Grafting in the bulk is also possible but only other techniques can verify this. In most cases, films grafted after extraction of additives seem to have been more homogeneously grafted in the bulk.

Separation of PPg

Polypropylene is hydrophobic in contrast to PAA which is water-soluble. Thus, the classical solvents of PP like ODCB at 140°C should allow the separation of soluble, ungrafted PP chains (or slightly modified) from insoluble, highly grafted chains. *Figure 3* schematically shows the method used. We generally observe a more or less rapid dispersion of the films in ODCB at 140°C. An insoluble part is always present for all the grafting rates tested, whether the antioxidants were extracted or not.

After being separated, the insoluble part cannot be dissolved in PP solvents like ODCB at 140°C or in PAA solvents like methanol or water at high pH, even after prolonged soaking. Nevertheless, a pure PAA sample treated as above can be readily and completely solubilized in water, at alkaline pH. Consequently, the insoluble fraction separated in ODCB cannot correspond to a PAA homopolymer. It swells greatly in PAA solvents (methanol and water) and seems to remain quite unchanged in hot ODCB. The i.r. spectrum of this product (*Figure 4*) is very close to that of pure PAA. Nevertheless, we notice the presence of a band of low intensity at 1376 cm^{-1}, characteristic of the PP structure. Thus, the insoluble fraction should consist only of highly grafted PP. It is important to mention the large difference which exists between the extinction coefficients of the C=O and CH_3 bands. Thus, it is not possible to detect the presence of PP in mixtures of PAA and PP above 80 wt% PAA.

If we consider the fact that grafting takes place in an heterogeneous medium, we can easily conceive that this particular radical polymerization of AA will occur preferentially at the surface of the films, especially at the PP–water interface. The reaction starts from monomer molecules adsorbed on the samples.

Thus, for G_T values of 3–4, a film grafted without extraction of the antioxidants, after irradiation at 4 Mrad, is characterized by an insoluble fraction 10 times greater than the one obtained in the case of a film for which the additives were extracted (*Table 1*). In the first case, the insoluble fraction appears in the form of a very thin film with a fibrous texture. The latter could correspond to a superficial layer giving the main response in the i.r. analysis (by a.t.r.) obtained in this case. For the extracted films, the grafting is distributed in the bulk of the samples. Thus, for similar global grafting rates, the superficial layer

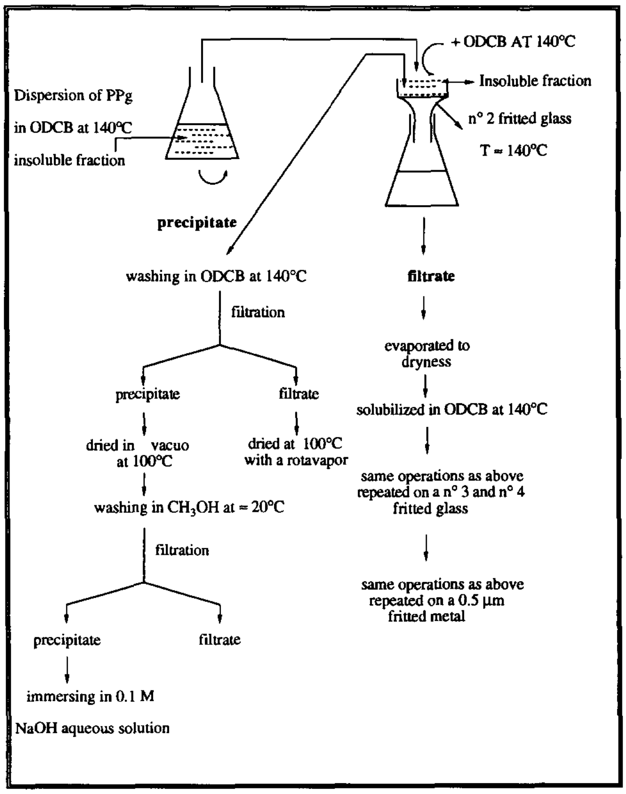

Figure 3 Separation of the various fractions of PPg

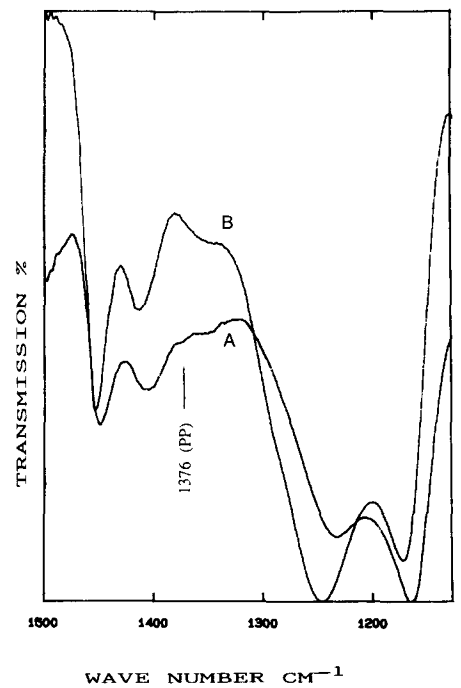

Figure 4 Transmission spectra of: the insoluble fraction obtained after the filtration of a PPg dispersion in ODCB at 140°C (A), and the PAA homopolymer (B)

Table 1 Results of the separation of the different fractions of PPg films: apparent grafting rates of the films, measured by a.t.r. and by transmission (T), and of the filtrates obtained on fritted glass

	$A_{1710\ \mathrm{cm}^{-1}}/A_{975\ \mathrm{cm}^{-1}}$					
Nature of the films	Initial films T	Filtrates obtained on fritted glass			Fritted metal 0.5 μm	Insoluble (wt%)
		no. 2	no. 3	no. 4		
Extracted and irradiated at 2 Mrad	4.1	1.8	1.7	0.8	0.4	~1
	1.0	1.0	0.8	0.6	–	<1
Non-extracted and irradiated at 4 Mrad	3.1	1.1	1.3	0.6	0.4	~11

has necessarily a *G* value much below that of the above case. Thus, the only PP–water interface initially accessible for the unextracted films would be the external surface of the films. Conversely, in the case of extracted films, this kind of interface also seems to exist in the bulk, as a result of the extraction of the antioxidants.

If we now consider the first filtrates on a no. 2 fritted glass (*Figure 3*). PAA homopolymer, especially of low molecular weight, could be solubilized or dispersed in a very divided state leading to its presence in the filtrate. In fact, we show that pure PAA with low molecular weight ($\overline{M}_w \sim 2000\ \mathrm{g\,mol^{-1}}$) is not solubilized in hot ODCB. Conversely, a small amount goes through a fritted glass of large porosity (no. 2). Filtration on a no. 2 fritted glass of a dispersion of a PPg film in ODCB at 140°C gives, after evaporation of the solvent, a white powder. Even after a prolonged immersion under stirring in methanol, this powder cannot be dissolved. Although it is synthesized in a large amount in the polymerization medium, the total absence of PAA homopolymer in the insoluble part as in the filtrate allows us to conclude that grafted films are fully devoid of this homopolymer in isolated form. We can also add that the method of washing, used at the end of the polymerization in order to eliminate the homopolymer adsorbed on the grafted film, is sufficiently efficient.

The amounts of products isolated after the successive filtrations on no. 3 and no. 4 fritted glasses are too small to be analysed. Nevertheless, as is shown in *Table 1*, we observe a continuous decrease in *G* in the products in the successive filtrates. Thus, the systems containing PPg which go through each fritted glass would not correspond to true solutions.

As PAA homopolymer is absent from the medium, the mixture contained in each filtrate can be only a mixture of PP and PPg whose grafted rate remains largely below that of the first insoluble fraction. We can also notice that for high grafting rates, there is a large difference between the residual grafting rate after passage through a no. 2 fritted glass and the initial *G* value. This is related to the proportion of insoluble material obtained in each case and to its *G* value (*Table 1*). Thus, if we compare the results for high grafting rate, a more important decrease in *G* in the filtrate, together with an insoluble fraction 10 times higher, is obtained in the case of unextracted films. The more important decrease in *G* observed in the latter case agrees quite well with the other results described above. Nevertheless, the very important insoluble fraction separated in this case should consist of less grafted polymer. This is not the case, as shown in the i.r. (a.t.r.) analysis of the corresponding film. Thus, we must imagine, as proposed by Rao *et al.*[16,17], that some crosslinking could occur under the condition of high concentrations of propagation chains. These networks could be formed either between PPg grafts of various lengths or between propagative chain ends and oxo radicals of PP chains, the former being the most likely. This agrees quite well with the large and small amounts of insoluble products obtained in the case of unextracted and extracted films, respectively. In addition, in the first case, due to the presence of both high irradiation dose and antioxidants, the grafting density at the surface should be the highest within the samples studied and, therefore, should favour crosslinking by recombination of chain ends.

When the porosity of the filters decreases, whatever the film, *G* in the filtrate decreases (*Table 1*). We can assume that the successive filtrations allow the separation of lower particle sizes. These could correspond to aggregates or microgels formed in ODCB whose lengths increase with *G*. Therefore, we could imagine that whatever *G*, a true solution is never obtained with PPg chains. Nevertheless, an experiment to filter, on a 0.5 μm pore size fritted metal, the solution obtained after filtration on a no. 4 fritted glass shows that (*Table 1*), whatever the case, PPg always remains in the filtrate. Thus, we can conclude that below a residual *G* (in the filtrate) of $\leqslant 0.4$, the grafted polymer is soluble in ODCB.

Proposed grafting mechanism

The various operations for separation of PPg prevent any ambiguity in the possible presence of PAA homopolymer in the modified films. They show the coexistence of two types of copolymers: one extremely grafted with a chemical structure very close to PAA, the other less grafted, with a large distribution of grafted rates. The first probably consists of PP chains bearing both numerous and very long grafts, with part of them being crosslinked to others belonging to PP chains. This copolymer should be essentially formed on the film surface. The presence of a distribution of grafting rates in the second case must be related to the decrease in G from the surface to the centre of the films.

I.r. (a.t.r.) analyses at a constant incident angle of the film surfaces by a.t.r. do not allow analysis of the deep layers of the sample. However, Uchida *et al.*[22] proposed that grafting should lead to a loss of cohesion of the PP chains and therefore to an increase in the thickness of the film, and, in particular, of the superficial layer. This phenomenon reduces the access of the i.r. beam to the internal layers.

The difference between the two kinds of films, extracted or not, can be interpreted as follows. The unextracted PP should maintain a pronounced hydrophobic character even after an irradiation at 8 Mrad, as shown by preliminary experiments of the wetting of non-extracted films irradiated at this dose. This must be related to the inhibiting role of the antioxidants regarding chain hydroperoxidation which occurs during and after irradiation in air[23]. Thus, for a given irradiation dose, the concentration of initiating sites is much lower than in the absence of antioxidants. This would make the diffusion of AA molecules dissolved in water difficult.

In such conditions, the initial grafting can be only produced on the PP chains located at the film surface, after physical adsorption of the monomers[24]. The polymerization will continue on this external layer as long as the monomer is unable to diffuse into the film. As the grafting goes on, the polarity of the grafted chains increases simultaneously with their loss of cohesion allowing the access of monomers to the deeper chains in the film. Nevertheless, this diffusion should be limited to the surroundings of the chains already grafted. It must be also mentioned that grafting involves only the amorphous parts of PP[24]. For a similar irradiation dose, PP whose antioxidants were extracted contains many more hydroperoxides. Moreover, in all cases, the electron beam goes through all the film and the peroxides are formed throughout the material. This important presence of polar functions could alone make the PP more hydrophilic, thus improving the diffusion of AA. The absence of antioxidants means the loss of their role of polymerization inhibitors. The loss of material created after extraction of antioxidants generates free volume which could be also a factor in the improvement of gas diffusion in water. The preliminary experiments of gas diffusion (H_2O vapour) through the films show that after extraction or not of the antioxidants, diffusion through the films is very weak and independent of whether the films were irradiated or not[25]. Nevertheless, we showed that an increase in diffusion is obtained in the case of extracted PPg films ($G_T = 1.5$). No modification was observed in the case of unextracted films of the same grafting rate.

All these observations contribute to show that grafting is a progressive phenomenon going from the surface to the bulk of the material. It depends on water diffusion in relation to the accessibility of initiating sites by the monomer. This process is kinetically controlled by a progressive change in the balance between hydrophilic (PPg, hydroperoxides) and hydrophobic (PP) parts as the grafting evolves, and also by the free volume created by the extraction of additives which is certainly increased at the grafting temperature. For these reasons, we can explain the rapid progress of the grafting in the bulk of extracted films. In the latter case, accessibility to a large amount of initiating sites leads to smaller graft lengths. The initial superficial mechanism of grafting is in agreement with those reported in the literature for all systems in which the polymerization solvent is not a solvent of the polymer to be grafted[26]. During a study of the grafting of poly(ethylene terephthalate) by acrylamide using e.s.c.a. at various stages of the grafting, Uchida *et al.*[22] proposed a mechanism which was initiated at the surface of the film and progressively propagated towards the deeper layers of the material. In this case and others[13], where the solvent is not a solvent of the polymer to be grafted, the initiation was photochemical and since the action of u.v. radiation is always limited to the surface, grafting was only obtained at the surface. Although electrons go through all the material and thus can create initiating sites everywhere, our results show that it is possible to control the depth of radiochemical grafting by means of antioxidants. Three parameters must act on the polymerization process: the monomer concentration, the local concentration of initiating species and the temperature. Munari *et al.*[6], in a study of the grafting of PP by vinyl pyrrolidone in solution in methanol showed that, from a radiochemical initiation, the grafting initially superficial could be obtained uniformally in the bulk by increasing the monomer concentration. Mori *et al.*[27] studied the electron beam irradiation induced grafting of acrylonitrile (AN) onto polyethylene (PE). He found that the grafting, first limited to the film surface shifted to the centre as the reaction proceeded, whatever the temperature and the dose rate. Moreover, he observed the role of the grafting temperature on the diffusion of AN into PE. As mentioned above, in our case, the study of the influence of these parameters is limited by viscosity problems. To our knowledge, the role of extraction of the antioxidants on the grafting mechanism has not yet been reported in the literature. Our results show that in this case it is possible to graft a film in the bulk even with a relatively low monomer concentration.

Considering the above results, and the model proposed by Uchida *et al.*[22], we can schematically show the evolution of grafting at the surface of a PP film by the diagram given in *Figure 5*. As supposed above, in the case of unextracted film of high G, we can consider that the grafting is also accompanied by crosslinking between the various layers involved.

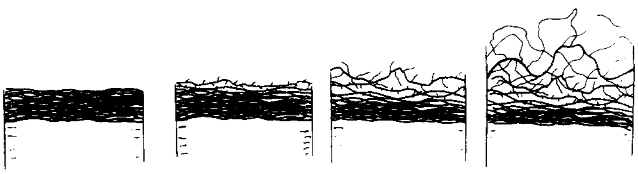
Figure 5 Model of the grafting mechanism of the PP film

CONCLUSIONS

From various methods of characterization of the grafting we have shown one kind of grafting which takes place at the PP–water interface. When the initial hydrophilic/hydrophobic ratio is increased in conjunction with morphological accessibility, in particular after extraction of the antioxidants, the grafting is progressively and rapidly displaced towards the bulk. Conversely, the presence of additives leads to the decrease in hydrophilicity and also inhibition of polymerization thus favouring a superficial grafting.

We can conclude that it should be possible to control the location of the grafting both by the content of antioxidants and by their extraction.

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