Gas Transport in Surface Grafted Polypropylene Films with Poly(acrylic acid) Chains

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ABSTRACT: This work describes the grafting reaction of poly(acrylic acid) (PA) onto the surface of polypropylene (PP) films carried out with ultraviolet radiation, using benzophenone as photoinitiator and water as solvent. By increasing the reaction time, graft percentages of 3.5, 6.5, 12.9, 19.8, 29.4, and 36.0% were obtained. Micrographs of the modified films show that grafting exclusively occurs on the PP films surface. The values of the permeability coefficient of oxygen, nitrogen, carbon dioxide, carbon monoxide, argon, methane, ethane, ethylene, and propane across the grafted films undergo a sharp drop. The interpretation of the permeation results suggest that radicals created in the tertiary carbons of the grafted chains by effect of UV light or by chain transfer reactions may highly crosslink the PA grafted layer. A rigid layer involving both strong hydrogen bonding and chains crosslinking is formed at grafting percentages of 3.5% that strongly hinders gas permeation across that layer. Destruction of hydrogen bonding by partially replacing protons of acrylic acid residues by sodium/silver cations increases the permeability of the surface grafted films. Finally, the films permselectivity is hardly affected by the grafted layer. ©2007 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 45: 2421–2431, 2007

Keywords: diffusion; gas; permeation; permselectivity; photografting; poly(acrylic acid); polypropylene films

INTRODUCTION

Owing to its useful properties, easy workability, and low manufacturing costs, polypropylene (PP) is widely used for the preparation of films, fibers, plates (sheets), injection-molded as well as blow molded articles, and so forth However, the low surface tension hinders dyebility, printability, paintability, and adhesivity of fibers, films, and sheets prepared from PP unless their surfaces are modified. Surface modification can be accomplished by increasing the polarity introducing special chemical functionalities like carboxylic groups, or by coating the surfaces with polar thin films, for example, poly(acrylic acid) (PA). In this way paint adhesion or metal-polymer bonding,[1–5] polymer-polymer bonding,[4,5] and so forth are enhanced. It is worth noting that even biofunctional PP surfaces can be generated, allowing the application of PP in the biomedical field for vascular grafts, catheters, heart valves, and so forth. In this case, and as a first step, reproducible functionalization, for example, with carboxylic groups, is required.[6–9]

In the last two decades, efforts have been devoted to the preparation of polar PP surfaces, using for this purpose different kinds of oxidation techniques in gas phase.[10–12] or solution-state

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oxidative etching.[13–16] However, PP surfaces thus treated tend to reorganize or reconstruct rendering ineffective the modification in many cases.[17–19] This drawback can be overcome by using grafting chemistry wherein the introduced surface groups are polyfunctional polymers or oligomers. Surface grafting techniques including photoinitiated grafting,[20–24] living radical grafting,[25] ceric ion induced grafting,[26] layer-by-layer ionic grafting,[27] and plasma polymerization[28,29] have proved to be effective to graft polyfunctional monomers or polymers onto PP surfaces.

Although gas transport in modified polymeric materials has widely been investigated,[30–36] up to our knowledge no study on the permeation characteristics of PP films coated with PA has been reported. Recently, gas permeation studies across surface modified low density polyethylene (LDPE) have shown that a thin grafting layer of PA reduces nearly six times the values of the permeability coefficient of gases in unmodified LDPE films.[37] The drop of permeability was attributed either to ordered structures of the grafted chains or to highly crosslinked structures developed onto the films surface. The strong effect of the relatively thin layer of PA on gas transport across surface grafted LDPE led us to investigate how the surface graft percentage of the hydrophylic polymer may affect the gas barriers of PP, a polyolefin widely used in the packaging industry. In this context, the transport of oxygen, nitrogen, carbon dioxide, argon, carbon monoxide, methane, ethane, and propane was measured at 30 °C. Also, the pressure and temperature effects on gas transport were investigated. To obtain a deeper insight into the influence of PA layers on the barrier properties of surface grafted PP, the permeation characteristics of PP films prior grafting were also studied.

EXPERIMENTAL

Reagents

Acrylic acid (Basf), acetone (Cicarelli), ethanol (Porta), NaOH (Cicarelli), benzophenone (Fluka AG), and $AgNO_3$ (Merck) were commercially acquired and used as received, without further purification.

Isotactic PP films 32-μm thick were kindly provided by Arcor Flexibles (Argentine). The crystallinity was determined from the melting endotherm of the polymer measured with a Perkin-Elmer Pyris DSC calorimeter at a heating rate of 10 °C/min, assuming that the enthalpy of 100% crystalline isotactic PP is 138 J/g. The value of the degree of crystallinity thus obtained was 48%.

Graft Copolymerization Procedure and Characterization

Graft copolymerization reactions onto PP films were carried out via UV light using the method previously described for PA grafting onto the surface of PE films.[37] In brief, a clean film of PP was placed in a glass Petri dish to which 0.5 mL of a 0.2 M solution of the initiator (benzophenone) dissolved in acrylic acid, and 0.5 mL of the solvent (distilled water) were added. The dish containing the film and the reactive products was irradiated with UV light (medium pressure UV lamp Engenlhard–Hanovia), at room temperature, under a nitrogen atmosphere. Removal of unreacted monomer, homopolymer formed and rests of initiator was accomplished by exhaustively washing the grafted sample with a very dilute NaOH solution (pH = 8) first and with distilled water further. The —COOH groups grafted onto the surface of the films were also quantified by volumetric titration with a 0.01 M NaOH solution. The grafting percentage was obtained from

$$\% \text{ Grafting} = 100 \times \left(\frac{\text{weight of grafted PP} - \text{weight of PP}}{\text{weight of PP}} \right) \qquad (1)$$

Infrared Spectroscopy

The samples were characterized by Infrared spectroscopy (IR). The FTIR spectra were obtained on films (10 scans and 32 resolutions) with a Nicolet 5 SXC.

Surface Analysis

To highlight the contrast of the grafted PA layers, the samples were immersed in a 1 M NaOH solution and then washed with distilled water (pH = 6) until all the NaOH was removed. Sodium ions were replaced by silver cations by immersing the grafted films in a silver nitrate solution. Finally the samples were washed with water and dried. The surface grafted films were sputter-coated with gold–palladium before examination under a Philips XL 30 SEM apparatus with tungsten filament. Cross-sectional area micrographs were taken with an angle of 45° in order that a perspective of the surface of the films is displayed. The microscope operated at an accelerating voltage of 25.0 kV. The magnification of the microphotographs obtained varied from 2000× to 4000×.

Gas Permeation Measurements

High vacuum was made in an experimental permeation device made up of two compartments separated by the film. One of the compartments, the upstream chamber, was filled with the pertinent gas at a given pressure and the permeation of the gas through the film to the other compartment, or downstream chamber, was monitored as a function of time with a MKS pressure sensor (10^{-4}–1 mmHg) via a PC. The permeation equipment was immersed in a water thermostat at the temperature of interest.

The permeation coefficient, P, was obtained by means of the following expression

$$P = \frac{273}{76}\left(\frac{V_{\mathrm{d}} l}{A T p_{\mathrm{u}}}\right) \lim_{t \to \infty}\left(\frac{\mathrm{d}p_{\mathrm{d}}(t)}{\mathrm{d}t}\right) \tag{2}$$

where V_{d}, A, l, and T represent, respectively, the volume of the downstream chamber, the barrier of the permeation area, the membrane thickness and temperature. The variables p_{d} and p_{u} are the pressures of the downstream and upstream chambers, respectively. Usually, the permeability coefficient is given in barrers [1 barrer = 10^{-10} × cm^3(STP)cm/(cm^2 s cmHg)]. The diffusion coefficient was obtained from the expression[38]

$$D = \frac{l^2}{6\theta} \tag{3}$$

where the time lag, θ, is the time at which the extrapolation of the p versus t plot covering the gas flow in steady-state conditions intersects the abscissa axis. Finally, the apparent solubility coefficient, S, was calculated from P and D by the following equation

$$S = P/D \tag{4}$$

The transport parameters, D and S, are usually given in cm^2/s and cm^3 (STP)/(cm^3 cmHg) units, respectively.

RESULTS

Chemical Modification

Previous studies have shown that the photografting process of hydrophylic monomers onto polyolefinic film surfaces is conditioned by the solvent. For example, Tazuke et al.[39] reported that the grafting of acrylamide onto PP films using benzophenone as initiator may take place not only on the polymer surface but also in the polymer bulk if the solvent is compatible with PP. In fact, if acetone–water is used as solvent, grafting mainly occurs on the films surface. However, acrylamide grafting extends to the bulk if tetrahydrofuran-methyl nitrile replaces acetone/water as solvent, In this case, the PP-solvent compatibility facilitates diffusion of the monomer to the radicals created inside the films.[40] Water has been used as solvent for the copolymerization graft reaction of PA onto low density polyethylene.[41] It was found that the hydrophilic character of the reaction medium prevents the diffusion of the monomer inside the hydrophobic films. Moreover, the fact that the photoinitiator and the growing chains are soluble in water facilitates radical reaction propagation outside the polymer surface. An additional bonus in the use of water as solvent is that it is inert to the triplet excited state of the photoinitiator benzophenone, thus the grafting reaction is not inhibited.

A general scheme for the grafting mechanism of PA onto the surface of PP films is shown in Figure 1. A radical formed in the benzophenone by effect of a UV light quantum removes a hydrogen atom from a tertiary C—H bond of PP, creating a free radical that initiates the grafting reaction. Owing to the hydrophobic character of PP and the hydrophilic nature of the reaction medium, diffusion of the photoinitiator inside the films is unlikely, so the creation of free radicals is mainly restricted to the films surface.

The variation of the grafted PA with time was determined by both gravimetry and volumetric titration, and the pertinent results are shown in Table 1. Representative IR spectra of the films after homopolymer removal are presented for different grafting times in Figure 2. Typically, the intense —C=O absorption (1718 cm^{-1}) characteristic of PA is seen in the spectra. It is obvious that the intensity of the peak increases while increasing grafting time. Other characteristic bands of PP were observed, such as the peaks at 2850 and 1451 cm^{-1} (CH_2 and CH_3 stretching). The graft of PA onto PP films is

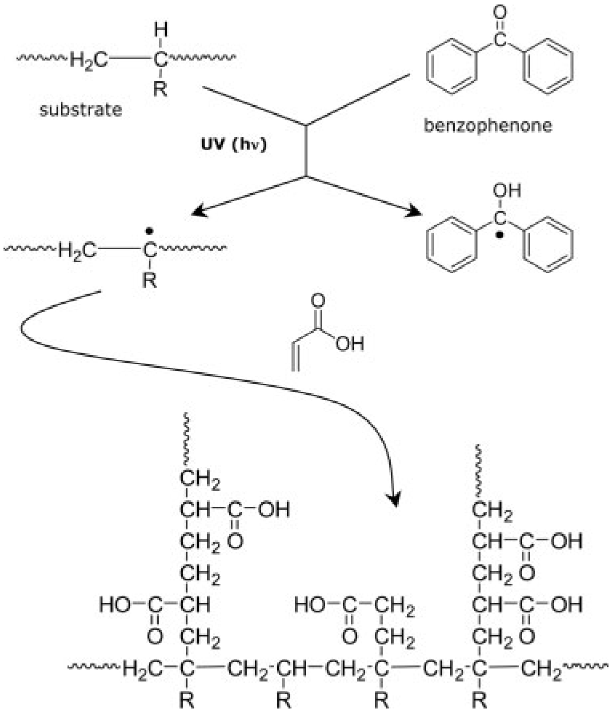


Figure 1. Scheme of the photografting reaction of acrylic acid onto the surface of isotactic PP films. (R = $-CH_3$).

only detected by FTIR after 5 min of radiation time. As shown in Table 1, the grafting percentage of PA seems to be a linear function of the reaction time for grafting times larger than 5 min.

Table 1. Graft Percentage and Surface Density of COOH groups on Polypropylene Films Using Benzophenone as Initiator and Water as Solvent

Sample	Time, Min	Microequiv. COOH/cm^2	% Graft
PP1	2.5	–	–
PP2	5		3.5
PP3	7.5	3.9	6.5
PP4	10	4.3	12.9
PP5	15	6.6	19.8
PP6	20	9.7	29.4
PP7	25	12	36

Figure 3 shows scanning electron micrographs of the surfaces of modified PP films after grafting times of 5, 10, and 20 min. The micrographs highlight a grafted PA layer coating the PP films, without observing the presence of PA polymer inside the PP films. For a graft percentage of 3.5%, a spongy layer of PA coats the PP film through which apparently uncoated tiny paths are detected. The spongy character of the surface of the grafted polymer decreases as the graft percentage increases, and the uncoated paths disappear. Besides, the PA coated surfaces display irregularities that increase with increasing graft percentage.

Gas Permeation

Permeation experiments were performed placing the grafted surface of the films facing the

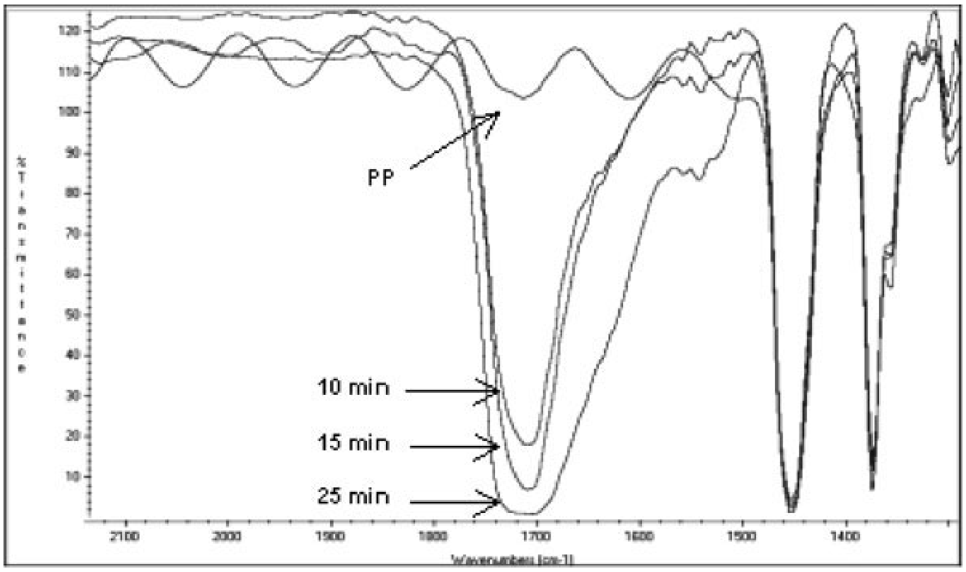
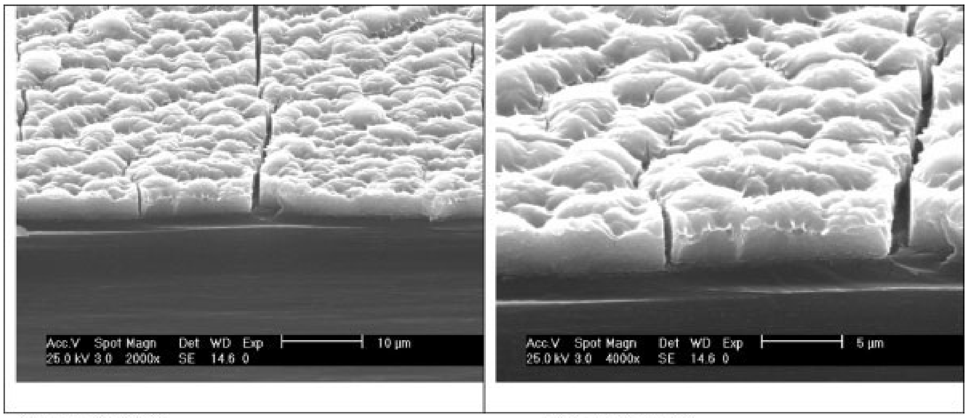
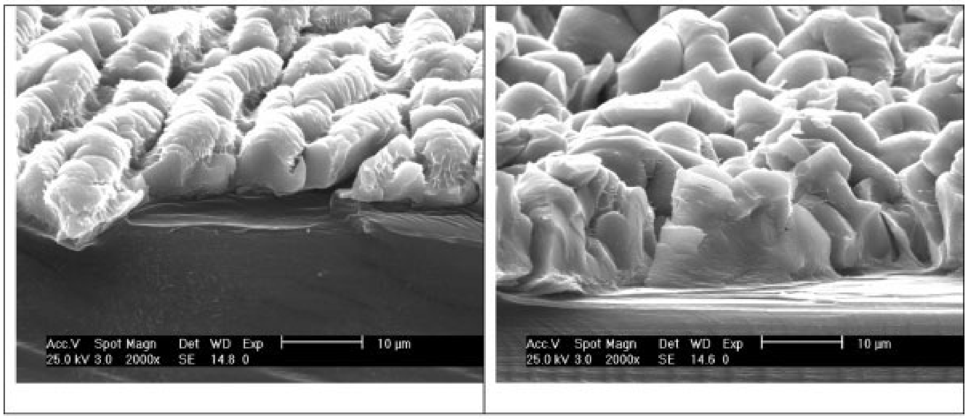


Figure 2. IR spectra of surface grafted PP films with acrylic acid for different grafting times indicated in the Figure.



PP_graft 3.5% PP graft 3.5%



PP graft 12.9% PP graft 29.4%

Figure 3. SEM micrographs for PP films surface grafted with PA. Top: micrographs corresponding to the 3.5% graft [PP2(3.5%G)]. Bottom: left PP4 (12.9%G); right PP6 (29.4%G).

upstream chamber in some experiments and the downstream chamber in others, no detecting any asymmetry effect on the permeation characteristics. As usual, isotherms describing the evolution of the pressure of the gas in the downstream chamber with time exhibit a transitory process at short times, followed by a linear dependence of pressure on time once steady state conditions are reached. Illustrative curves showing the permeation curves of oxygen across PP films as well as films grafted with PA for 5 min [PP2 (3.5%G)] and 20 min [PP6 (29.4%G)] are shown in Figure 4. In the acronyms of the different grafts, the grafting percentage is shown between brackets. The expression resulting of integrating Fick's second law using appropriate boundary conditions fit the experimental results as the continuous curves shown in Figure 4.

The results at 30 °C for the permeability, diffusion, and solubility coefficients of hydrogen, oxygen, nitrogen, carbon dioxide, methane, ethane, ethylene, propane, argon, and carbon monoxide through PP, PP1(0%G), PP2(3.5%G), PP4(12.9%G), and PP6(29.4%G), are gathered in Table 2. The

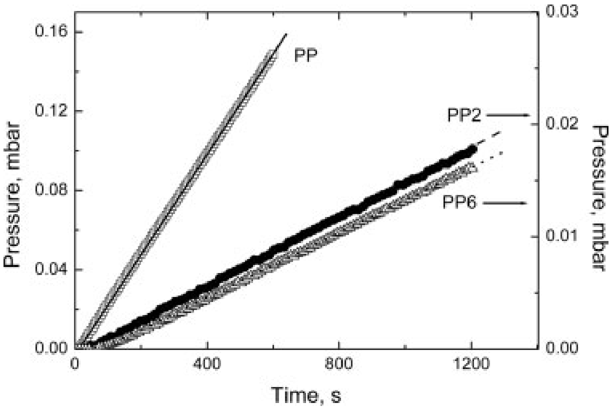


Figure 4. Isotherms showing the variation of the pressure in the downstream chamber with time for PP, PP2(3.5%G), and PP6(29.4%) films.

Table 2. Values of the Permeability, *P*, Diffusion, *D*, and Solubility, *S*, Coefficients for Several Gases, at 30 °C and 1 Bar, in PP, PP1, PP2(3.5%G), PP4(12.9%G), and PP6(29.4%G) Films

Gas	Film	*P*, barrers	$D \times 10^7$, cm^2/s	$S \times 10^3$, cm^3/cm^3 cmHg
H_2	PP2	3.51	29.04	0.12
	PP4	2.77	10.12	0.27
	PP6	2.40	11.08	0.22
O_2	PP	0.79	1.31	0.60
	PP1	0.72	1.53	0.47
	PP2(3.5%G)	5.8×10^{-2}	0.61	9.5×10^{-2}
	PP4(12.9%G)	6.8×10^{-2}	0.30	0.23
	PP6(29.4%G)	5.7×10^{-2}	0.29	0.19
N_2	PP	0.17	2.59	6.6×10^{-2}
	PP1	0.17	0.87	0.19
	PP2	1.1×10^{-2}	0.35	3.0×10^{-2}
	PP4	6.6×10^{-3}	9.45×10^{-2}	7.0×10^{-2}
	PP6	6.4×10^{-3}	8.98×10^{-2}	7.2×10^{-2}
Ar	PP	0.54	0.94	0.57
	PP2	3.0×10^{-2}	0.37	8.2×10^{-2}
	PP4	2.0×10^{-2}	0.16	0.12
	PP6	1.7×10^{-2}	0.17	0.10
CO	PP	0.26	0.80	0.33
	PP2	1.5×10^{-2}	0.32	4.8×10^{-2}
	PP4	9.1×10^{-3}	0.11	8.6×10^{-2}
	PP6	8.6×10^{-3}	0.17	5.0×10^{-2}
CO_2	PP	2.71	0.72	3.78
	PP1	2.28	0.59	3.83
	PP2	0.16	0.14	1.12
	PP4	0.19	2.93	6.4×10^{-2}
CH_4	PP	0.34	0.31	1.11
	PP2	2.0×10^{-2}	0.13	0.16
	PP4	5.8×10^{-3}	5.88×10^{-2}	9.9×10^{-2}
C_2H_6	PP	0.32	3.66×10^{-2}	8.79
	PP2	1.8×10^{-2}	1.76×10^{-2}	1.02
C_2H_4	PP	0.45	7.78×10^{-2}	5.72
	PP1	0.42	7.33×10^{-2}	5.76
	PP2	2.5×10^{-2}	3.61×10^{-2}	0.70
C_3H_8	PP	0.23	0.68×10^{-2}	33.3
	PP1	0.24	0.62×10^{-2}	38.9
	PP2	1.7×10^{-2}	2.91×10^{-3}	5.9

The quantity between brackets indicates the surface grafted PA percentage.

permeability coefficient of the gases through PP follows the trends $P(N_2) < P(C_3H_8) < P(CO) < P(C_2H_6) < P(CH_4) < P(C_2H_4) < P(Ar) < P(O_2) < P(CO_2) < P(H_2)$. Similar trends are observed in the surface modified films, though in this case the values of the permeability coefficients are in average nearly 16 times smaller than those corresponding to the unmodified PP films.

The values at 30 °C of the diffusion coefficient of the gases in PP films vary as $D(H_2) > D(N_2) > D(O_2) > D(Ar) > D(CO) > D(CO_2) > D(CH_4) > D(C_2H_4) > D(C_3H_8) > D(C_2H_6)$. Slight changes are observed in the order of the diffusion coefficient of the gases in modified films. For these cases, $D(H_2) > D(O_2) > D(Ar) > D(N_2) > D(CO) > D(CO_2) > D(CH_4) > D(C_2H_4) > D(C_2H_6) > D(C_3H_8)$.

Finally, the most condensable gases experience the highest solubility coefficients. For unmodified films, $S(C_3H_8) > S(C_2H_6) > S(C_2H_4) > S(CO_2) > S(O_2) > S(Ar) > S(CO) > S(N_2) > S(H_2)$. These trends are kept in the modified films, observing in some cases a high decrease in the values of the solubility coefficient. For example, the apparent

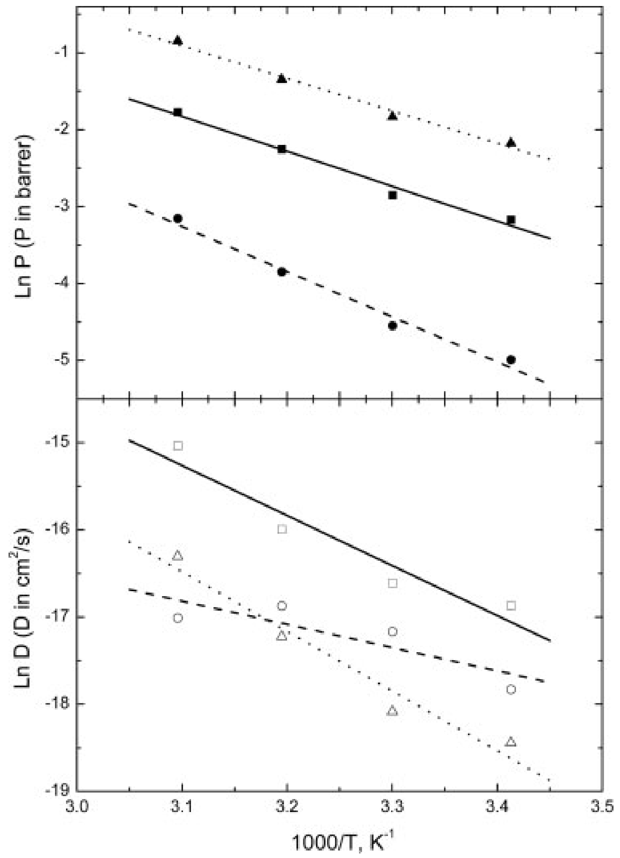


Figure 5. Arrhenius plots showing the temperature dependence of the permeability (filled symbols) and diffusion coefficients (open symbols) in PP2(3.5%G) films for oxygen (squares), nitrogen (rhombus), and carbon dioxide (triangles).

solubility coefficient of propane in PP, in cm^3 (STP)/(cm^3 cmHg) units, decreases from 33.34×10^{-3} in PP to 5.87×10^{-3} in PP2(3.5%G).

The influence of temperature on the transport properties of oxygen, nitrogen, and carbon dioxide through PP2(3.5%G) films was investigated. The transport coefficients follow Arrhenius behavior as the plots shown in Figure 5. The activation energies associated with the parameters that define the transport process, presented in Table 3, shows that $E_P < E_D$ for O_2 and CO_2, where E_P and E_D are, respectively, the activation energies associated with the permeation and diffusive processes. As a result, the solubility of these gases in the modified films is an exothermic process. For nitrogen $E_P > E_D$ and the solubility of this gas in the PP2(3.5%G) films is an endothermic process. One would expect that the solubility of the most condensable gases (propane, ethylene, and ethane) in the modified PP films is an exothermic process while that of the less condensable gases (carbon monoxide, argon, and methane) is endothermic.

The sensitivity of the transport properties of the grafted films to the pressure of the upstream chamber was studied using carbon dioxide as permeation agent. The results showed that the permeability coefficient is independent on pressure in the low pressure region (0.23–1.07 bars).

DISCUSSION

The results of Table 2 show that a 3.5% of PA grafted onto the surface of PP reduces by a factor of 16 ± 2 the permeability coefficients of the gases corresponding to unmodified PP films. For the less condensable gases the highest reduction mainly occurs in the diffusion coefficient, whereas for the most condensable gases the highest decrease takes place in the solubility coefficient. Owing to the hydrophilic character of the reaction medium that precludes the diffusion of the photoinitiator and the monomer inside the hydrophobic films, it is expected that grafting only proceeds on the films surface. This assumption was tested by SEM. To get a good contrast for the grafting layers, the protons of PA were partially replaced by silver ions following the procedure described earlier. An exhaustive inspection of the thickness of the grafted layer in the micrographs reveals a significant heterodispersity in the layers thickness.

By viewing the PP2(3.5%G) films as a sort of laminated formed by a layer of PA covalently attached to the surface of PP, the decrease in pressure Δp across the laminated can be written as

$$\Delta p = \Delta p_{PP} + \Delta p_{PA} \tag{5}$$

where Δp_{PP} and Δp_{PA} represent the drop of pressure across the PP and the PA layers, respectively. In steady state conditions, gas flow across the individual layers and the overall grafted film

Table 3. Activation Energies Associated with the Permeability and Diffusion Coefficients of O_2, N_2, and CO_2 in PP2(3.5%G) Films, Represented by E_P and E_D, Respectively; the vant' Hoff Heating Sorption is also Shown

Gas	E_P, kJ/mol	E_D, kJ/mol	ΔH_S, kJ/mol
O_2	38.0	48.0	−10.0
N_2	49.1	22.3	26.8
CO_2	35.3	57.3	−22.0

Table 4. Comparison of the Values of the Transport Parameters, at 30 °C and 1 bar, for Different Gases in Polypropylene Grafted with Acrylic Acid for 5 min, PP2(3.5%G), and in the Same Films Where the Protons of Acrylic Acid were Partially Replaced by Silver Ions PP2Ag(3.5%G)

Gas	Membrane	P, barrer	$D \times 10^7$, cm^2/s	S $\times 10^3$, cm^3 (STP)/cm^3 cmHg
O_2	PP2	5.8×10^{-2}	0.61	9.5×10^{-2}
	PP2Ag	0.11	0.44	0.25
N_2	PP2	1.1×10^{-2}	0.35	3.0×10^{-2}
	PP2Ag	2.5×10^{-2}	0.22	0.12
CO_2	PP2	0.16	0.14	1.12
	PP2Ag	0.38	0.23	1.65
CH_4	PP2	2.0×10^{-2}	0.13	0.16
	PP2Ag	5.1×10^{-2}	0.12	0.44
C_2H_6	PP2	1.8×10^{-2}	1.8×10^{-2}	1.02
	PP2Ag	5.1×10^{-2}	2.2×10^{-2}	2.28
C_2H_4	PP2	0.45	7.8×10^{-2}	5.72
	PP2Ag	6.4×10^{-2}	3.2×10^{-2}	1.98
C_3H_8	PP2	0.23	0.7×10^{-2}	33.34
	PP2Ag	3.0×10^{-2}	1.2×10^{-2}	2.59

must obey Fick's first law, converting eq 5 into

$$\frac{1}{P}=\frac{l_{PP}}{l}\frac{1}{P_{PP}}+\frac{l_{PA}}{l}\frac{1}{P_{PA}} \tag{6}$$

where l, l_{PP} and l_{PA} are, respectively, the average thickness of the grafted film, the unmodified PP film and the PA layer, respectively, whereas the parameters P, P_{PP}, and P_{PA} represent the respective permeability coefficients. The average thickness of the grafted PA layer can be estimated from

$$l_{PA}=w(\rho_{PP}/\rho_{PA})l_{PP} \tag{7}$$

where w is the mass of PA grafted per gram of unmodified PP and ρ_{PP} and ρ_{PA} are, respectively, the densities of the PP and the PA layers. The density of PA is strongly dependent on the water content and the degree of neutralization. The density of dry 100% PA is 1.40 g/cm^3 that drops to 1.08 g/cm^3 if the water content in gram referred to 1 g of dry polymer is 0.03.[42] Assuming that $l \approx l_{PP}$ for PP2(3.5% G) films, eq 6 becomes

$$\frac{P}{P_{PA}}\simeq\frac{l_{PP}}{l_{PA}}\left(1-\frac{P}{P_{PP}}\right)=\frac{15}{16}\frac{l_{PP}}{l_{PA}} \tag{8}$$

Then, the permeability coefficient across the grafted PP sample is $P_{PA} \approx 0.025\,P \approx 0.0015\,P_{PP}$.

Previous experiments carried out on the transport properties of ethylene across bulk PA films using a Cahn balance have shown that the value of the permeability coefficient is ~4.4 barrers, significantly higher than the value of this coefficient in PP films.[37] In view of the relatively high permeation characteristics of bulk PA films, the only way of explaining the sharp drop of the permeability coefficient of ethylene and other gases in PP2(3.5%G) films is that either order develops in the grafter layer or the PA chains are highly crosslinked. The first assumption is unlikely owing to the asymmetry of PA chains. Concerning the second assumption, the high concentration of monomer in the films solution facilitates the increase of the length of the growing grafting chains in the hydrophilic PP-solution interface. Radicals created in the tertiary carbons of the grafted chains by effect of UV light or by chain transfer reactions may crosslink the PA grafted layer. Hydrogen bonding combined with crosslinking may severely restrict local segments fluctuations in the glassy PA layer. As a result, the probability that chain fluctuations produce non permanent channels through which a gas molecule wandering in a cavity slides through it to a nearby one will decrease, with the consequent diminution of the diffusion coefficient. Also, restrictions in chains fluctuations presumably decrease the solubility of the gases in the grafted layer.

A surprising result is the similarity of the permeability coefficients of PP2(3.5%G), PP4(12.5%G), and PP6(29.4%G). However, eq 7 suggests that P_{PA} should increase with increasing values of w if the permeability is analogous across the whole layer thickness. The results of Table 4 shows that the transport parameters of O_2, N_2, CO_2, CH_4, C_2H_4, C_2H_6, and C_3H_8 in PP2Ag (3.5%G) films, where the protons of the carboxylic acid moieties replaced by sodium/silver ions, are nearly two times those measured in PP2(3.5%G) films suggesting that the partial destruction of hydrogen bonding between carboxylic acid groups increases the permeability of the gases. All these facts lead to postulate the formation of a rigid primary PA layer arising from hydrogen bonding and crosslínking chains cause a sharp drop in gas permeation. This primary layer is already formed in the PP2(3.5% G) films. As the grafting percentage increases, PA chains probably grow in the radicals formed in the tertiary carbons of the grafted primary layer giving rise to the formation of wrinkly surfaces with rigid pores that facilitate gas transport to the primary permeability layer formed at short grafting times. If this hypothesis is true, the primary layer could be responsible for the severe reduction of gas permeation across the surface modified films.

It is worth noting that the permeability coefficient for oxygen across surface modified low density polyethylene with 3.7% grafting of PA is 0.087 barrers, nearly two times higher than that found for oxygen in PP2(3.5%G). Differences in the crystallinity of the films (25% for LDPE vs. 48% for PP) may be partially responsible for the differences observed between the permeations of modified LDPE and PP films. Notice that as a consequence of the difference of crystallinity, the surface area available for gas transport processes in the PP films is nearly one half of that for linear low density polyethylene.

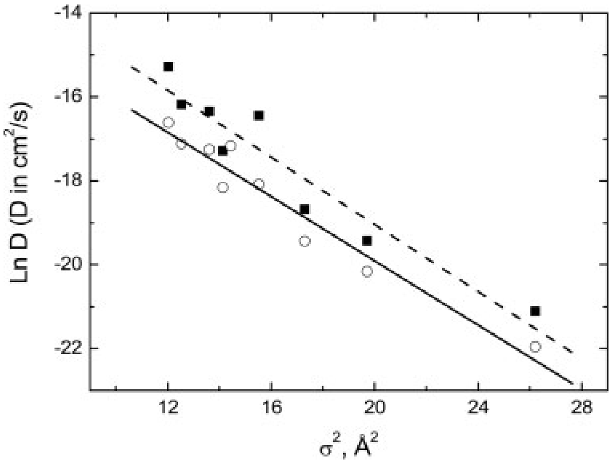


Figure 6. Variation of the diffusion coefficient with the square of the collision diameter of the gases permeating across the PP (filled squares) and PP2(3.5%G) (open circles) films.

Table 5. Comparison of the Permselectivity of the PP2(3.5%G) and PP2Ag(3.5%G) Films for Different Pairs of Gases, at 30 °C.

Permselectivity	PP	PP2 (3.5%G)	PP2Ag (3.5%G)
$\alpha(O_2/N_2)$	4.6	5.5	4.3
$\alpha(CO_2/O_2)$	3.4	2.8	3.5
$\alpha(CO_2/N_2)$	15.9	15.1	14.9
$\alpha(CO_2/CH_4)$	8.0	7.9	7.5
$\alpha(CO_2/C_2H_6)$	8.5	8.9	7.5
$\alpha(CH_4/C_2H_6)$	1.1	1.1	1.0
$\alpha(CH_4/C_3H_8)$	1.5	1.5	1.7
$\alpha(C_2H_6/C_2H_4)$	0.7	0.7	0.8

PP2(3.5%G) and PP2Ag(3.5%G) represent, respectively, PP surface coated with 3.5% of acrylic acid and the same films in which protons were partially replaced by silver cations.

The diffusive step in rubbery films is carried out by jumping the diffusant from a nonpermanent hole to a nearby one. The activation energy associated with the formation of a hole to host the diffusant, presumably depends on the cohesive energy density of the molecular chains and the cross-sectional area of the diffusant. In the case of glassy polymers, the jumping process from a hole or cavity to a neighboring one could be carried out through channels formed by chain fluctuations, the walls of which are formed by the segments of the polymer matrix. The radius of the channels should be at least equal to the van der Waals radius of the diffusant, σ. At first glance, one would expect that the activation energy associated with the diffusion process across rubbery or glassy film should be proportional to σ^2, so that $D \sim \exp(-\sigma^2)$, or $\ln D \sim -\sigma^2$.[43,44] In other words, the plot $\ln D$ versus σ^2 should be a straight line of negative slope. The size of the molecule of a gas can be estimated from the Lennard-Jones collision diameter σ_c, determined on the basis of the molecular interactions of a gas, and the kinetic diameter which is close to the molecular sieving dimension of the molecule.[45,46] Both the collision and kinetic diameters are widely accepted correlation parameters for diffusivity in the rubbery and glassy states. The values of the natural logarithm of the diffusion coefficients of O_2, N_2, CO, Ar, CO_2, CH_4, C_2H_4, C_2H_6, and C_3H_8 through modified and unmodified films, represented as a function of the square of the collision diameter in Figure 6, roughly fit to a straight line. Notice that the straight line for the modified PP lies below that of the unmodified one, presumably as a result of the fact that the large cohesive energy density of PA renders more difficult to form channels through which the diffusant can slide to a nearby hole in this latter polymer than in PP.

Finally, the permselectivity coefficient of the films to a pair of gases A and B are currently expressed by

$$\alpha(A/B) = \frac{P(A)}{P(B)} = \frac{D(A)}{D(B)}\frac{S(A)}{S(B)} \tag{9}$$

Values of the permselectivity coefficients for different pairs of gases, at 30 °C, are shown in Table 5. The results indicate that $\alpha(O_2/N_2)$ is ~4.6 in PP films, the permeability coefficient of oxygen being 0.79 barrers. The permselectivity of oxygen with respect to nitrogen increases to 5.5 in the PP2(3.5%G). This increase in permselectivity is at expenses of decreasing the permeability of oxygen from 0.79 to 5.8×10^{-2} barrers. The value of $\alpha(O_2/N_2)$ in PP2Ag (3.5%G) is only 4.3, but in this case the permeability coefficient of oxygen is two times higher than that obtained in PP2 (3.5%G) films. The analysis of the rest of gases in Table 5 shows that surface modification of PP does not increase the permselectivity of the unmodified PP films. The approximately similar permselectivities of PP and PP2(3.5%G) arise (I) from approximately similar diffusivity, as well as solubility, for the gas pairs CH_4/C_2H_6, CH_4/C_3H_8, CH_4/C_2H_4, and C_2H_6/C_2H_4 and (II) from a decrease of diffusivity selectivity by a factor of ~2 and a concurrent increase of similar magnitude of solubility for the gas pairs CO_2/O_2, CO_2/CH_4, and CO_2/C_2H_4. This difference between hydrocarbon gas pairs and CO_2/C_xH_y or CO_2/O_2 pairs are in line with the anticipated specific interaction effects of CO_2 with carbonyl groups containing polymers.[47]

CONCLUSIONS

PA layers grafted onto PP films using UV light techniques exhibit a spongy texture at grafting percentages of 3.5%. The grafting of PA onto the surface of isotactic PP is associated with induction times larger than 2.5 min. The spongy texture, as well as the relative regularity of the surface of PP2(3.5%G), tends to disappear as the grafting percentage of PA increases.

The permeability coefficient of gases through PP2(3.5%G) is in average nearly 16 times lower than that measured in PP. The fact that the decrease in permeability for higher grafting percentages is nearly similar to that found for PP2(3.5%G) suggests that some sort of primary PA layer is formed where hydrogen bonding combined with crosslinking chains is formed that severely restricts gas transport across the grafted films.

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