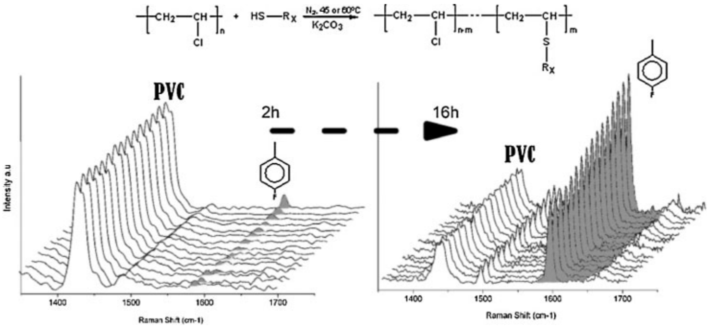
Surface Modification of PVC Membranes Using Fluorothiophenol Compounds

Marta Corrales, Karina Bierbrauer, Javier Sacristan,* Carmen Mijangos

The controlled chemical surface modification of PVC films by means of three fluoride aromatic compounds, 4-fluoro thiophenol, 3,4-difluorothiophenol and penta fluorothiophenol is reported. To obtain information about the surface selectivity of the reactions, the degree of modification of the polymer across the film was determined by depth profiling carried out using confocal Raman microscopy. It is shown that the gradient of the modification degree and the surface selectivity depend on the relationship between the rate constants of the substitution reaction and the diffusion process of the reactant. Therefore it is function of reaction time, temperature and the proportion of solvent/non-solvent used for the reaction.



Introduction

Today's sophisticated polymer-based devices are more likely to be successful if they are engineered with optimal bulk properties and precisely controlled surface chemistry.[1–3] For polymers, the bulk properties provide structural integrity and determine properties such as tensile strength, Young modulus and permeability.[4–6] It is mostly surface chemistry that determines biocompatibility, adhesion and barrier properties among others.[7–12] To satisfy both sets of requirements, material selection is critical. However, materials with optimal bulk properties rarely have optimal surface properties. Generally, to obtain the desired surface chemistry, a material is chosen primarily for its bulk properties and then its surface is modified/functionalized by means of different surface modification methods.[2,8,13] In the past several practical approaches have been explored for the modification of polymer surfaces, including chemical reactions,[11,14–17] blending,[18] plasma treatments,[19] corona discharge treatments,[20] grafting reaction[21] and adsorption of block copolymers.[22] Unfortunately, many of these surface modification methods may come with drawbacks such as added costs, a limited range of chemistries, lack of durability and increased potential for bulk polymer degradation.[23]

In fact, to improve the properties of poly(vinyl chloride) (PVC), our group has been devoted to investigate the modification of the pristine material, via nucleophilic substitution of chlorine atoms, in bulk[11,24,25] and at the surface using mixtures of solvents and non-solvents for the polymer.[16,26–29] The application of polymer analogue reactions on PVC has been shown to open even more fields for useful applications for this polymer. Wet-surface modification has been proved as the most controllable and efficient method to modified surface chemistry in PVC, polystyrene and other polymers.[26–28] It has been shown

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that PVC films can be chemically modified while preserving their form, optical properties and smoothness when reactions are carried out in an appropriate solvent/non-solvent mixture as the reaction medium.[16,27] The proportion of polymer solvent and non-solvent greatly influences the degree of modification achievable. However, in order to control the modification degree, the distribution of the modified groups and selectivity towards the surface, reaction time, temperature and reactivity of the modifier are also parameters of paramount importance[26–30] allowing to control useful surface properties like hydrophobicity and cell adhesion[12] while at the same time keeping the valuable mechanical properties of the bulk material.

Fluorinated surfaces of polymers have attracted much interest because of their advantageous properties, such as low wettability, low adhesion and low coefficient of friction.[31–33] These surfaces derive their characteristics from the unique molecular properties associated with the C−F bond that imparts a specific, unique chemistry and physics at interfaces. In this sense, fluoride compounds can be used as modifier in order to introduce these kinds of properties to different commodity polymers. For example, in situ fluorination processes for polymers such as polyethylene or poly(propylene) have been found to be effective for reducing permeation of small molecules such as oxygen and water which is an important fact in packaging applications.[34–35] It is has been shown very recently that functionalized PVC membranes, in bulk, with relatively bulky chemical moieties containing fluorine atoms in their structure display very different diffusion properties than pristine PVC.[36]

Therefore taking advantage of our experience in the selective surface chemical modification of PVC the purpose of this work is twofold, on the one hand, to prepare diverse samples of surface functionalized polymer films by reacting in a controlled way PVC chains with 4-fluoro-, 3,4-difluoro- and pentafluorothiophenol in solvent/non-solvent mixtures as a reaction medium. On the other hand, the second objective is to understand under which conditions a modification reaction evolves with time towards a homogeneously modified film or towards a film selectively modified at the surface. To this end confocal Raman microscopy was used to analyze the modified transparent polymer films of up to 50 μm thickness, obtaining profiles with a depth resolution of 1–2 μm.

Experimental Part

Materials

Commercial bulk polymerized PVC was obtained from Rio Rodano Industries, Spain. The average molecular weights determined by GPC were $\overline{M}_w = 112\ 000$ and $\overline{M}_n = 48\ 000\ g \cdot mol^{-1}$. The tacticity measured by ^{13}C NMR was syndio = 30.6%, hetero = 49.8% and iso = 19.6%.

As the nucleophiles for the modification reactions, 4-fluorothiophenol, 3,4-fluorothiophenol and pentafluorohiophenol were purchased from Aldrich with purities of 90, 95 and 97%, respectively. Cyclohexanone was doubly distilled prior to use and dimethylformamide was of commercial high-purity grade, and used without further purification.

Homogeneous Modification of PVC

PVC [8 mmol based on monomer units ($M = 62.5\ g \cdot mol^{-1}$)] and 8 mmol of the respective thiol aromatic compound were dissolved in 50 mL of cyclohexanone, 1.6 g of potassium carbonate was added and the reaction started under nitrogen atmosphere at 60 °C. The reaction was stopped by precipitating the mixture in cold methanol/water (2:1). The modified polymer was purified using methanol/tetrahydrofuran as a solvent/precipitant system.

Film Modification

PVC films have been prepared by casting from THF solutions. They were dried at 50 °C for 2 weeks prior to use. To allow the film to react on both sides and avoid folding or contact with the reactor wall, PVC films with dimensions $20 \times 10\ mm^2$ and thickness of about 60–70 μm were clamped in Teflon frames. The frames were immersed in a 50 mL reactor containing a 0.5 M solution of modification reactants and 1.6 g potassium carbonate in solvent/non-solvent, DMF/H_2O, mixture under nitrogen atmosphere to avoid oxidation of the modifier. The temperature of the reactor was controlled by a thermostat. In order to follow the kinetics of the reaction and obtain films of different degree of modification, samples were taken out from the solution at different time intervals, washed with water, extracted for 24 h in ether and dried.

Characterization

Calibration curves were necessary in order to quantify the modification of the PVC films using samples modified homogeneously in solution. The degree of modification had previously been determined by means of elemental analysis in the case of PVC functionalized with pentafluorothiopehenol and by means of ^1H NMR in the case of PVC modified with 4-fluorothiophenol and 3,4-fluorothiophenol.

NMR spectra were recorded in 5–10 wt.-% $CDCl_3$ solutions with a Varian Gemini 300 (300 MHz, 25 °C, 16 scans, pulse width 20 ms).

Elemental analysis of the pentahalogenated samples was performed on a Leco CHNS-932.

Confocal Raman Microspectroscopy

Raman spectra were recorded on a Renishaw Invia microspectrometer using the 514-nm line of an Ar laser. This instrument was equipped with a Peltier-cooled charge-coupled device (CCD) detector, a holographic grating (1 800 grooves · mm^{-1}) and a Raman holographic edge filter, which prevented the backscattered laser radiation from entering the spectrograph. The Ramascope was set up in the confocal mode with a 100× short-working-length

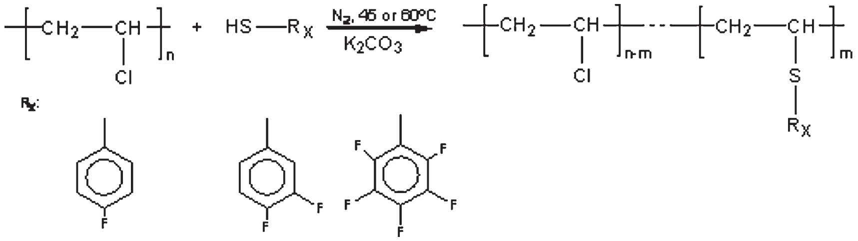

Figure 1. Modification reaction of PVC with different fluoride aromatic thiols.

objective [numerical aperture (NA) = 0.90], a slit width of about 4 μm and a CCD of 576 × 384 pixels. A depth profile of a sample was obtained by focusing the microscope stepwise (1 μm steps) through the polymer film and recording a spectrum at each step. For apparent penetration depths of up to 30 μm, accumulation times (*t*) per spectrum (window from 1 000 to 1 800 cm^{-1}) were usually *t* = 30 min. To correct the obtained depth profiles for the influence of the refractive index of the sample the length scale of the obtained profiles is multiplied by the refractive index of the polymer.[37–38]

Results and Discussion

In this work surface modification of PVC was carried out using three different commercial fluoride aromatic thiols, mono-, di- and pentasubstituted ones. Surface modification reactions have been carried out at two different reaction temperatures, 45 and 60 °C and reaction mixtures H_2O/DMF 1:2 and 1:4. This allowed us to study not only the influence of modifier reactivity and size but also the effect of temperature and solvent/non-solvent mixture in the selectivity towards the surface and in the progress of the modification reaction itself. The general reaction and the structures of the modifiers used in this work are depicted in Figure 1. The reaction conditions are described in the Experimental Part.

In order to calculate the absolute degree of modification of the modified PVC films it was needed to use calibration curves obtained from homogeneously modified samples whose modifier content has previously been determined by NMR spectroscopy and/or elemental analysis.[24] The kinetic of the modification reactions of PVC with 4-fluorothiophenol, 3,4-flurothiophenol and pentafluorothiophenol is shown as a function of time in Figure 2. As can be seen in all cases it is possible to reach very high modification degrees, up to 30% after very short reaction times ≤3 h which in principle make this modification reaction very promising for industrial applications. It is worthy of remark that the three modifiers display a very different behavior. The highest degree of modification reached with 4-fluorothiophenol is approximately 80% and the lowest with pentafluorothiophenol is 40% meanwhile the 3,4-fluorothiophenol present an intermediate behavior with modification degrees of about 60% after 5 h. These differences correspond with the acidity and nucleophilicity of the modifier which is influenced by the inductive and mesomeric effects of the substituents. The mesomeric effect is very similar for all the three compounds but the negative inductive effect due to the fluorine atoms is obviously less strong in 4-fluorothiophenol than in 3,4- and pentafluorthiophenol. Therefore it exhibits the highest nucleophilicity which should have a strong influence on the surface modification reaction and can be expected to be the most surface selective agent.

Information about the modified groups within the membrane depth profile was obtained by focusing the Raman microscope stepwise (1 μm) through the polymer membrane while recording at each step the spectral region which contains modifier bands at 1 580 cm^{-1} due to the stretching vibration of the aromatic rings and a constant reference signal of 1 425 cm^{-1} due to the C–H deformation of the PVC structure.[30] This procedure gives rise to a series of spectra such as those shown in Figure 3a. Comparison of the spectra shows that both bands show changes in intensity on penetrating the interior of the film. Since the intensity of the PVC band can be expected to remain unaffected by the reaction, the increasing intensities

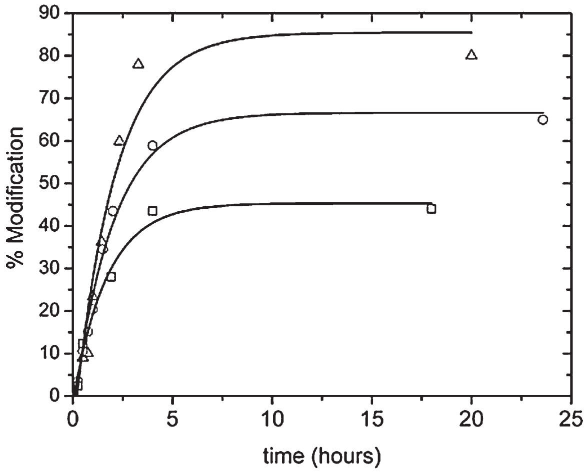

Figure 2. Kinetics of PVC modification in ciclohexanone at 60 °C with 4-fluorothiophenol (Δ), 3,4-fluorothiophenol (○) and pentafluorothiophenol (□) using a 2:1 molar ratio of PVC and thiol compound.

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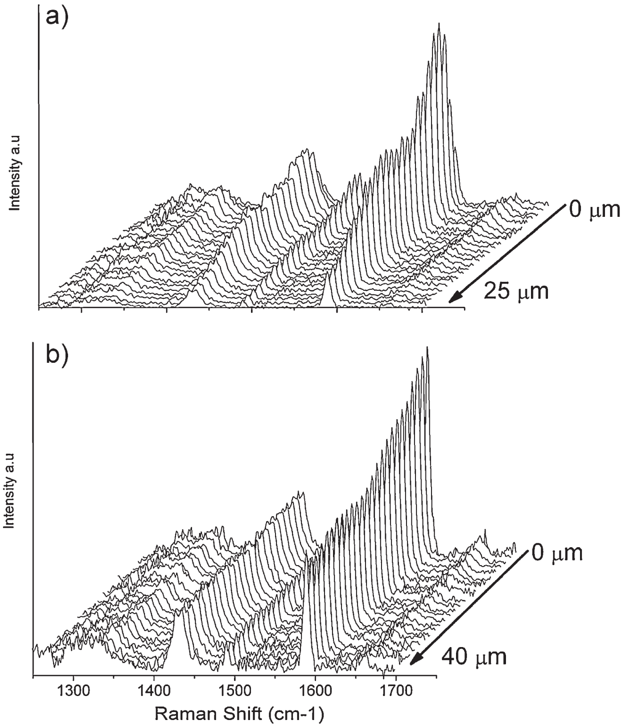

Figure 3. Series of Raman spectra as a function of depth of a PVC film modified with 4-fluorothiophenol in H_2O/DMF 1:4 at 45 °C (a) uncorrected spectra and (b) corrected spectra according to ref.[25].

measured in the first 4 μm below the surface and the decrease of the signal intensity in the last 4 μm before reaching the opposite surface must be due to the confocal Raman spectroscopy limitations. This feature may be explained simply by the fact that in the region of the film surfaces the scattering volume giving rise to the Raman spectrum is not entirely confined within the film. Indeed, this effect is utilized in estimating the depth resolution of the technique, by measuring the scattered intensity as a function of depth for a silicon wafer. The half-width of the confocal profile is found to be approximately 1.4 μm, and the intensity falls rapidly in the wings of the profile. A similar effect can be observed for the aromatic band, which increases from the surface up to a depth of about 4 μm. The signal then decreases until it begins to increase again and finally falls off when approaching the opposite surface of the membrane.

Therefore before any analysis of the Raman spectra it is necessary to mathematically correct these two effects following the procedure shown elsewhere.[38–39] On the one hand, in order to avoid the effect of intensity variations near the surfaces, where the scattering volume is not entirely confined within the film the raw data are normalized with respect to the reference band at 1 425 cm^{-1}. On the other hand, to correct the effect of polymer refractive index on measured depth profiles that leads to an incorrect apparent thickness scale,[38–39] it have been shown that in combination with the peak normalization described above, an expansion of the scale of apparent thickness to the measured film thickness (by multiplication of the apparent values with the refractive index of the polymer) results in a good approximation to the true depth profile.[26,37,40] Figure 3b displays the spectra after the scale expansion and normalization.

Influence of Modifier Type on the Modification Profile and Surface Selectivity

Raman spectra of PVC modified with the three reactants, 4-fluorothiophenol (PVCF), 3,4-fluorothiophenol (PVC2F) and pentafluorothiophenol (PVC5F) are shown in Figure 4 as a function of depth. First of all, one can see at least qualitatively that in all cases the reaction takes place preferentially at the surface. The modification occurred at the outermost layers of the polymer film, that is, at

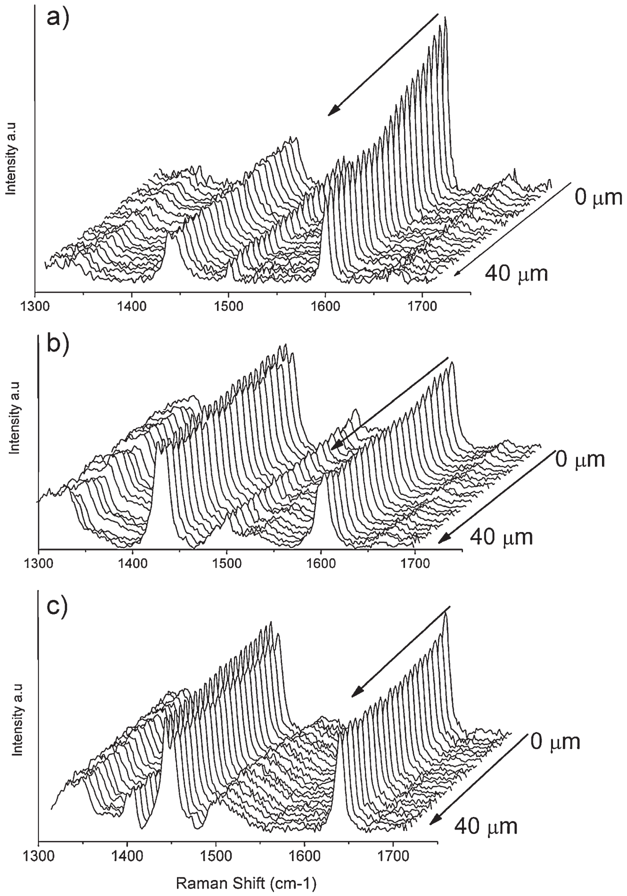

Figure 4. Series of Raman spectra as a function of depth of a PVC films modified 16 h at 45 °C with (a) 4-fluorothiophenol, (b) 3,4-fluorothiophenol and (c) pentafluorothiophenol. The spectra are normalized with respect to the intensity of the PVC band at 1 425 cm^{-1}.

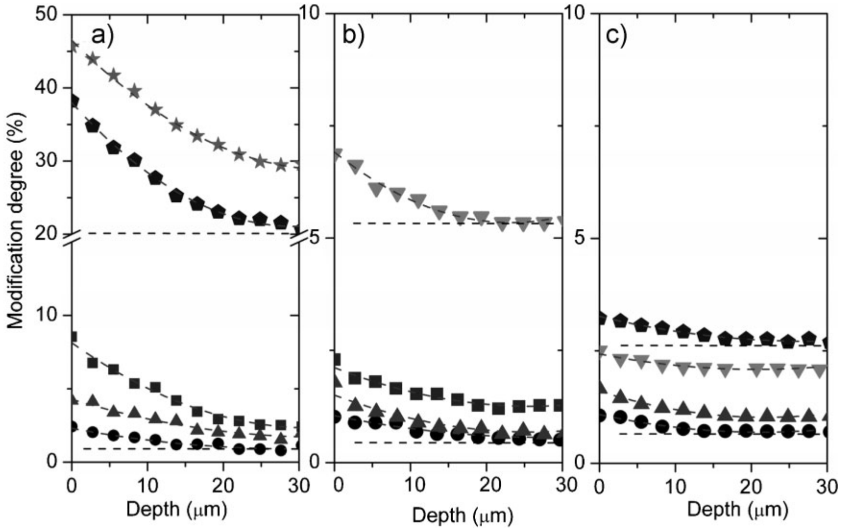

Figure 5. Depth profiles of ≈60 μm thickness PVC films modified with (a) 4 fluorothiophenol, (b) 3,4-fluorothiophenol and (c) pentafluorothiophenol in H_2O/DMF 1:4 at 45 °C for for 2 h (●), 4 h (▲), 6 h (■), 16 h (▼), 24 h (⬟) and 30 h (★). Lines are simply guides to the eye.

microscale. The relative degree of modification of the film can be calculated from the ratio of the integrals of the deconvoluted aromatic ring signal at 1 580 cm^{-1} to that of the PVC band at 1 425 cm^{-1}, absolute values are obtained using a calibration curve. In order to quantify and easily compare the gradient of modification through the film, depth profile curves of the modifying groups are shown in Figure 5. Moreover, films modified at different reaction times were analyzed in order to investigate the evolution of the profiles with time. The three modifiers displays a similar behavior, the shape of the curves, decreasing from a maximum value close to the surface to a minimum at the center of the film demonstrates the surface selectivity of this reaction. However, some differences can be appreciated in this figure. PVCF presents the highest modification degree at the surface while PVC5F has the lowest modification degree and the flatter modification profile curves. It is worthy of remark that for PVC5F the modification degree at the surface it is very low ≤ 5% which do not allow to unequivocally confirm the selectivity towards the surface of this reaction whereas PVCF and PVC2F display differences between the conversion at the surface and at deeper layers that goes from 5% at the shortest reaction times to 50% at the largest ones. For each of the three materials the modification degree at the surface and in the interior of the film increases also as a function of reaction time due to more penetration of the reactive. The reaction continues inside and at the outermost layers of the film. These results highlight that in principle the modification degree at the surface and the modification gradient can be varied over a wide range as a function of the modifier and reaction time.

One of the most important aspects of a surface modification reaction is the surface selectivity because it gives us a quantitative idea about the distribution of the modifier within the polymer film. Moreover, it can be directly calculated from depth profile Raman spectra[26] using expression 1 where d is the thickness of the film, f(M) a function which describes the evolution of the degree of modification with depth x and M_{surf} is the degree of modification at the surface of the film. Both values can be obtained from the depth profile curves. According to the definition of the surface selectivity (SS), values between 0 and 1 are possible, with 0 corresponding to a completely homogeneously modified film and 1 to a film with an infinitely thin modified outer surface layer,

$$SS = 1 - \frac{\int_0^{d/2} f(M)\mathrm{d}x}{(1/2)\mathrm{d}M_{surf}} \qquad (1)$$

Figure 6a and b display the evolution of the degree of modification at the surface and the surface selectivity of PVCF, PVC2F and PVC5F in H_2O/DMF 1:4 mixture at 45 °C, respectively. From these figures it becomes evident that the highest degree of modification at the surface and selectivity is obtained with 4-fluorothiophenol and the lowest with pentafluorothiophenol. These differences observed in the degree of modification at the surface, in the selectivity towards the surface and in the shape of the modification profiles, Figure 4, can be explained by the different acidity and nucleophilicity of the modifier and by their different size. 4-fluorothiophenol is the smaller modifier and has the lower negative inductive effect therefore it is a comparatively better nucleophile than 3,4-fluorothiophenol and pentafluorothiophenol. Consequently, PVCF exhibits the highest modification degree at the surface and surface selectivity among the three modifiers. For PVC5F the situation is very different in spite of the larger size of the modifier, the low electron density of the sulfur atom and consequently its nucleophilicity is the most reduced by the five fluorine substituents with a strong negative inductive effect.[24] It leads to lower degrees of modification at the surface. However, at the same time the modifier has more time to diffuse through the film and react but as the reaction progress the diffusion of the modifier is hindered due to steric hindrance resulting in larger SS than in the case of

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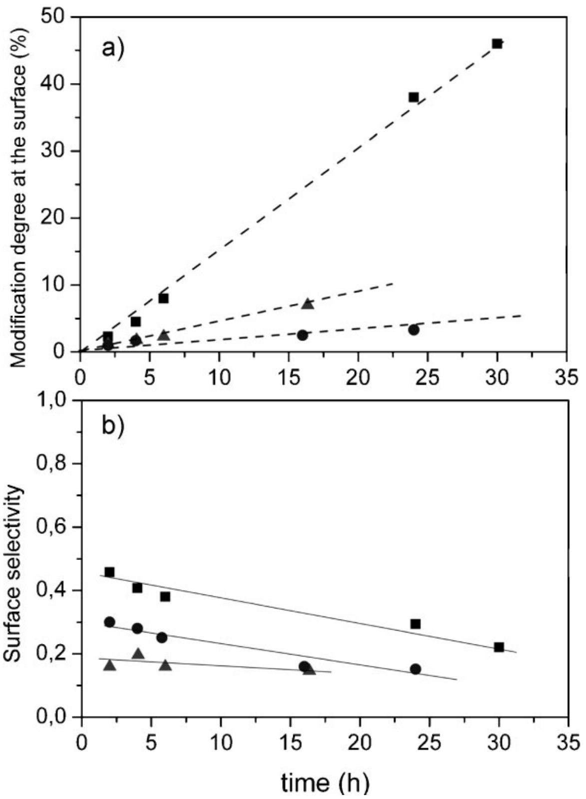

Figure 6. (a) Influence of modifier characteristics on the degree of modification at the surface and (b) evolution of surface selectivity with reaction time of PVC films modified in H_2O/DMF 1:4 at 45 °C with 4-fluorothiophenol (■), 3,4-fluorothiophenol (▲) and penta-fluoro thiophenol (●). Lines are guides to the eye.

PVC2F. PVC modified with 3,4-fluorothiophenol can be considered as an intermediate case. Its size is comparable to 4-fluorothiophenol but the reactivity is lower. As a consequence of that it displays lower modification degrees at the surface than PVCF but higher than PVC5F. In general surface selectivities decrease with reaction time, however at this temperature PVC modified with 3,4-fluorothiophenol shows the lowest SS. This behavior is interpreted due to the lower reactivity of the modifier and to its size which allow it to diffuse throughout the film prior to react and consequently, a nearly homogeneously modified film is obtained at the largest reaction times studied in this work.

These results are better understood taking into account that the modification reaction of polymer films in solvent/non-solvent mixtures is composed of three steps,[26,29] each of them with its own reaction rate constant. The first step after immersing the film into the reaction solution is the swelling of the polymer film by the reaction medium. The second step is the transport of the modification reactant to the functional groups of the polymer and the third step is the reaction itself. It is worthy of remark that diffusion of relatively small solvent molecules proceeds very fast in comparison to the transport of the reactant that is why the existence of a gradient of modification degree across the film indicates that the transport of the solvent and the reactant through the membrane must be slow in comparison to the nucleophilic substitution reaction. These results suggest that is not just one rate constant responsible of the observed concentration gradients, but the relationship between the reaction and the reactant diffusion constant which mainly controls the modification reaction.

Dependence of Modification Profile and Surface Selectivity on the Reaction Temperature

The reaction temperature at which a polymer film is modified can be expected to have a very strong influence in the distribution of the modifier groups within the polymer film.[29] Based in our previous experience, in this work two temperatures have been selected, 45 and 60 °C which should lead to modified PVC films with different concentration gradients across them. Figure 7a and b displays the depth profiles of PVC films modified with 4-fluorothiophenol, and pentafluorothiophenol in H_2O/DMF 1:4 mixtures at 60 °C (Figure 5 shows the depth profiles of PVC films modified with 4-fluorothiophenol, and pentafluorothiophenol in H_2O/DMF 1:4 mixtures at 45 °C). Similar results were obtained for PVC films modified with 3,4-fluorothiophenol (not shown here). From these curves its evident that the modification reaction has taken place selectively towards the surface. It can be seen that higher reaction temperatures favor both higher degrees of modification at the surface and deeper penetration of the reactant. The curves are considerably flatter at 60 °C than those at 45 °C (Figure 5). A similar behavior can be expected after an increment in polymer solvent concentration in the reaction medium as we will see in the next section. However, it should be taken into account that higher temperatures not only produce a stronger swelling of the films but do also activate the reactivities of the modifiers, which should affect the selectivity of these reactions towards the surface.

Figure 7c displays the evolution of the degree of modification at the surface of PVC films modified in H_2O/DMF 1:4 mixture at 45 and 60 °C. It is clear that the highest degree of modification at the surface is obtained with 4-fluorothiophenol and the lowest with pentafluorothiophenol. Furthermore the surface selectivity as function of time was calculated from the depth profiles of the modified PVC films according to Equation (1) and is depicted in Figure 7d. As expected, the values decrease with increasing reaction temperature and time. From these curves two conclusions can be drawn: on the one hand, the enhanced swelling of the film facilitates both the contact between polymer and reactant leading to higher degrees of modification at the surface (at the same reaction times), and a faster distribution of the reactant within the film. As a consequence,

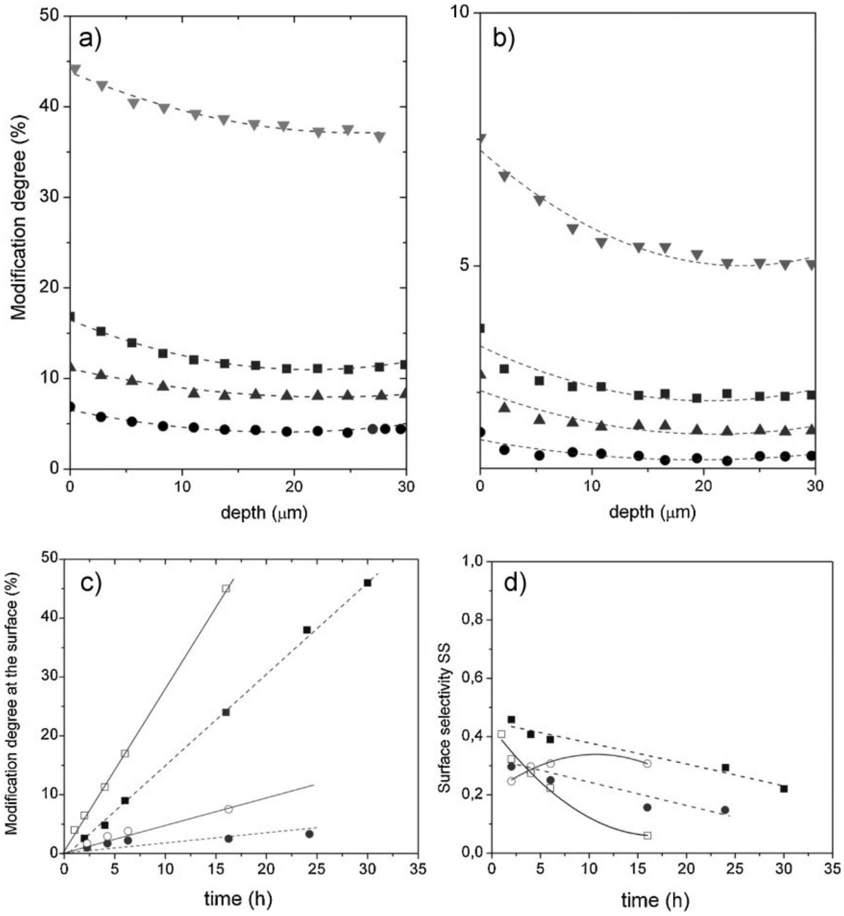

Figure 7. Evolution of depth profiles with time, (●) 2 h, (▲) 4 h, (■) 6 h and (▼) 16 h of PVC films modified in H_2O/DMF 1:4 with (a) 4-fluorothiophenol at 60 °C, (b) pentafluorothiophenol at 60 °C, (c) degree of modification at the surface of PVC films and (d) evolution of surface selectivity with reaction time for PVC films modified in 1:4 H_2O/DMF 4-fluorothiophenol at 45 °C (■) and 60 °C (□) and with pentafluorothiophenol at 45 °C (●) and 60 °C (○) as a function of time. Lines are guides for the eyes.

we observe lower surface selectivities at the highest temperature, which decrease more rapidly with reaction time. A second result deduced from Figure 7d is the fact that SS of PVC5F at 60 °C slightly increases with reaction time becoming more surface selective. This is due to the steric hindrance of the relatively bulky modifier present at the surface that decrease its diffusion coefficient through the polymer film with conversion.

Dependence of Modification Profile and Surface Selectivity on the Reaction Medium

A third parameter that strongly influences both modification degree and surface selectivity is the reaction medium in which a polymer film is chemically modified. It can be expected to be of paramount importance in the final distribution of modifier groups within the polymer film. The use of a swelling/non-swelling mixture as a reaction medium implies that the polymer film is in a swollen state during the reaction but does not solve. In this situation, the concentration of the swelling solvent in relation to the non-swelling solvent is very relevant with respect to the final selectivity of the reaction towards the surface. Reaction mixtures with high content of polymer solvent will lead to nearly homogeneously modified films, whereas reaction mixtures with higher concentration of non-solvent gives rise to polymer films modified selectively at the surface. It also leads to higher selectivities towards the surface but lower degrees of modification.

Depth profiles of modified PVC films with 4-fluorothiophenol and pentafluorothiophenol at 60 °C in H_2O/DMF 1:2 are depicted in Figure 8a and b. As could be expected the poorer the solvent quality the higher the SS and the lower the amount of fluoride aromatic units detected at the polymer surface. This is due to the lower mobility of reactive species and functional groups in the less swollen films. In addition, the highest degree of modification reached in the highest swelling solvent is approximately 50% what is in agreement with the value found for PVC modified in homogeneous solution with this compound. In Figure 8c the evolution of of the surface selectivity with reaction time of PVC films modified with, 4-fluorothiophenol and pentafluorothiophenol at 60 °C in different H_2O/DMF mixtures is shown. From these curves, it is clear that lower selectivity towards the surface is observed for the reaction mixture with a higher proportion of DMF (H_2O/DMF 1:4) but when the reaction is carried out in a bad reaction medium (H_2O/DMF 1:2) higher SS is reached. These results can be explained on the basis of swelling behavior of PVC films in solvent/non-solvent mixtures. After immersing the film into the reaction solution the first step is the swelling of the polymer film by the reaction medium. Reaction mixtures with very low concentration of polymer solvent lead to very low swelling degrees of the polymer film. Therefore the reaction it is mainly restricted to regions near the surface where the modifier is found. However, the situation is completely different in reaction mixtures with larger concentration of polymer solvent where the polymer film reaches high swelling degrees. It opens the structure facilitating the diffusion of the modifiers through the polymer starting the

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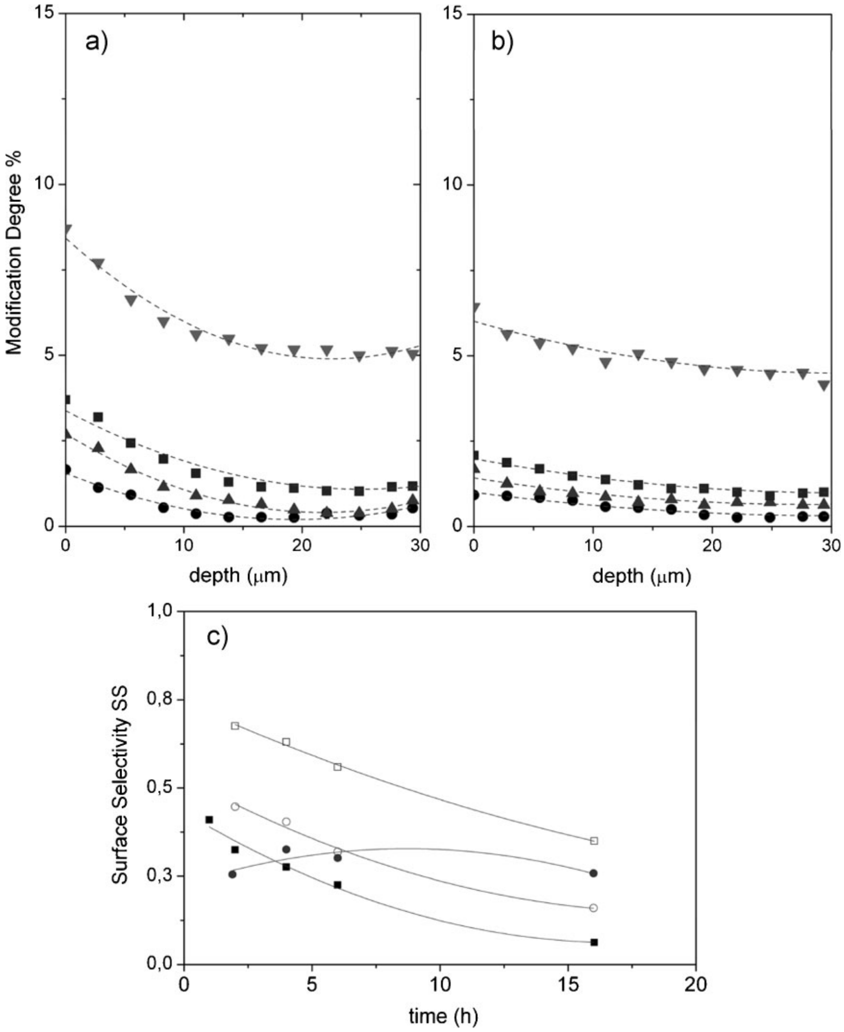

Figure 8. Evolution of depth profiles with time for modification of PVC films at 60 °C in H_2O/DMF 1:2, with (a) 4-fluoro thiophenol, and (b) penta fluoro thiophenol at (●) 2 h, (▲) 4 h, (■) 6 h and (▼) 16 h and (c) surface selectivity as a function of reaction time for PVC modified with: 4-fluorothiophenol in H_2O/DMF 1:2 (□), in H_2O/DMF 1:4 (■) and pentafluorothiophenol in H_2O/DMF 1:2 (○) and in H_2O/DMF 1:4 (●) at 60 °C. Lines are guides for the eyes.

reaction simultaneously in all the film leading to a more or less homogeneous modification. Remarkably, in PVC films modified with pentafluorothiophenol in poorly swelling reaction media (H_2O/DMF 1:2) selectivity towards the surface decrease as a function of time leading to nearly homogeneously modified films with SS values near zero at the largest reaction times studied while better solvents (H_2O/DMF 1:4) and/or higher reaction temperatures (Figure 8) lead to an inversion of this tendency; surface selectivity increases with reaction time reaching a almost constant value at reaction times >10 h. On one side, in the poorly swelling reaction medium the unfavorable reaction conditions, low reactivity of the modifier and low swelling degree favors a good distribution of the modifier within the PVC film prior to the reaction itself leading to SS that decrease with reaction time. However, when the reaction takes place in good polymer swelling mixture, the balance between the favorable reaction conditions that increase the diffusion coefficient of the modifier and its low reactivity are responsible of the very noticeable change in SS. Furthermore, it has to be taken into account the steric hindrance due to the bulky aromatic groups incorporated to the polymer chain that hinder the transport of the modifier itself to the inner layers of the polymer film especially at the largest reaction times.

Conclusion

In this work it has been shown that the surface of PVC films can be successfully modified with 4-fluorothiophenol, 3,4-difluorothiophenol and pentafluorothiophenol in a controlled way by wet chemical reactions in the appropriate solvent/non-solvent reaction medium and reaction temperature. We have shown that Raman microscopy is an excellent technique to analyze wet-chemically modified polymer films. It can be used in the confocal mode to record depth profiles, which allows the determination of the distribution of modified groups within samples. By depth profiling of modified PVC laminates it has been shown that the reactions have taken place preferentially at the surface and it allowed us to determine the gradient of modification all the way along the PVC films.

In conclusion, the use of modifiers with very different reactivity towards a nucleophilic substitution reaction and size highlight the importance of the relationship between the modifier reaction constant and its diffusion constant through the swelled polymer film with respect to the selectivity towards the surface and surface modification degree. In addition, PVC modified with 4-fluorothiophenol seems to be very attractive (high degrees of modification at the surface and SS > 0.6) for future applications in gas separation membranes where it is well known that the introduction of bulky side groups brings considerable increments in the diffusion coefficients. At this moment, experiments are underway to further evaluate the diffusion properties of these selectively surface modified PVC films in comparison to homogeneously modified PVC.[36]

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