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Wetchemical surface modification of plasticized PVC. Characterization by FTIR-ATR and Raman microscopy

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Abstract

The chemical modification of plasticized PVC films with amino thiophenol in mixtures of DMF/H_20 has been studied. The degree of modification and the distribution of modified groups within the films were determined using Raman spectroscopy and FTIR-ATR. The amounts of plasticizer (bis-2-ethylhexyl phtalate, DOP) bleached out during the reaction and the amount of dimethylformamide (DMF) penetrated into the film were analysed in control reactions without the reactant using ^1H NMR spectroscopy and Raman spectroscopy.

Reaction kinetics and surface selectivity of the modification reaction were compared with the corresponding reactions of PVC films without plasticizer.

Keywords: Plasticized PVC; Wet-chemical surface treatment; Confocal Raman spectroscopy

1. Introduction

The surface properties of polymeric materials are important to many of their applications. These properties include adhesive and barrier characteristics, chemical resistance and physical corrosion. A desired polymer surface sometimes cannot be obtained from the material itself but through modification. Modification of a polymer surface can be achieved by means of various chemical or physical processes [1–3]. Of special interest are wet-chemical treatments of films [4] because they present the best method to produce well-defined and reproducible products.

In previous work it has been shown that PVC films can be modified and functionalised at the surface via nucleophilic substitution of chlorine atoms by wet-chemical treatments using mixtures of solvents and non-solvents for the polymer [5]. The solvent tends to expand the chains, facilitating in this way the penetration of the reactant into the polymer chains and the reaction itself. The proportion of solvent and non-solvent greatly influences the degree of modification achievable. Further parameters which allow to control the modification, the distribution of the modified groups and the surface selectivity of the reaction are the reaction time and temperature.

In many applications, however, it is not pure PVC from which an article is prepared but PVC with an important amount of plasticizers and stabilizers. These additives change the flexibility of the polymer chains and will therefore have a strong influence on the reactivity of the surface towards modification reactions.

In this work we study possibilities to modify surfaces of plasticized PVC films by wet-chemical modification methods and compare the results with those obtained on non-plasticized PVC films.

2. Experimental Part

2.1. Film preparation

The samples of plasticized PVC have been prepared using a homogeneous mixture of PVC/DOP (50% weight). The mixture was degassed and samples of 4 g were processed in a hot-plate press at 170 °C and 50 bars during 90 s.

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2.2. Film modification

In order to allow the film to react on both sides and avoid folding or contact with the reactor wall, plasticized PVC films with dimensions 60 mm × 20 mm and a thickness of about 50 μm were clamped in teflon frames. The frames were immersed in a 0.5 molar solution of amino thiophenol. In order to follow the kinetics of the reaction, samples were taken out from the solution at different time intervals, washed with water, extracted for 24 h in ether and dried.

2.3. Confocal Raman microspectroscopy

Raman spectra were recorded on a Renishaw Ramascope 2000 spectrometer using the 632.8 nm line of a He–Ne laser. This instrument was equipped with a Peltier-cooled charge-coupled device (CCD) detector, a holographic grating (1800 grooves/mm), and a Raman holographic edge filter, which prevented the backscattered laser radiation from entering the spectrograph. The stigmatic single spectrograph was attached to a Leica microscope. The Ramascope was set up in the confocal mode with a 100 × short-working-length objective (numerical aperture (NA) value of 0.95), a slit width of about 15 μm, and a CCD of 576 × 384 pixels (pixel size 22 μm). The long axis (576 pixels) defines the spectral dimension, and the short axis describes the height of the image. The arrangement of the CCD and the slit acted as a synthetic confocal aperture. The depth resolution of the confocal arrangement in air has previously been checked, using a silica sample as a reference material and has been determined as 4.5 μm by the full width at half-maximum criterion [7].

A depth profile of a sample was obtained by focussing the microscope stepwise (2 μm steps) through the polymer film and recording a spectrum at each step. For apparent penetration depths of up to 20 μm, accumulation times (t) per spectrum (window from 1200–1750 cm^{-1}) were usually $t = 3$ min. Greater depths required $t = 5–10$ *min* to obtain adequate signal to noise ratio. When different accumulation times were used for recording the different spectra of a set, scattering intensities were normalized, using the appropriate accumulation time.

2.4. NMR spectra

Spectra were recorded at 80 °C on a 200 MHz XL Varian spectrometer operating at 200 MHz using 5% solutions in deuterated dimethyl sulfoxide.

2.5. ATR measurements

Spectra were recorded at ambient temperature on a Spectrum One FTIR spectrometer of Perkin Elmer equipped with an internal reflection element of diamond using an accumulation of 4 runs and the same pressure of the crystal on the surface in each sample.

3. Results and discussion

When plasticised films are the subject of a wet-chemical modification reaction the presence of plasticizer can be expected to have great influence in the reaction kinetics, distribution of the modified groups in the film and surface selectivity. A problem one has to face is the fact that the plasticizer concentration in the polymer will not be constant during the reaction as it is extracted by the solvent/ non-solvent mixture that enters the system.

Therefore, before studying the influence of the plasticizer on the modification reaction itself, the kinetics of plasticiser and solvent diffusion are determined.

3.1. Control reaction without reactant

In order to study the plasticizer bleach out and the DMF/H_20 migration into the films, PVC/DOP films are immersed at 60 °C in solutions of DMF/H_20 1:1, 2:1, 3:1 and 4:1 being DMF a solvent of PVC while H_2O is the non-solvent necessary to avoid the solution of the films. After 2, 4, 6, 8 and 24 h samples are withdrawn and analysed by ^1H NMR, and confocal Raman microscopy.

As an example, Fig. 1 shows a NMR spectrum in DMSO (recorded at 80 °C in order to assure complete solution of the whole sample) of a PVC/DOP sample treated for 6 h in DMF/H_2O 3:1. DMF shows signals at 8.05 ppm (1H, s), 2.7 ppm (3H, s) and 2.9 ppm (3H, s), the characteristic peaks of DOP appear at 7.6 (4H, s), at 4.2 ppm (4H, d) and between 1.7 and 0.8 ppm (30H, m). Quantification of DOP and DMF with respect to PVC is performed by integration of the different peaks.

The results of the NMR analysis are used to present the time dependence of the DOP extraction and the swelling by the solvent/non-solvent mixture shown in Fig. 2 for the different reaction mixture used. It can be seen that in all cases the swelling by DMF is very quick and that an equilibrium state is reached after about 3 h. It is remarkable that the DMF content in the films at equilibrium is relatively low. This becomes evident when it is compared with the values found for unplastized PVC films swollen in the same conditions (Table 1). The reason for the huge difference observed is most likely of entropic origin.

On the other hand, the samples loose DOP, a process that is slower than the DMF migration due to the larger size of

Table 1
Content of DMF in PVC films at equilibrium swelling (at 60 °C)

Reaction medium	PVC films without plasticizer		PVC films with plasticizer	
	mol%	Vol%	mol%	Vol%
DMF/H_20 1:1	1.3	2.2	0.7	1.0
DMF/H_20 2:1	8.6	14.0	1.2	1.7
DMF/H_20 3:1	11.4	18.2	1.9	2.7
DMF/H_20 4:1	15.9	24.7	2.3	3.5

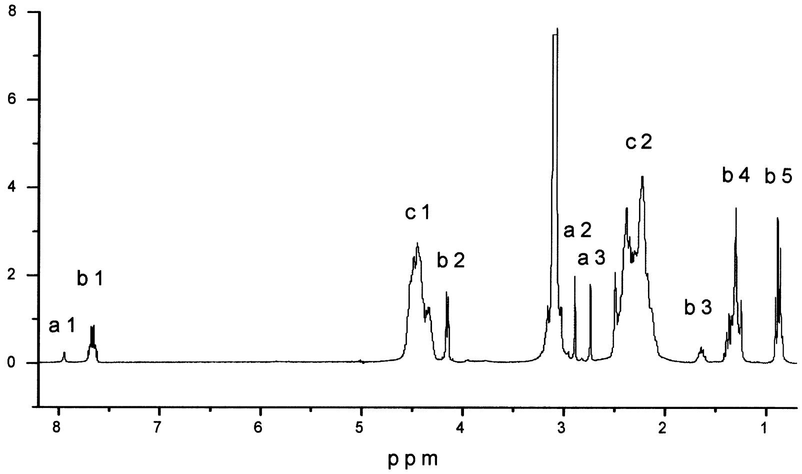

Fig. 1. ^{1}H NMR spectrum of plasticized PVC after 6 h exposition to a solution of DMF/H_20 3:1 at 60 °C. DMF signals ((a1)–(a3)), DOP signals ((b1)–(b5)) and PVC signals ((c1), (c2)).

the plasticiser. The equilibrium state is reached here after 6–10 h, depending on the quality of the solvent used. In no case the plasticizer is completely extracted under the chosen conditions. Depending on the reaction medium between 10 and 25% of the initial amount of DOP remains in the films.

From the NMR analysis the total loss of DOP and the total amount of DMF penetrated into the samples have been determined. However, no information about the distribution of these compounds inside the films could be obtained with this technique. Confocal Raman microscopy has recently been shown to be an excellent mean to measure depth profiles of transparent films with a thickness of up to 80 μm with a depth resolution of about 2 μm [8–12].

In Fig. 3, the Raman spectra of PVC (a), DOP (b) and DMF (c) are presented. For the depth profiling measurements the window from 1800 to 500 cm^{-1} was selected, as it contains characteristic bands of the three compounds, namely the C=O and C–O valence bond at 1725 and 1050 cm^{-1} of DOP, the C=O valence bond at 1660 cm^{-1} of DMF and the C–Cl valence bond at 650 cm^{-1} of PVC. The loss of DOP and the swelling by DMF can be quantified using the ratio of the intensities at 1050, 650, 1660, and 650 cm^{-1}, respectively.

Depth profiles of the samples were measured, with Raman spectra recorded from near the surface down to the center of each film in steps of about 2 μm. As an example, Fig. 4 shows one such set of Raman spectra for a PVC/DOP sample exposed for 4 h to a mixture of DMF/H_2O 3:1 at 60 °C. All spectra are normalized with respect to the C–Cl valence band at 650 cm^{-1} which is considered to be constant during the bleaching out/swelling of DOP and DMF although both compounds exhibit small peaks at this wave length. However, their contributions to the total intensity is negligible in comparison to the huge PVC signal.

All depth profiles measured, independent of the exposition time of the samples, show that no gradients of DOP or DMF exist inside the samples, but that both components are distributed homogeneously in the films. This finding confirms what has been seen in the kinetic study (Fig. 2), that the diffusion of DMF is considerably quicker than that of DOP. The solvent migrates into the film and begins a continuous extraction process of the plasticizer. If the diffusion rate of the solvent would be the slower step of the

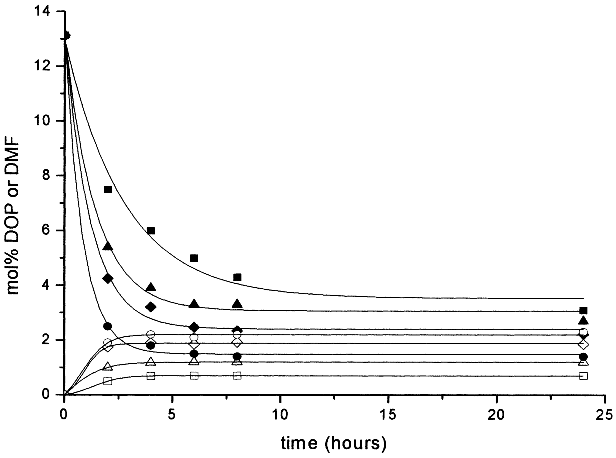

Fig. 2. Kinetics of DOP (solid symbol) loss and swelling with DMF (hollow mark) in different reaction media at 60 °C: DMF/H_20 1:1 (■, □), DMF/H_20 2:1 (▲, △), DMF/H_20 3:1 (◆, ◇) and DMF/H_20 4:1 (●, ○).

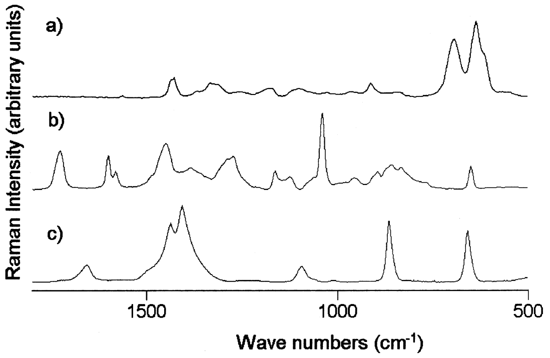

Fig. 3. Raman sprectra of (a) PVC, (b) DOP and (c) DMF.

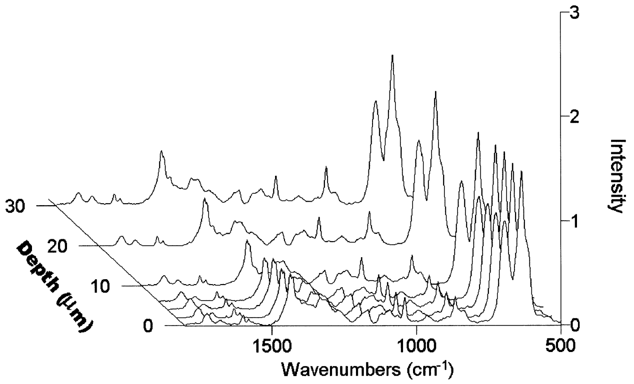

Fig. 4. Series of Raman spectra as a function of depth of a plasticized PVC film after exposition to a solution of DMF/H_20 3:1 for 6 h at 60 °C.

process, concentration gradients of both components would have been expected.

3.2. Modification with amino thiophenol

In order to study the modification reaction of plasticized PVC films with amino thiophenol, films were immersed in solutions of different proportions of DMF and H_20 which contained the reactant. Samples were withdrawn after 2, 4, 6, 8, and 24 h.

IR and Raman spectra of these systems are complex and bands necessary to analyse the modifier content are overlapped. Therefore, before analyzing the films, they were extracted during 24 h in ether in order to eliminate DOP and DMF and simplify the analysis. The films were studied using FTIR-ATR and Raman microscopy.

3.2.1. FTIR-ATR

FTIR-ATR is a very surface selective technique [13,14] and allows to study the modification and its kinetics in the outermost 1–2 μm of the films. An example, a series of FTIR-ATR spectra of a PVC film modified in DMF/H_20 3: 1 at 60 °C and different reaction times is shown in Fig. 5.

The presence of free amino groups in the polymer is reflected by three characteristic peaks between 3200 and 3500 cm^{-1},(not shown in the figure), which are due to the N–H valence bonds [15]. Additional peaks in the modified polymer can be assigned to the N–H deformation at 1620 cm^{-1}, the aromatic C–C valence bond (1597 cm^{-1} and 1495 cm^{-1}), the C–N valence bond at 1177 cm^{-1} and to the C–H deformation for para-substituted aromatics (826 cm^{-1}). These bands increase with increasing reaction time.

The absolute degree of modification of the film surfaces was obtained from these spectra using a calibration curve recorded on homogeneously modified samples whose modifier content had previously been determined by NMR spectroscopy.

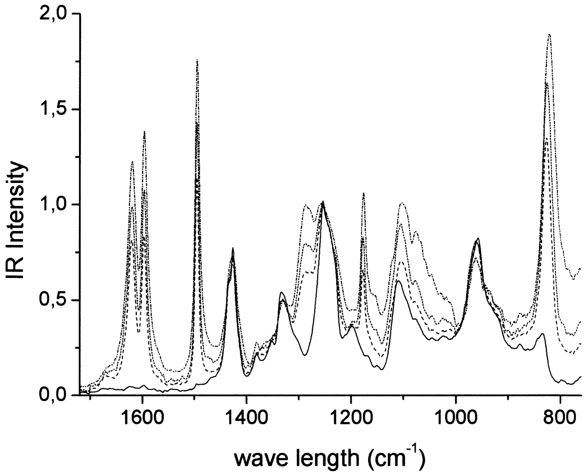

Fig. 5. Evolution of FTIR-ATR spectra at the surface of a plasticized PVC film modified with 4-amino thiophenol for 0 h (solid), 4 h (dash), 8 h (short dash) and 24 h (dash-dot-dot) in DMF/H_20 3:1 at 60 °C and subsequent extraction with ether.

The kinetic of the modification in the different reaction media is shown in Fig. 6. As could be expected the better the solvent quality the faster the reaction and the higher the amount of amino thiophenolate units detected at the polymer surface. This is due to the higher mobility of reactive species and functional groups in the stronger swollen films.

The equilibrium is reached in all cases after about 24 h. The highest degree of modification reached in the highest swelling solvent is approximately 30% what is in agreement with the value found for PVC modified in homogeneous solution with this compound [15]. 30% is generally found to be the limiting degree of substitution whenever this polymer is modified with aromatic thiol compounds carrying functional groups capable to form hydrogen bonds [16]. These lead to a physical crosslinking of the system and avoid mobility and accessibility of further reactant to the remaining chlorine atoms.

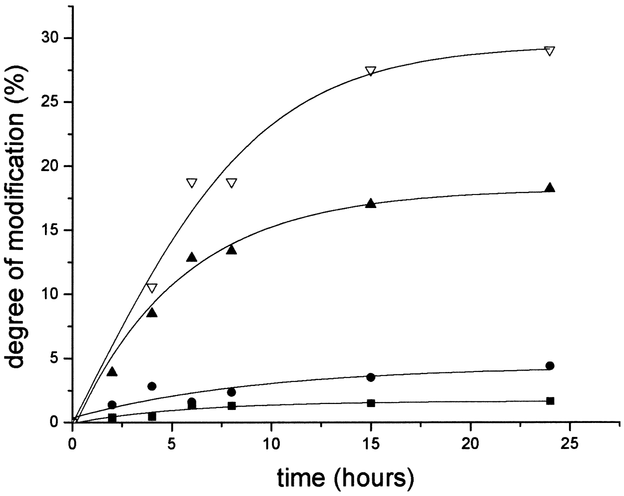

Fig. 6. Kinetics at the surface as determined by FTIR-ATR of the modification with 4-amino thiophenol at 60 °C of a plasticized PVC film in DMF/H_20 1:1 (■), DMF/H_20 2:1 (●), DMF/H_20 3:1 (▲) and DMF/H_20 4:1 (▽).

3.2.2. Raman microscopy

The before-mentioned FTIR-ATR study was useful to gain information about the modification reaction of the outermost 1–2 μm of the films. However, it is also interesting to analyze the interior of the modified samples and see how the plastizicer influences the evolution of the reaction and the distribution of the modified groups. For this purpose a Raman microscope was used. Two different kinds of studies were carried out, one in the non-confocal mode and a second one using the confocal principle. In both cases, the laser light is focused through the objective of the microscope on the surface of the sample and the Raman diffusion emitted from there is collected by the same objective and analyzed in a charge-coupled device (CCD) detector. If the microscope works in the non-confocal mode the slit in front of the detector is completely open and a large area of Pixels in the detector is used. Under these conditions no resolution in depth can be achieved and the spectrum obtained gives a mean value of the modification across a thickness of about 25 μm.

On the other hand, one can also limit the analysis to a few pixels of the CCD detector and open the slit in front of the detector only to 15 μm. This is the so-called confocal principle which allows to discriminate spectra at different depths, because the contribution of Raman emission of out of focus planes is efficiently blocked out. The depth resolution of our instrument in the confocal mode has been determined to be 4.5 μm.

The evolution of the Raman spectra recorded in non-confocal mode at the surface of a PVC film modified at 60 °C with amino thiophenol in DMF/H_20 4:1 is shown in Fig. 7. The Raman spectra show bands at the same wave numbers than the corresponding IR spectra (Fig. 5), being the main difference the intensities of the signals. In general, strong signals in IR (for example at 1620 and 1500 cm^{-1}) have weak Raman activity and vice versa (1100 cm^{-1}). As in the FTIR-ATR case also here absolute degrees of modification were obtained from the spectra using a calibration curve recorded on homogeneously modified PVC films.

The kinetic of the modification in the different reaction media is shown in Fig. 8. Qualitatively, the curves resemble those obtained by FTIR-ATR, that is to say that higher reaction rates and higher degrees of modification are observed for the solvents with a higher proportion of DMF. However, there are two important differences. While the modification at the surface had reached an equilibrium state after about 24 h (Fig. 6) the reaction in the interior of the films is considerably slower. The reason for this finding lies obviously in the diffusion process of the reactant. This becomes especially evident in the case of the solvent mixtures DMF/H_20 1:1 and 2:1 where the conversions after 24 h have hardly reached 20% of the equilibrium conversion at the surface as determined by FTIR-ATR. On the other hand, when the reaction is carried out in a better solvent (DMF/H_20 3:1 and 4:1) the reaction rate is faster and conversions of about 60% are reached after 24 h.

The equilibrium degree of modification in these cases can be estimated by curve fitting of the Raman data points. This treatment yields a limiting degree of modification of 16.8% when a solvent mixture of DMF/H_20 3:1 is used for the reaction. This value corresponds within the experimental error to the degree of modification of 18.2% found by FTIR-ATR at the film surface, that is to say that after a sufficiently long reaction time a homogeneously modified film will be obtained.

On the other hand, when the reaction is carried out in DMF/H_20 4:1, one observes a large discrepancy between the degree of modification of 29.8% as found at the surface and 19.6% as estimated using the curve fit of the Raman data points. Obviously, in this case, the transport of

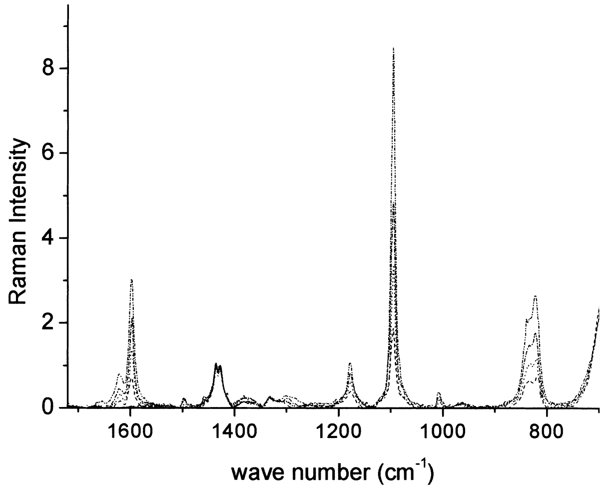

Fig. 7. Evolution of Raman spectra at the surface (non-confocal mode) of a plasticized PVC film modified with 4-amino thiophenol for 0 h (solid), 2 h (dash), 4 h (dot), 8 h (dash dot) and 24 h (dash-dot-dot) in DMF/H_20 3:1 at 60 °C and subsequent extraction with ether.

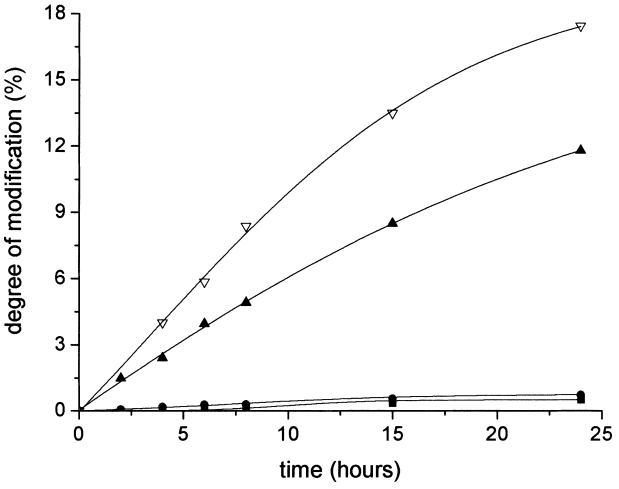

Fig. 8. Kinetics at the surface as determined by Raman microscopy (non-confocal mode) of the modification with 4-amino thiophenol at 60 °C of a plasticized PVC film in DMF/H_20 1:1 (■), DMF/H_20 2:1 (●), DMF/H_20 3:1 (▲) and DMF/H_20 4:1 (▽).

aminothiophenol in the interior of the film is efficiently hindered. It is likely that this strong reduction of the diffusion coefficient of the reactant is due to the formation of a physical network formed by hydrogen bridges between amino group carrying polymer chains. This network becomes sufficiently dense when a critical amount of amino groups is exceeded. As a consequence, a pronounced gradient of modifier content from the surface to the inner of the film is built up.

Gradients across the thickness of the film can be measured using the Raman microscope in the confocal mode as has been described elsewhere [6]. In order to construct these depth profiles Raman spectra are recorded from near the surface down to the center of each film in steps of 1 μm. As an example, Fig. 9 shows one such set of Raman spectra for a plasticized PVC sample modified in DMF/H_2O 3:1 at 60 °C after a reaction time of 6 h and subsequent extraction with ether. The raw data have been normalized with respect to the reference band at 1425 cm^{-1} (which corresponds to the C–H bending mode of the unmodified polymer main chain) in order to avoid the effect of intensity variations near the surfaces, where the scattering volume is not entirely confined within the film.

Relative degrees of modification of the modified polymer were obtained from these spectra by taking the ratio of integrated peak areas [$I(1050\ cm^{-1})/I(1425\ cm^{-1})$]. Absolute values were calculated using a calibration curve recorded on homogeneously modified samples, whose degree of modification had previously been determined by ^1H NMR spectroscopy. One of the effects of polymer refractive index on measured depth profiles has been shown to be an incorrect apparent thickness scale [17,18]. We have recently 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 [19]. This scale expansion has been carried out before constructing the depth profiles shown in Fig. 10.

The shape of the curve demonstrates clearly that, in this case, substitution of chlorine atoms has taken place preferentially at the surface of the laminate while in the interior the amount of amino groups is only about 10% of its value at the surface. The depth profile shown has a similar shape than those found in modification reactions of non-plasticized PVC films [6] and can be fitted with a Gaussian curve indicating a Fickian diffusion process of the reactant.

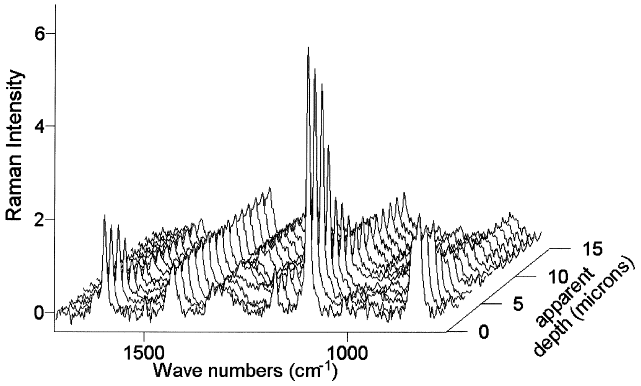

Fig. 9. Series of Raman spectra as a function of the apparent depth of a plasticized PVC film modified for 6 h with 4-amino thiophenol in a solution of DMF/H_20 3:1 at 60 °C and subsequent extraction with ether.

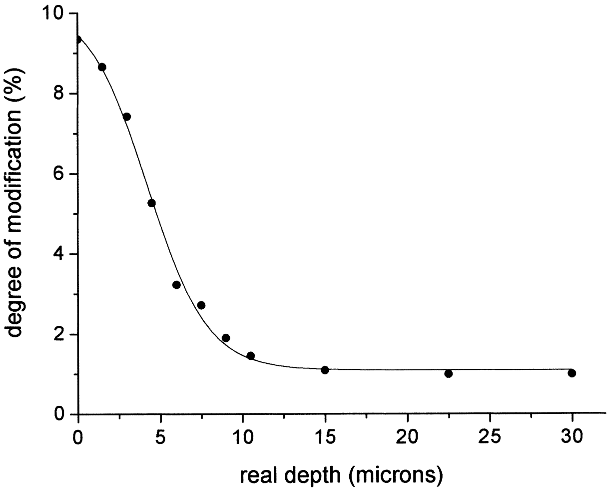

Fig. 10. Depth profile of a plasticized PVC film modified for 6 h with 4-amino thiophenol in a solution of DMF/H_20 3:1 at 60 °C.

It is instructive to compare the degree of modification at the surface obtained from the Raman measurements and that determined by FTIR-ATR. While with FTIR-ATR a value of 12.8% had been found (Fig. 6), the Raman microscope gives only 9.3% in the confocal mode and even less, 3.9%, in the non-confocal mode (Fig. 8). The reason for these large discrepancies is the different depth resolution of the three techniques. FTIR-ATR is the most surface selective one which analyses the outer 1–2 μm of the film. With the confocal Raman microscope used here the depth resolution had been determined to be 4.5 μm. The first spectrum recorded when focussing on the surface does therefore also contain contributions from layers deeper inside the film that are less modified and reduce thereby the true value at the surface. Finally, when measuring in the non-confocal mode, where the resolution curve is extremely flat over a large depth range being the resolution more than 25 μm the obtained spectrum at the surface can more correctly be considered as a quasi-transmission spectrum giving a mean values across the film.

4. Conclusions

It was shown that plasticized PVC can be modified with aminothiophenol moieties in a similar way than non-plasticized films. A concentration gradient of modifier groups is established across the films. The surface selectivity and overall degree of modification depends essentially on the solvent quality and reaction time. The modified films contain a reduced but homogeneously distributed amount of plasticizer what is due to its partial extraction by the reaction medium.

The combination of FTIR-ATR and Raman microscopy in the confocal and non-confocal mode are an excellent mean to elucidate the structure and distribution of modified groups within transparent polymer films.

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References

[1] Clark DT, Feast WJ. Polymer surfaces. Chichester: Wiley; 1978.
[2] Garbassi F, Morra M, Occhiello E. Polymer surfaces. Chichester: Wiley; 1994.
[3] Chan CM. Polymer surface modification and characterization. Munich: Hanser Publishers; 1993.
[4] Mittal KL, Lee KW. Polymer surfaces and interfaces: characterization modification and application. Utrecht: VSP; 1997.
[5] Sacristán J, Mijangos C, Reinecke H. Polymer 2000;41:5577.
[6] Sacristán J, Mijangos C, Spells S, Yarwood J, Reinecke H. Macromolecules 2000;33:6134.
[7] Tabaksblat R, Meier J, Kip BJ. Appl Spectrosc 1992;46:60.
[8] Barbillat J, Dhamelincoourt P, Delhaye M, Da Silva E. J Raman Spectrosc 1994;25:3.
[9] Huong PV. Vibr Spectrosc 1996;11:17.
[10] Hajatdoost S, Olsthoorn M, Yarwood J. Appl Spectrosc 1997;51: 1784.
[11] Sacristán J, Mijangos C, Spells S, Yarwood J, Reinecke H. Macromol Rapid Commun 2000;21:894.
[12] Sacristán J, Mijangos C, Spells S, Yarwood J, Reinecke H. Macromol Chem Phys 2002;203:678.
[13] Harrick NS. Internal Reflection Spectroscopy. New York: Wiley; 1967.
[14] Ohta K, Iwamoto R. Appl Spectrosc 1985;39:418.
[15] Reinecke H, Mijangos C. Polymer 1997;38:2291.
[16] Herrero M, Tiemblo P, Reyes-Labarta JA, Mijangos C, Reinecke H. Polymer 2002;43:2631.
[17] Everall N. Appl Spectrosc 2000;54:773.
[18] Everall N. Appl Spectrosc 2000;54:1515.
[19] Reinecke H, Spells S, Sacristan J, Mijangos C, Yarwood J. J Appl Spectrosc 2001;55:1660.