

Surface modification of PVC films in solvent–non-solvent mixtures

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Abstract

Appropriate reaction conditions for the selective surface modification of PVC films with sodium azide and amino thiophenol were investigated. Whilst the use of a phase-transfer agent makes it possible for the nucleophilic substitution reaction to occur, the morphology of the film is changed by the reaction, leading to a loss in both surface smoothness and transparency of the film. On the other hand, performing the reaction in mixtures of a good and a non-solvent for PVC modification takes place in a controlled manner and the film remains both smooth and transparent. The degree of modification can be varied as a function of time, of temperature and the proportion solvent to non-solvent used in the reaction. The determination of the overall degree of modification of films of different thickness allows one to draw conclusions about the surface selectivity of the reaction. According to this study, the reaction with sodium azide occurs homogeneously through the film, whilst the use of amino thiophenol leads to a polymer film which is preferentially modified at the surface. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(vinyl chloride); Films; Surface modification

1. Introduction

The surface properties of polymeric materials are important in many of their applications, and include adhesive and barrier properties, chemical resistance and physical corrosion. A desired polymer surface sometimes cannot be obtained from the polymer alone, and modification of the material is required. Modification of a polymer surface can be achieved by means of various chemical or physical processes, the most common techniques including plasma-ion beam treatment, electric discharge, surface grafting, chemical reaction, vapour deposition of metals, and flame treatment [1–3].

It is well known that PVC can be chemically modified and functionalized in solution and in the melt using thiol compounds [4–9], and these reactions are particularly selective when aromatic thiols are used [10–13]. Other nucleophiles such as the azide group can also be introduced into PVC chains without side reactions, when apolar solvents with a high dielectric constant like DMSO or DMF are used [14].

Attempts have also been made to modify PVC powder in aqueous suspensions [15], a very attractive procedure from an economic point of view. Although it has been demonstrated that no modification of the polymer takes

place when only water is used as the solvent, in the presence of small quantities of a phase-transfer catalyst a degree of modification between 10–30% can be achieved. Alternatively, a good solvent for PVC can be added to the water suspension to yield highly modified polymers, as described by Levin et al. [16].

In the present paper we report the applicability of the aforementioned reaction conditions on the modification of PVC films with sodium azide and aminothiophenol, respectively. It is particularly interesting to examine whether it is possible to find conditions which favour surface selective reactions, i.e. modification of the polymer which is limited to the surface of the film whilst the bulk remains unreacted.

2. Experimental

Commercial bulk polymerized PVC was obtained from Rio Rodano Industries, Spain. The average molecular weights determined by GPC were $M_w = 112\,000$ g/mol and $M_n = 48\,000$ g/mol.

The tacticity measured by ^{13}C NMR was syndio = 30.6%, hetero = 49.8% and iso = 19.6%.

For the modification reactions, PVC films of different thickness (20–80 μm) were prepared by casting from THF solutions. The films were extracted in a Soxhlet apparatus during 24 h using diethyl ether, and then dried under reduced pressure for a further 2 h.

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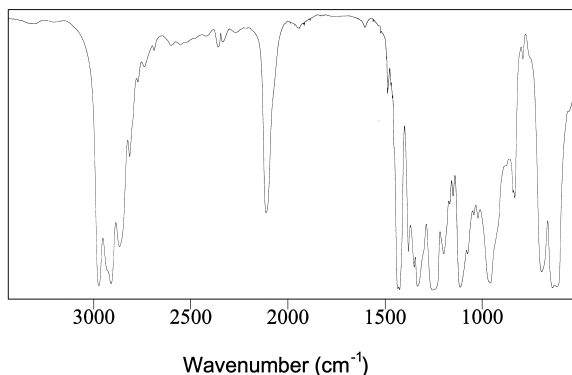


Fig. 1. IR-spectrum of a PVC laminate modified with NaN_3 in H_2O using a PTC.

The modification agent sodium azide was purchased from Fluka and used without further purification. Amino-thiophenol was purchased from Acros and was distilled under reduced pressure prior to use.

Modification of the films: in order to allow the film to react on both sides and avoid folding or contact with the reactor wall, PVC films with dimensions $60 \text{ mm} \times 20 \text{ mm}$ and different thickness were clamped in Teflon frames. The frames were immersed in a 0.5 M solution of the respective modification agents. In order to follow the kinetics of the reaction, smaller pieces ($10 \text{ mm} \times 10 \text{ mm}$) of the film were cut at different time intervals, washed with water, extracted for 24 h in ether and dried. The reproducibility of the reaction was tested by performing each reaction five times under the same conditions.

The degree of swelling H of the samples during the reaction is determined by weighing the samples before (w_b) and after (w_a) the reaction. H is calculated according to: $H = w_a/w_b$. Thereby, the films are also checked for

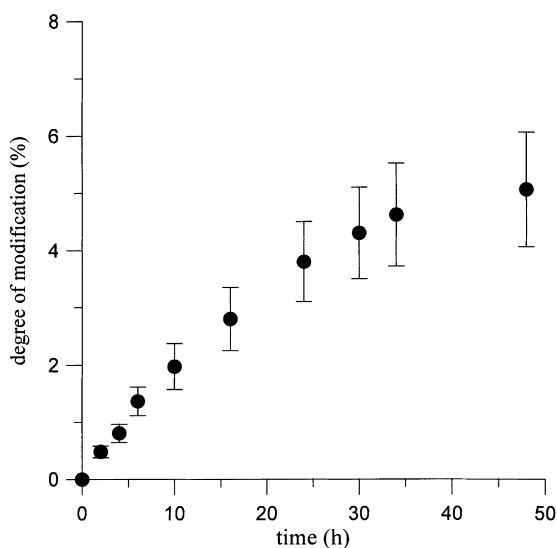


Fig. 2. Kinetics of the modification of PVC films with NaN_3 in H_2O using a PTC.

possible weight loss through partial solubility of the polymer in the reaction medium.

Analysis of the modified films was performed by infrared spectroscopy on a Nicolet 520 FT-IR spectrometer. In order to obtain the relative degree of modification, the following absorption ratios (areas) were used:

PVC modified with sodium azide (PVC-N3): $\nu(\text{N}_3)$ -azide stretching vibration, at 2110 cm^{-1} vs. $\nu(\text{C-H})$ at 2930 cm^{-1} ,

PVC modified with amino thiophenol (PVC- ϕ -NH₂): $\nu(\text{N-H})$ between $3500\text{--}3200 \text{ cm}^{-1}$ vs $\nu(\text{C-H})$ at 2930 cm^{-1} .

The error determining the relative degree of modification using band ratios is less than 0.5% as we deal with an internal reference. In order to obtain absolute values for the modification of the films, calibration curves were calculated from the IR spectra of PVC films prepared from polymers homogeneously modified in solution, with degrees of modification previously determined by elemental analysis in the case of PVC-N3, and ^1H NMR in the case of PVC- ϕ -NH₂. The relation between band ratios as calculated for eight samples as a function of their degree of modification is linear, with regression coefficients of 0.9935 (PVC-N3) and 0.992 (PVC- ϕ -NH₂), respectively, indicating the accuracy of the method.

Proton NMR spectra were recorded at 25°C in 5% (w/v) DMSO-d solutions with a Varian Gemini 200 MHz under standard conditions.

3. Results and discussion

A basic problem for the selective modification of polymeric surfaces is the choice of the appropriate reaction conditions and, in particular, the reaction medium. On the one hand, the polymer must not dissolve or change its morphology by interaction with the solvent, and on the other, the functional groups of both the polymer and the modification agent must be able to achieve intimate contact. It is known [15] that PVC cannot react with nucleophiles in pure water because of the large polarity differences between water and the polymer. One possibility to overcome this problem is the use of a phase-transfer catalyst.

3.1. Phase-transfer catalyst (PTC)

The azide is an interesting functional group which can be converted into an amine by reduction or form radicals when heated, it is a strong nucleophile, and appears to be an appropriate surface modification agent for PVC, with the added advantage of its strong IR activity useful for monitoring purposes. In order to study the influence of a phase-transfer catalyst on the modification reaction and the resulting surface quality, PVC films were reacted with sodium azide in H_2O in the presence of tetrabutylammonium bromide. The degree of modification of a film

Table 1
Conditions for the reaction of PVC with sodium azide

H ₂ O/DMF ratio	Temperature (°C)	Reaction time (h)	Film thickness (μm)	Degree of modification (%)
1:2	45	200	25, 50	No reaction
1:2	60	200	25, 50	No reaction
1:3	30	100	25, 50	0.1
1:3	45	200	25, 50	0.5
1:4	30	170	25, 50	0.5
1:4	45	275	25, 35, 50, 60	1.3
1:4	60	70	50	3.7
1:6	30	150	50	1.2
1:6	45	320	10, 25, 50	2.0
1:6	52	220	50	6.1
1:6	60	48	50	5.3
1:7	45	160	50	5.2
1:8	30	150	20, 50	2.0
1:8	45	200	25, 50	6.4
1:8	60	5	25, 50	Film dissolves
1:9	30	1	25, 50	Film dissolves

of 60 μm thickness was determined as a function of reaction time and at different temperatures, as indicated in the Section 2.

The analysis of the film by IR spectroscopy (Fig. 1) clearly shows that a modification reaction takes place, as indicated by the variation of the characteristic band of the azide group at 2110 cm⁻¹. The conversion of the modified film was determined by measuring the area of the azide band at 2110 cm⁻¹ with respect to that of the C–H valence bond at 2930 cm⁻¹. Absolute values for the degree of modification were obtained using a calibration curve recorded on samples whose degree of modification had been determined by elemental analysis.

Measuring the kinetics of the modification shows that the reaction has finished after about 50 h (Fig. 2). A degree of modification of up to 6% was detected under the given reaction conditions. However, the films lose both their

transparency and the smoothness of their surfaces as is evidenced by its aspect and gritty feel. This is most likely due to partial crystallization of the polymer. Furthermore it can be observed that chlorine substitution is strongly inhomogeneous, as indicated by the fact that deviations from a mean value of about 20% are found when reproducing the reaction. Strong inhomogeneities are typical for chemical solid–liquid phase reactions.

3.2. Solvent/non-solvent mixture

An alternative to the use of a phase-transfer catalysts might be the addition of a good solvent to the PVC/water system. In order to investigate this effect, films were reacted in different proportions of water/dimethyl formamide and at different temperatures (Table 1).

The results from the IR analysis show that PVC films do

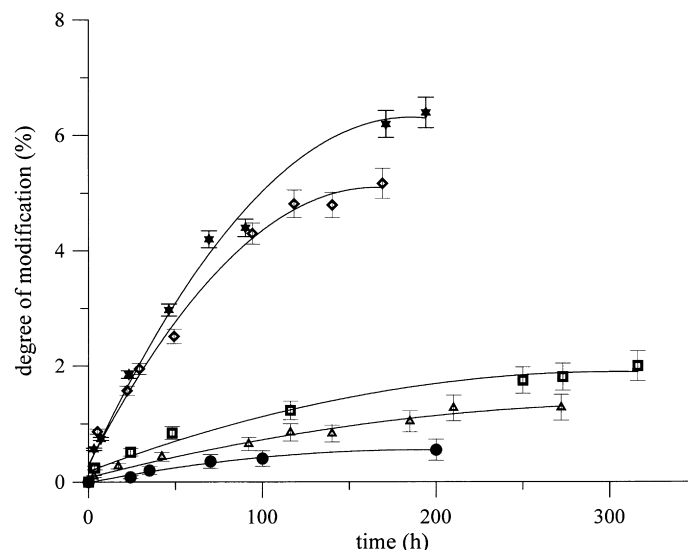


Fig. 3. Kinetics of the modification of PVC films with NaN₃ at 45°C in different H₂O/DMF mixtures: 1:3 (●); 1:4 (△); 1:6 (□); 1:7 (◇); 1:8 (★).

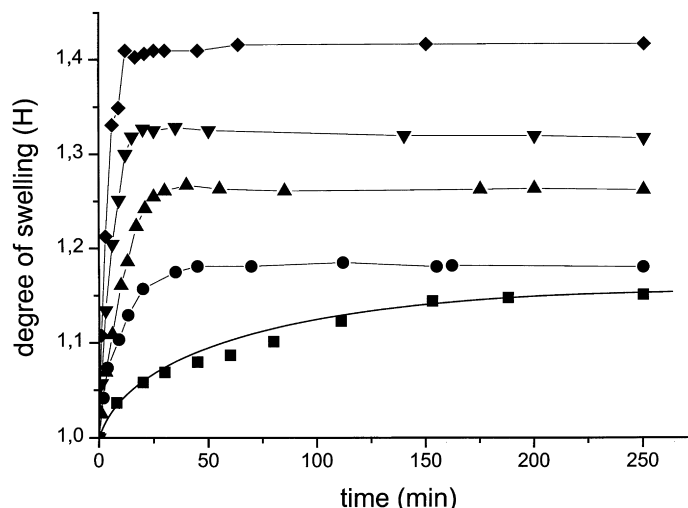


Fig. 4. Swelling of PVC films (50 μm) in different $\text{H}_2\text{O}/\text{DMF}$ mixtures at 45°C : 1:3(■); 1:4(●); 1:5(▲); 1:6(▼); 1:7(◆).

indeed react with azide groups when an appropriate solvent/non-solvent proportion is chosen. When the percentage of the non-solvent is higher than 33 vol%, no modification of the polymer films takes place, and when the proportion of DMF is increased, a wide range of possible mixtures exists which permit the nucleophilic substitution reaction to take place without unwanted side-reactions or degradation. If the proportion of solvent to non-solvent is further increased, dehydrochlorination is favoured and the surfaces become coloured. Finally, if the reaction medium contains considerably more DMF than water (>90 vol%) the PVC films begin to dissolve.

The important difference to the modification reactions using a phase-transfer catalyst is the fact that in this case the films remain completely transparent and their surface quality appears to be unaffected. Furthermore, the results are reproducible with an error of less than 5%, indicating

that the reaction under these conditions takes place in a homogeneous manner.

Within the appropriate range of solvent mixtures, the degree of modification of the films and the reaction rate strongly depend on the solvent to non-solvent ratio. This is shown in Fig. 3, where the progress of the reactions is illustrated. With an increasing proportion of DMF the substitution reaction occurs faster, and higher ultimate modification levels are achieved. This is due to the swelling of the polymer, which depends on the solvent quality. In non-solvents the interaction between polymer and solvent is almost zero, chain-chain contacts are dominant and the molecules of the modification agents cannot get into close contact with the reactive sites of the polymer. A good solvent tends to expand the chains. In this way the nucleophiles can penetrate the polymer, and modification can take place. The degree of swelling, H , of the films in the different reaction media was measured by weighing the film samples before and after the reaction. The higher the proportion of solvent to non-solvent, the higher the degree of swelling, and thus the maximum degree of modification observed (Fig. 4).

A second parameter which influences the reaction rate and the final degree of modification of the polymer, is the temperature. This is shown in Fig. 5, where the progress of the reaction of three films modified in the same medium but at different temperatures is compared. It is observed that increasing the temperature has a similar effect to that observed by improvement of the solvent quality, that is, the modification reaction is faster and higher ultimate conversions are reached.

Of special interest is the question as to whether chlorine substitution occurs homogeneously within the membrane, or if it is possible to modify the film selectively at the surface. The modification reaction of a polymer film comprises three steps, each with its own reaction rate constant. The first step is the swelling of the polymer film by the reaction medium,

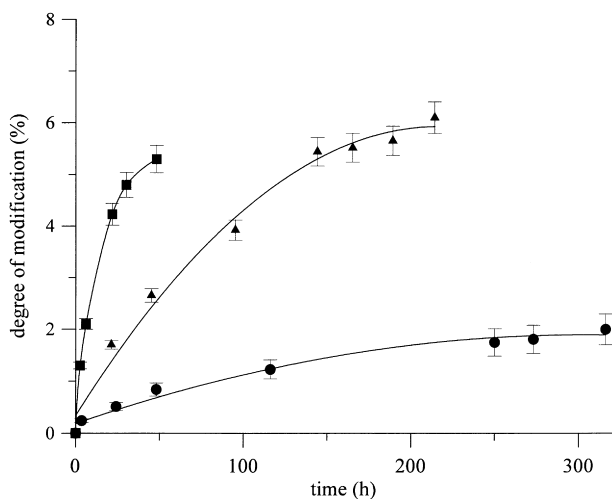


Fig. 5. Kinetics of the modification of PVC films with NaN_3 in $\text{H}_2\text{O}/\text{DMF}$ 1:6 at different temperatures: 45°C (●); 52°C (▲); 60°C (■).

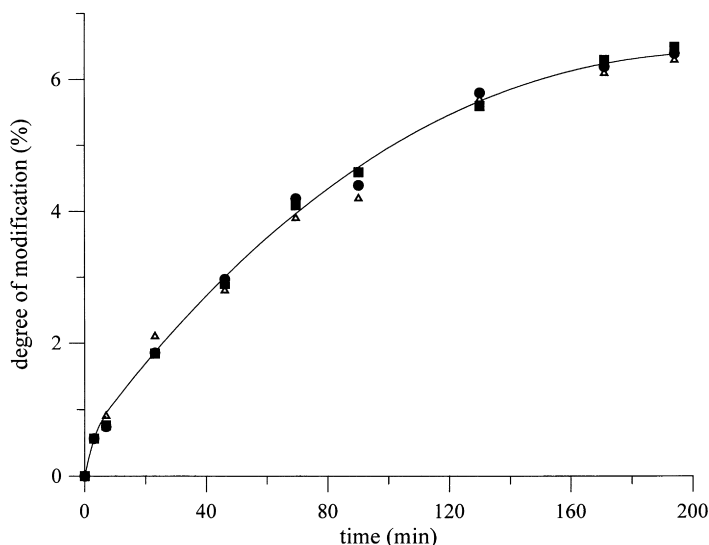


Fig. 6. Kinetics of the modification of PVC films of different thickness with NaN_3 in $\text{H}_2\text{O}/\text{DMF}$ 1:8 at 45°C : $10\ \mu\text{m}$ (■); $25\ \mu\text{m}$ (●); $50\ \mu\text{m}$ (Δ).

which contemplates the diffusion of the solvent into the membrane (k_1), the second step is the transport of the modification agent to the functional groups of the polymer (k_2), and the third step is the reaction itself (k_3). Generally, the swelling of the polymer is the fastest process. As can be observed in Fig. 4, complete swelling of the systems to equilibrium is generally achieved after about 30 min (only in the case of mixture 1:3 does it take 2.5 h). The relation between the rate constants for step two and three conditions the modification reaction of a polymer film to occur either homogeneously through the film or selectively at the surface. If $k_2 > k_3$, the modification agent is distributed throughout the polymer film until the reaction begins and a homogeneously modified film is obtained. On the other hand, if $k_2 < k_3$, membrane modification can be stopped until the agent has completely penetrated the film, and a modification gradient through the film will be observed. The larger the ratio k_3/k_2 , the higher the selectivity of the reaction with respect to the surface.

In order to obtain qualitative information concerning the surface selectivity of the modified films, the reactions were performed with membranes of different thickness. In the case where the membrane is homogeneously modified, the final degree of modification should be independent of thickness, whilst on the other hand, if the reaction takes place only at the surface a thick membrane is expected to exhibit a considerably lower mean degree of modification than a thin one.

The kinetics for reactions of sodium azide with PVC films of different thickness are compared in Fig. 6. The curves show that the final degrees of modification do not vary with thickness, within experimental error. This indicates that the azide groups are homogeneously distributed throughout the film, and that no modification gradient exists. This is possibly due to the small size of the agent, comparable to that of the solvent. Obviously, in this case the rate constant for the diffusion of azide groups is higher than k_3 .

In order to increase the ratio k_3/k_2 facilitating the

Table 2
Conditions for the reaction of PVC with 4-aminothiophenol

$\text{H}_2\text{O}/\text{DMF}$ ratio	Temperature ($^\circ\text{C}$)	Reaction time (h)	Film thickness (μm)	Degree of modification (%)
1:4	30	120, 72	35	1.9
1:4	45	45	30	6
1:4	55	2.5, 2	25, 70	0.9, 0.7
1:4	60	46, 30	40, 60	16, 10
1:5	30	100, 30	20, 50	4.8, 1.8
1:5	40	54	40	16
1:5	45	24, 24, 24	35, 50, 80	19, 17, 11
1:5	50	24	35	21
1:5	60	2, 4.5	55, 70	1.6, 1.2
1:6	30	30	45	2.4
1:6	45	9	50	4.5
1:6	60	1	50	Film dissolves
1:7	30	22.5, 30	50, 60	11.2, 10.4
1:7	45	0.5	50	Film dissolves

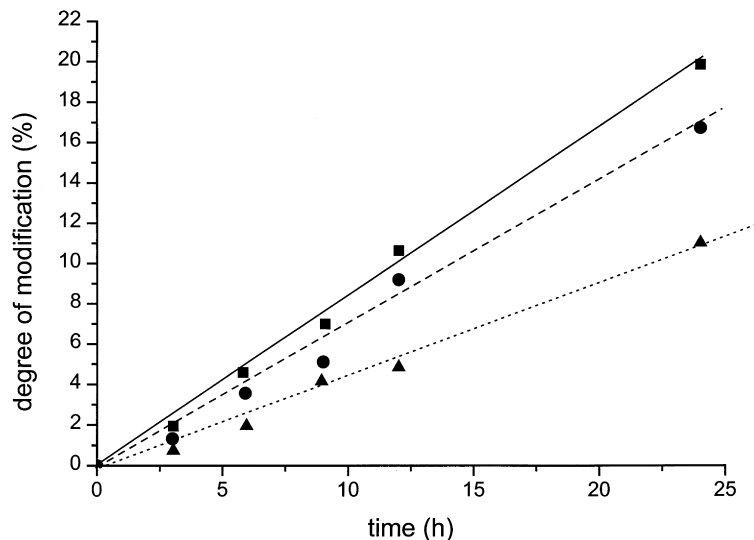


Fig. 7. Kinetics of the modification of PVC films of different thickness with aminothiophenol in H₂O/DMF 1:5 at 45°C: 30 μm (■); 50 μm (●); 80 μm (▲).

substitution reaction (increase of k_3) and hindering the transport of the modification agent in the interior of the PVC film (decrease of k_2), aminothiophenol was chosen, which is known to be both a strong nucleophile and around three times the size of the azide group.

In Table 2 the conditions and results for the modification reactions of PVC films with aminothiophenol at different temperatures and solvent to non-solvent ratios are summarized. As in the case of the system discussed above, the mean degree of modification can be varied over a wide range as a function of the reaction parameters.

Of special interest is the question as to whether the change of reactivity and size of the nucleophile has any influence on the surface selectivity of the reaction. Fig. 7 shows the kinetics of the reaction for films of different thickness. In contrast to the observations for PVC–N3, the course of the reaction depends strongly on film thickness, and the final degree of modification is inversely proportional to this parameter. This is a clear indication that the reaction has taken place selectively at the surface.

Experiments by confocal Raman spectroscopy which are now underway appear to confirm that no gradient exists in the case of modification with azide groups, whereas a gradient is observed in the case of modification with aminothiophenol, confirming the surface-selective character of the process.

4. Conclusion

It has been shown that PVC films can be modified chemically without loss of their transparency and surface smoothness when carrying out the reactions in appropriate mixtures of solvent and non-solvent for the polymer. The surface of the films can be selectively modified in cases where the rate constant of the substitution reaction is higher

than that of the transport process of the modification agent in the interior of the film and the reaction is stopped before the compound is homogeneously distributed in the laminate. From modification of PVC laminates of different thickness with aminothiophenol it can be deduced qualitatively that a gradient of the degree of modification is established.

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