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Systematic optimization of poly(vinyl chloride) surface modification with an aromatic thiol

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Abstract

The efficient covalent functionalization of poly(vinyl chloride) (PVC), which is widely used in medical device manufacture, allows an array of potential property-enhancing surface modifications to be made. To demonstrate a general method of functionalization *via* substituted (functional) thiols, we describe a systematic approach to the optimization of PVC surface modification by nucleophilic substitution with 4-aminothiophenol through control of reaction conditions: solvent composition, sonication, reaction time and presence of base and/or phase transfer catalyst (PTC). Efficient thiol attachment was confirmed using solid-state NMR and Raman spectroscopies, and the extent of surface modification was quantified using ATR-FTIR spectroscopy. Sonicated samples exhibited a lower degree of modification than their statically immersed counterparts (21.7 vs 99.6 $\mu g\ cm^{-3}$), and mechanical integrity was compromised. In DMSO/H_2O systems with a PTC, resultant degrees of PVC surface modification were up to 12.5% higher when caesium carbonate was employed as the base than in corresponding systems with potassium carbonate.

Keywords

PVC, thiol, nucleophilic substitution, surface modification

1. Introduction

Poly(vinyl chloride) (PVC) is one of the most extensively employed thermoplastic materials worldwide, with more than 31 million tons produced per annum [1]. The diverse applications of PVC, for example within transportation, construction, packaging and healthcare, result from its chemical and biological stability, relatively low cost and ready processability [2]. PVC currently accounts for almost 30% of all disposable polymeric devices used in medical screening, diagnosis, treatment and care [3].

Modification of the surface of PVC has been investigated as an approach to reduce leaching of additives into the surrounding media [4], aid polymer recycling [5], improve the mechanical and interfacial properties for applications with biofluid contact [6,7], and prevent biofouling, a phenomenon of major importance for medical grade PVC [8]. A variety of physical and chemical processes have been explored for PVC surface modification, including oxygen and argon plasma treatment [9], graft polymerization of polymer brush layers [7], UV irradiation [10], and nucleophilic substitution by wet-chemical treatment [11]. Aromatic thiols have been successfully employed as nucleophilic agents for the substitution of chlorine atoms on the PVC backbone in solution, aqueous suspensions or in the melt [12-14]. Sacristan *et al.* (2000) gave the first report of the importance of solvent conditions, in particular the solvent/non-solvent ratio, on the resultant degree of surface selectivity in PVC modification reactions with sodium azide and aminothiophenol [13]. To-date, however, the importance of an extended range of tuneable reaction conditions on the extent of PVC surface modification has not been systematically investigated. In particular, the ability to dramatically alter the surface chemistry of PVC through simple, efficient immersion chemistry, would afford opportunities to develop a range of novel surface properties for, among other applications, drug release, prevention of bacterial attachment or improving biocompatibility. This study, employing 4-aminothiophenol as a model thiol, provides the first methodical investigation of the effects of solvent composition, sonication, presence of a base and phase transfer catalyst (PTC), and reaction times on the degree of modification at the PVC surface during wet-chemical treatment of polymer films, and ultimately presents a platform for optimised PVC functionalization.

2. Experimental

2.1. Materials

All reagents were used as received. 4-Aminothiophenol was purchased from Apollo Scientific Limited, UK. Caesium carbonate and tetrabutylammonium bromide (TBAB) were obtained from Sigma Aldrich, UK. Potassium carbonate, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), ethylene glycol and diethyl ether were purchased from VWR International, UK. Unplasticised PVC films with a thickness of 0.2 mm were obtained from Goodfellow Cambridge Limited, UK.

2.2. Methods

Reaction conditions were varied as described below and the resulting polymers characterised by spectroscopic methods to determine the corresponding degrees of surface modification.

2.2.1. Wet-Chemical Treatment of PVC Films

2.2.1.1. Effect of Solvent/Non-Solvent Ratio

Unplasticised PVC film surfaces were modified by an adaptation of the methodology of Sacristan *et al.* (2000) [13]. Briefly, PVC samples (3 x 3 cm) were added individually to solutions of DMF/H_2O 4:1, 5:1 and 6:1 (50 mL) with 4-aminothiophenol (530.5 μL, 5 mmoL), and potassium carbonate (0.692 g, 5 mmoL) or caesium carbonate (1.629 g, 5 mmoL) as the base, and maintained at 60°C for 6 h. Samples were then washed thoroughly with deionised water. Residual nucleophile and solvent were removed by washing for 24 h with diethyl ether (3 x 100 mL), and samples were dried *in vacuo* prior to characterisation.

2.2.1.2. Effect of Sonochemistry

PVC samples were immersed in DMF/H_2O solutions (50 mL) containing potassium carbonate as the base and 4-aminothiophenol, as before, and sonicated at ambient temperature for 6 h (VWR Ultrasonic Cleaner, 230 V, 100 W). Samples were washed and dried as previously described.

2.2.1.3 Effect of Phase Transfer Catalyst

PVC samples were immersed in DMF/H$_2$O solutions (50 mL) containing caesium carbonate or potassium carbonate as the base and 4-aminothiophenol modifying agent, as previously described. After addition of the PTC, TBAB (59.7 mg, 0.19 mmoL), solutions were maintained at 60°C for 6 h. Deionised water was used to quench the reaction prior to washing and drying the modified PVC samples as before.

2.2.1.4. Effect of Solvent Selection

PVC surface modification reactions were carried out as before but using solvent systems containing THF, ethylene glycol or DMSO in place of DMF.

2.2.2. Characterisation

2.2.2.1. Fourier Transform Infrared (FTIR) Spectroscopy

Modified film surfaces were characterised by attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy. Spectra are an average of 12 scans acquired using an FT/IR-4100 spectrophotometer (Jasco, Great Dunmow, UK) equipped with a Pike MIRacle ATR accessory with diamond crystal at a resolution of 4 cm^{-1}. Infrared spectra of the 4-aminothiophenol modifying agent and unmodified (control) PVC films were obtained between NaCl windows and in the ATR mode, respectively. The degree of surface modification was determined from a calibration curve prepared using standard solutions of 4-aminothiophenol in methanol. The line equation determined from the calibration curve was y = 0.0002x - 0.0057 (r^2 = 1.00). Absorbance values of modified films at 1602 cm^{-1}, characteristic of aromatic ring stretching vibrations, were converted into surface concentrations (mg cm^{-3}) by rearranging the line equation to make x the subject and multiplying by the depth of penetration into PVC (1.33 μm).

2.2.2.2. Raman Spectroscopy

Raman spectra of modified films were obtained using a RamanStation R3 (Avalon Instruments, Belfast, UK) coupled with a RamanMicro 300 Raman microscope (PerkinElmer, Waltham, MA, USA) at 50x magnification. Raman scattered light from a 785 nm laser was

collected between 3200-400 cm^{-1} at a resolution of 2 cm^{-1} and total exposure time of 20 s.

2.2.2.3. Solid-State NMR Analysis

Solid-state ^{13}C spectra of modified and unmodified (control) PVC samples (2 x 2 mm) were obtained using a Varian VNMRS spectrometer operating at 100.56 MHz.
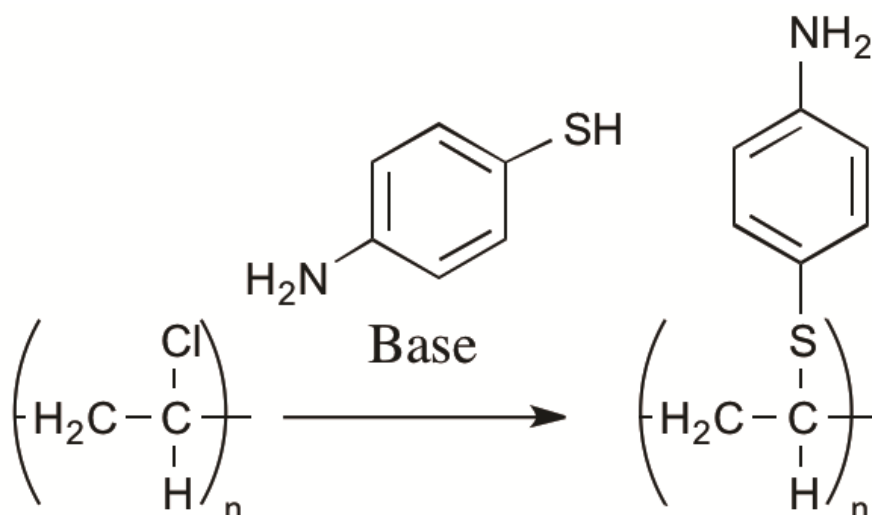
2.2.2.4. Tensile Analysis

Tensile analysis was performed using a Stable Micro Systems TA-XT Plus Texture Analyser (Goldaming, Surrey, UK) in conjunction with Texture Exponent 32 software. Rectangular samples (55 x 15 mm) of modified and unmodified (control) PVC films, with a thickness of 200 μm, were fixed between mobile upper and static lower clamps. The thickness of samples was not significantly altered by the surface modification process. The upper clamp was vertically elevated at a constant crosshead velocity of 1.0 mm s^{-1} until fracture. Ultimate tensile strength, Young's modulus and percentage elongation at break were determined from resultant plots of stress versus strain.

2.2.2.5. Statistical Analysis

Measurements were obtained at least in triplicate and results are expressed as mean ± SD. Statistical analysis was performed using GraphPad InStat software. Comparisons of individual mean values were made using the Kruskal-Wallis test, with post-hoc comparisons evaluated using Dunn's post-test. $P < 0.05$ was used to denote significance.

3. Results and Discussion

PVC was herein surface-functionalized with reactive thiol moieties *via* nucleophilic substitution of chlorine atoms of the PVC backbone with 4-aminothiophenol, as outlined in Scheme 1, under various reaction conditions of solvent composition, time, sonication, base and PTC.

Scheme 1: Nucleophilic substitution of C-Cl group of PVC with 4-aminothiophenol.

3.1. Spectroscopic Characterisation of Modified PVC Films

Surfaces of PVC films covalently modified with 4-aminothiophenol in DMF/H_2O 5:1, with potassium carbonate as the base, were characterised by ATR-FTIR, Raman and NMR spectroscopies.

3.1.1 FTIR Spectroscopy

Overlaid ATR-FTIR spectra of the 4-aminothiophenol modifying agent, unmodified (control) PVC and modified PVC are presented in Fig. 1. The spectrum of 4-aminothiophenol-modified PVC reveals the presence of additional bands not observed in the spectrum of control PVC. These bands, which are also present in the spectrum of the 4-aminothiophenol reactant, result from the presence of the covalently-bound aromatic modifier at the material surface, and can be ascribed to aromatic primary amine N-H stretching (3470 and 3350 cm^{-1}), aromatic C-C stretching (1600 and 1500 cm^{-1}), aromatic C-H stretching (3100 and 3028 cm^{-1}) and *para*-substituted C-H out-of-plane bending (825 cm^{-1}) modes of vibration of the attached aromatic thiol moiety [12,15]. Additional bands in the spectrum of modified PVC at 1620 and 1180 cm^{-1} are ascribed to N-H scissoring and C-N stretching vibrations, respectively, of the amino moiety of 4-aminothiophenol [15].
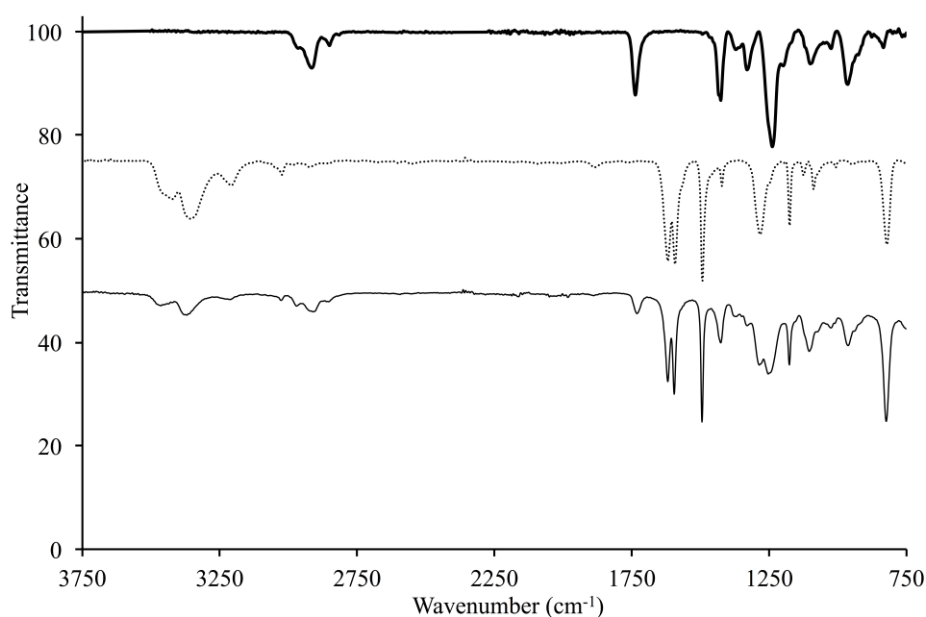
Fig. 1. ATR-FTIR spectra (3750-750 cm^{-1}) of 4-aminothiophenol (…), unmodified (control) PVC (—), and 4-aminothiophenol-modified PVC (—). Transmittance values are offset for clarity.

3.1.2. Raman Spectroscopy

Overlaid Raman spectra of control and modified PVC are displayed in Fig. 2. The Raman spectrum of 4-aminothiophenol-modified PVC shows distinct changes in comparison to control PVC, confirming successful tethering of 4-aminothiophenol to the PVC surface. Two new bands assigned to aromatic C-H stretching vibrations (3054 and 2973 cm^{-1}), an additional band ascribed to amino C-N stretching vibrations (1620 cm^{-1}), two bands corresponding to aromatic C-C stretching vibrations (1595 and 1496 cm^{-1}), and an intense band at 1095 cm^{-1} with shouldering of the band at 616 cm^{-1} corresponding to C-S stretching vibrations in the spectrum of 4-aminothiophenol-modified PVC indicate the presence of the covalently-bound aromatic thiol modifying agent at the polymer surface.
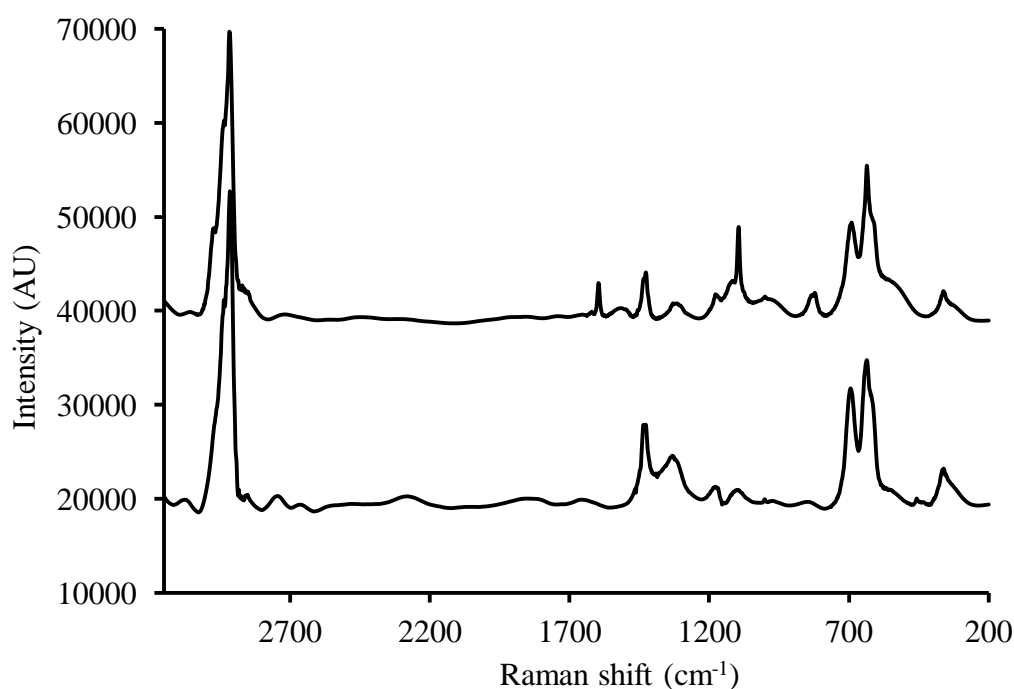
Fig. 2. Raman spectra of 4-aminothiophenol-modified PVC (top line) and unmodified (control) PVC (bottom line).

3.1.3. NMR Spectroscopy

The ^{13}C spectrum of 4-aminothiophenol-modified PVC exhibited analogous signals to that of control PVC, with some variation in intensity. Additional signals at 116, 138 and 148 ppm in the ^{13}C spectrum of modified PVC were consistent with signals observed at 115, 134 and 147 ppm during NMR analysis of 4-aminothiophenol in solution. A difference spectrum demonstrated a reduction in the intensity of the signal at 57 ppm, indicative of the shift for CH-Cl, and a concomitant increase in intensity of the signals at 16 and 22 ppm, ascribed to terminal methyl and adjacent methylene groups, respectively, upon modification, thus confirming successful substitution of chlorine atoms with aromatic thiol moieties.

3.2. Effect of Varying Reaction Conditions

In order to demonstrate an optimised method for the functionalization of PVC with thiol moieties, an array of reaction conditions, including sonication, base, presence of a PTC, solvent composition and reaction times, were herein varied and the effects of each reaction variable on the subsequent degree of thiol attachment are reported below.

3.2.1. Effect of Sonication

Interactions between the 4-aminothiophenol modifying agent and the PVC polymer chains lead to physical crosslinking of the polymer network, and are reported to limit the extent of PVC surface modification during wet-chemical treatment. This is due to the restricted mobility, and subsequent access, of the 4-aminothiophenol moiety to the chlorine atoms [12]. As such, the use of sonication as a method for attaining mass transfer of the reaction components at conditions of ambient temperature was investigated with concomitant changes in solvent compositions. Fig. 3 shows the resultant degrees of surface modification (mg cm^{-3}) following static immersion (at 60°C) and sonication (at ambient temperature) of PVC samples in DMF/H$_2$O 4:1, 5:1 and 6:1 systems (containing 20%, 16.7% and 14.3% water respectively), with potassium carbonate as the base. In order to assess homogeneity of the modified PVC surface, five points were analysed and the mean values are displayed in Fig. 3, with error bars representing surface heterogeneity.
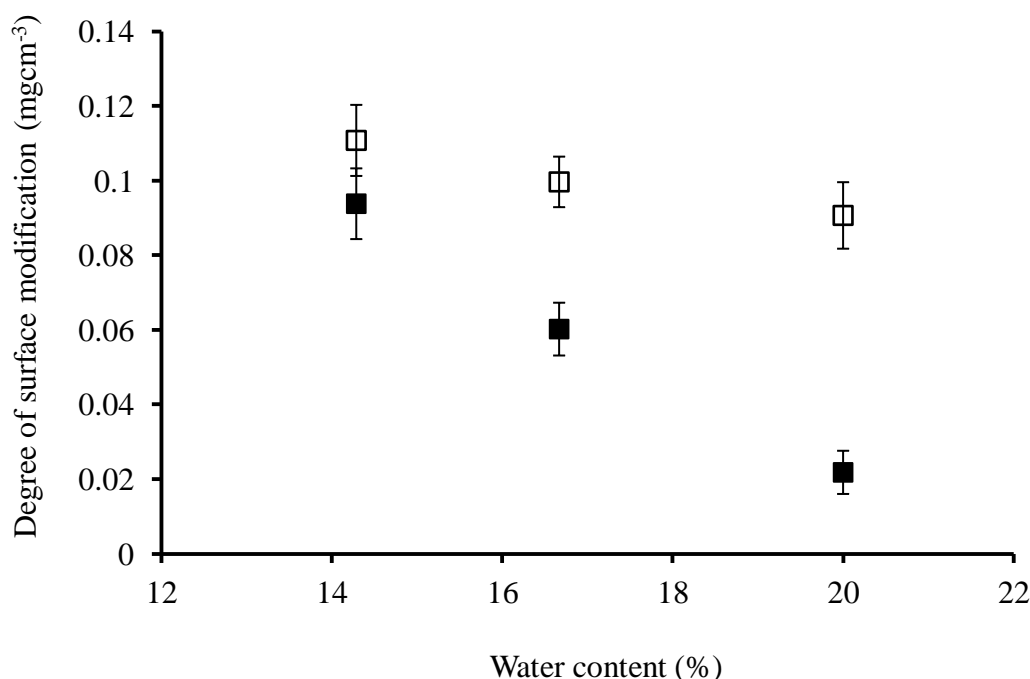

Fig. 3. Effect of sonication (at ambient temperature) (■) versus static immersion (at 60°C) (□) on the degree of PVC surface modification in DMF/H$_2$O systems with potassium carbonate as the base.

An increase in the degree of modification of both statically-immersed and ultrasonically-treated films was observed as the solvent concentration was increased, as demonstrated in

Fig. 3, due to enhanced penetration of the thiolate modifier into the expanded polymer chain network [12,13]. At concentrations of DMF higher than those presented here, the PVC dissolved, in accordance with previous reports [13].

The use of sonication at ambient temperature for modification of the PVC surface has been widely investigated, with metal ion chelation, and grafting of dyes such as Crystal Violet, Rose Bengal and Methylene Blue, and polymers such as PMMA, to PVC previously reported [16]. In addition to improving the mass transport of reagents, ultrasound was expected to enhance wetting of the PVC surface, thereby promoting contact between the PVC film and modifying agent, *via* high velocity impingement of the surface by microjets formed by the collapse of cavitation bubbles [16]. As displayed in Fig. 3, however, sonicated films exhibited lower degrees of surface modification compared to their statically-immersed counterparts, with these reductions becoming more pronounced as the water content of the reaction medium increased. For example, in DMF/H_2O 4:1 systems, the degree of modification of sonicated samples was four times lower than the corresponding statically-immersed samples. Furthermore, bombardment with base particulates caused pitting of the sonicated film surface, as displayed in Fig. 4. Due to the detrimental effect of sonication, even at ambient temperature, on integrity of film surfaces, and the inability to enhance the degree of chemical modification relative to that observed upon static immersion at 60°C, samples were statically immersed in all further wet-chemical treatment studies.
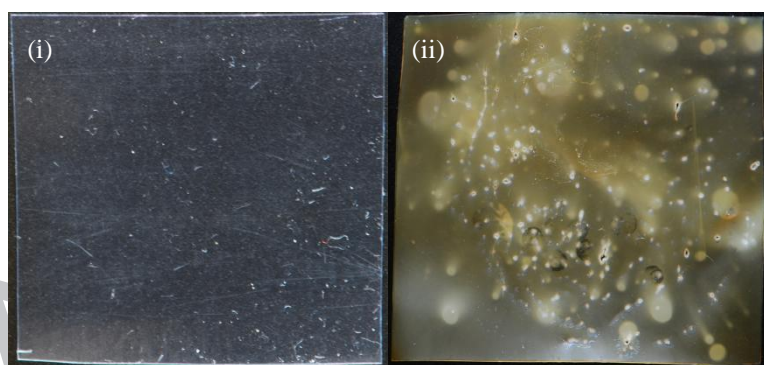

Fig. 4. Surfaces of (i) control PVC and (ii) 4-aminothiophenol-modified PVC following sonication in DMF/H_2O 6:1. The light spots represent surface irregularities caused by bombardment with base particulates.

3.2.2. Effect of Base

In the absence of a base, no variation in the IR spectra between treated and control PVC samples

was observed, suggesting conversion of 4-aminothiophenol to the thiolate is a pre-requisite for nucleophilic substitution. The effect of two alternative deprotonating agents, potassium carbonate and caesium carbonate, with respective solubilities in DMF of 7.5 mgmL^{-1} and 119.6 mgmL^{-1} [17], on the degree of PVC surface modification can be seen in Fig. 5.
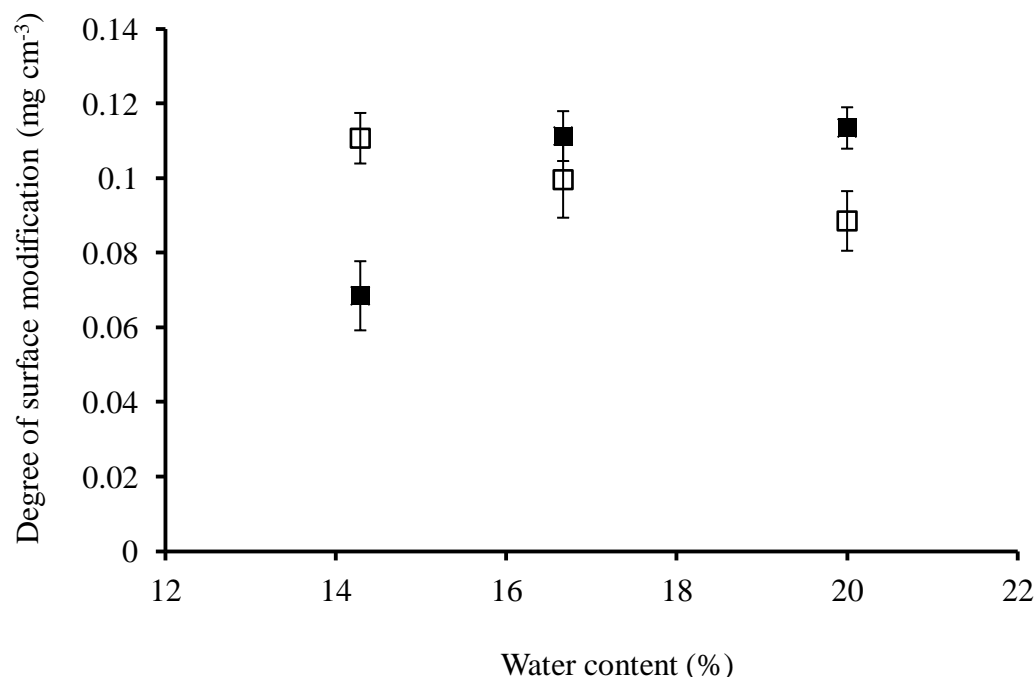

Fig. 5. The effect of potassium carbonate (□) and caesium carbonate (■) on the degree of PVC surface modification in DMF/H$_2$O systems.

ATR-FTIR analysis of the modified films suggests that substitution of potassium carbonate by caesium carbonate does not have a substantial effect on the extent of PVC surface modification with 4-aminothiophenol under the conditions of this study, as graphically demonstrated in Fig. 5. The detrimental effect of potassium carbonate particulates on surface integrity has previously been shown by the images in Fig. 4, therefore the more soluble base, caesium carbonate, was employed in further studies, unless stated otherwise.

3.2.3. Effect of Phase Transfer Catalyst

Phase transfer catalysts (PTCs) function to facilitate transfer of the nucleophile from the aqueous phase to the organic phase, allowing intimate contact at the polymer-solvent interface, and thereby promoting substitution of chlorine atoms at the PVC surface [18]. The effect of tetrabutylammonium bromide (TBAB), an effective catalyst for dehydrochlorination of PVC

[5], on the degree of PVC surface modification in DMF/H_2O systems with caesium carbonate as the base can be seen in Fig. 6.
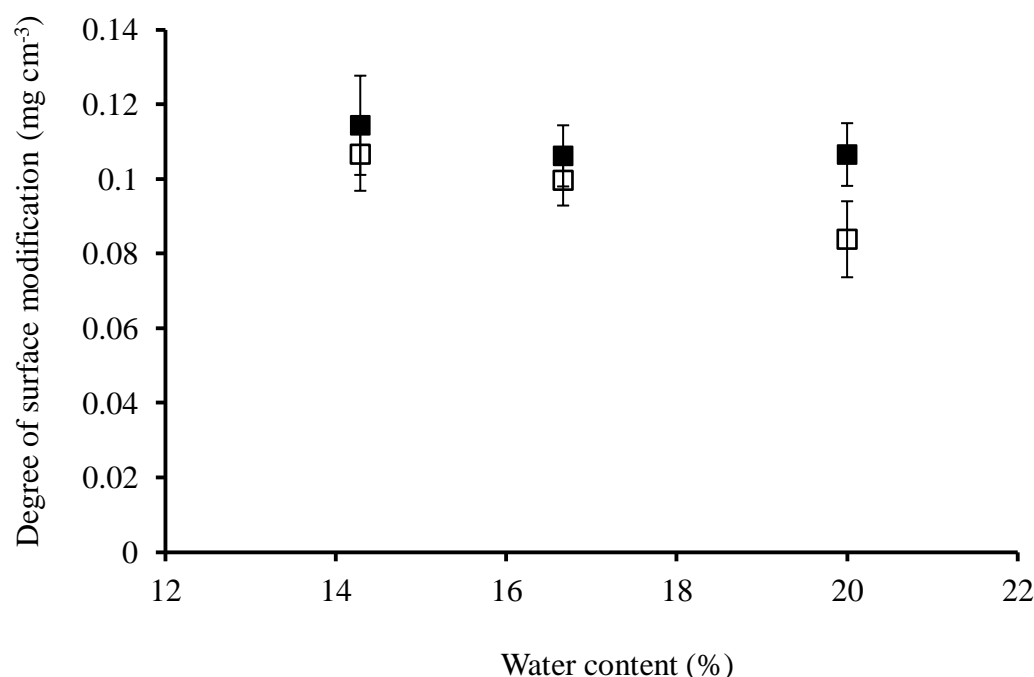

Fig. 6. Degree of PVC surface modification in DMF/H_2O systems with caesium carbonate in the absence (□) and presence (■) of TBAB.

Fig. 6 demonstrates that in the presence of TBAB as a PTC, the extent of PVC surface modification was up to 27% higher than in equivalent reaction media devoid of TBAB. The presence of a PTC in the basic DMF/H_2O systems was, however, detrimental to the mechanical integrity of the PVC samples, and induced surface irregularities can be seen in Fig. 7. Loss of optical transparency, with an associated increase in surface roughness, of PVC films has previously been reported during PTC-assisted surface modification by wet-chemical treatment [13].
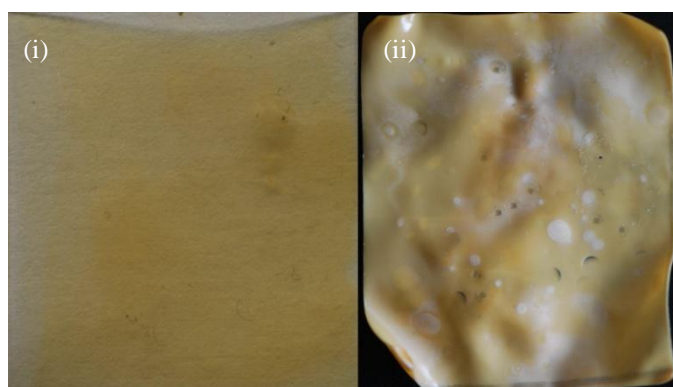
Fig. 7. PVC film modified in DMF/H$_2$O 6:1 in the absence (i) and presence (ii) of TBAB respectively.

This loss of mechanical integrity in the presence of TBAB was, however, found to be solvent-dependent, as reported below.

3.2.4. Effect of Solvent

A range of solvent systems have been successfully employed for chemical modification of powdered PVC *via* nucleophilic substitution, including tetrahydrofuran/dimethyl sulfoxide (THF/DMSO) [19] and DMF/H$_2$O [13], therefore the effect of alternative solvent compositions on the resultant degree of PVC surface modification was herein investigated.

Firstly, complete dissolution of the PVC film was observed within seconds of immersion in THF/H$_2$O systems, thus making this solvent unsuitable for surface modification of PVC. Secondly, no chemical modification of the PVC films occurred, as confirmed *via* spectroscopic characterisation, when ethylene glycol was employed as the solvent, irrespective of the base employed or presence of a PTC. In polar protic solvents, such as ethylene glycol, solvation of the nucleophile by hydrogen bonding occurs readily, thus hindering participation of this species in the nucleophilic substitution reaction. Thirdly, in systems employing DMSO/H$_2$O and potassium carbonate as the respective solvent and base, the extent of PVC surface modification was more than six-fold higher in the presence of TBAB than in equivalent solutions devoid of a PTC, as shown in Fig. 8.
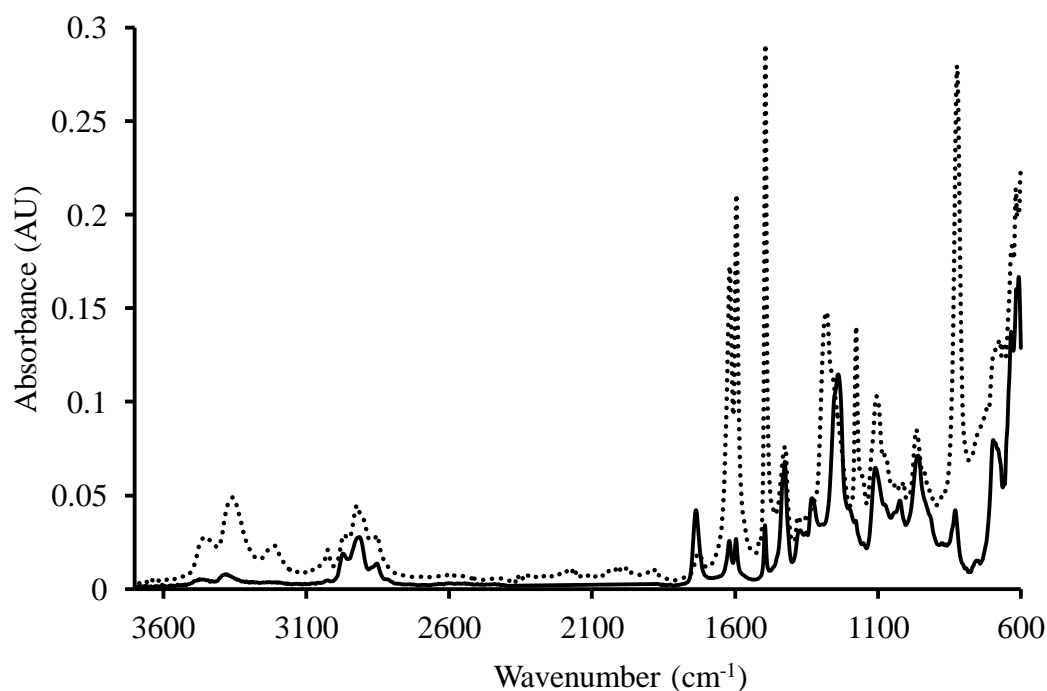
Fig. 8. Superimposed spectra of PVC films modified with 4-aminothiophenol in DMSO/H_2O 5:1 with potassium carbonate in the presence (…) and absence (—) of TBAB.

In the absence of a PTC, PVC surfaces were modified to a lower extent in DMSO systems than in the corresponding DMF systems, as a result of reduced polymer chain swelling in the former solvent. Upon addition of TBAB (3.5 mol%) to DMSO, however, approach of the nucleophile to the polymer surface was promoted, thus enhancing the resultant degree of surface modification. Furthermore, the modified films maintained their mechanical integrity in contrast to films modified in DMF/H_2O systems, which exhibited a warped and brittle nature due to extensive solvent-induced swelling of the polymer chains, as shown in the images in Fig. 7.

Increasing the quantity of TBAB from 3.5 to 7 mol% resulted in a 25% increase in the degree of surface modification, as determined *via* spectroscopic characterisation. This increase was, however, accompanied by visual changes, including an intensified yellow colouration and cloudiness of the films, as observed in Fig. 9, attributed to partial crystallization of the polymer, as previously reported during chemical modification of PVC with sodium azide [13].
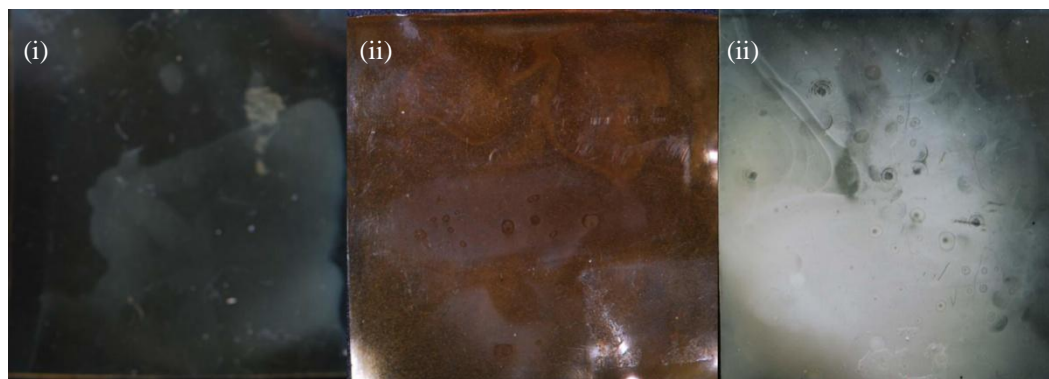
Fig. 9. PVC films modified with 4-aminothiophenol (5 mmoL) at 60°C for 6 h in DMSO/H_2O 5:1 in the presence of caesium carbonate (5 mmoL) and TBAB (0, 3.5 and 7 mol%) represented by (i), (ii) and (iii) respectively.

Furthermore, in DMSO solutions employing caesium carbonate as the base instead of potassium carbonate, degrees of surface modification were up to 12.5% higher, attributed to the greater solubility of the former base in DMSO (base solubilities were 362 mgmL^{-1} and 47 mgmL^{-1} in DMSO respectively) [17]. These findings support a TBAB concentration of 3.5 mol% and use of caesium carbonate as the base for optimal surface modification of PVC.

3.3. Tensile Analysis

Mechanical properties of the modified films, namely ultimate tensile strength, Young's modulus and percentage elongation at break, were determined following treatment in systems of DMSO/H_2O and DMF/H_2O, with caesium carbonate and TBAB (3.5 mol%), and results are reported in Table 1. No significant differences in ultimate tensile strength or Young's modulus of the PVC samples were demonstrated following treatment in DMSO/H_2O or DMF/H_2O systems, and optical transparency of the modified films was similar to unmodified PVC. In contrast, PVC modified in DMF/H_2O systems exhibited significantly lower elongation at break than control PVC and PVC treated in DMSO/H_2O systems. This reduced ductility was attributed to the higher levels of polymer chain entanglement in DMF, consequential to the extensive solvent-induced swelling.

Table 1 Mechanical Properties of PVC Films Modified with 4-Aminothiophenol in the Presence of Caesium Carbonate and TBAB in DMF/H_2O and DMSO/H_2O Systems

PVC Reaction Media	Ultimate Tensile Strength (Mean ± SD) ($N\ mm^{-2}$)	Young's Modulus (Mean ± SD) ($N\ mm^{-2}$)	Elongation at Break (Mean ± SD) (%)
Unmodified (control)	34.8 ± 1.3	63.7 ± 2.1	149.2 ± 8.8
DMF/H_2O	36.6 ± 4.4	70.8 ± 15.4	23.2 ± 4.8
DMSO/H_2O	32.1 ± 1.8	64.1 ± 9.3	127.3 ± 11.0

3.4. Kinetic Study of PVC Surface Modification with 4-Aminothiophenol

Through systematic investigation of varying reaction conditions, we have demonstrated that efficient thiol attachment to PVC, without compromising mechanical integrity, occurs in the presence of TBAB (3.5 mol%) and caesium carbonate in a solvent system of DMSO/H_2O 5:1. Kinetics of the PVC surface modification reaction were then investigated in the optimised reaction conditions by statically immersing PVC samples in media containing the 4-aminothiophenol modifying agent for time periods ranging from 2 to 42 h. Resultant degrees of surface modification were determined by FTIR, as previously described, using absorption bands of 4-aminothiophenol aromatic vibrational modes. The maximum degree of modification was quantified after 12 h as 149.7 μg cm^{-3}.
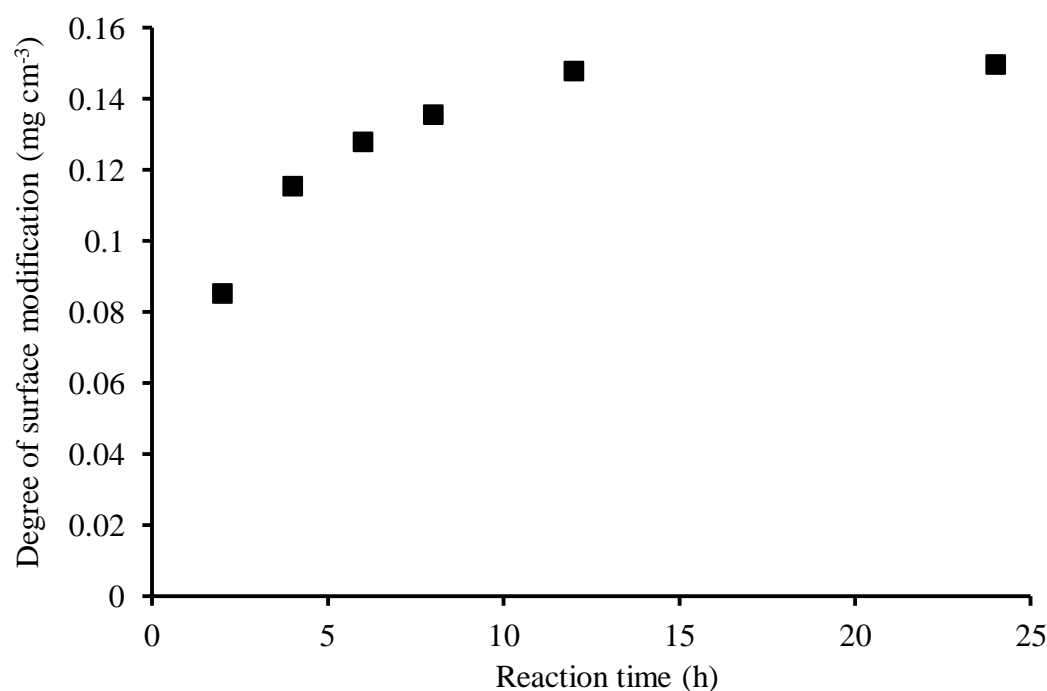
Fig. 10. Kinetics of the PVC surface modification reaction with 4-aminothiophenol in DMSO/H_2O 5:1 with caesium carbonate and TBAB (3.5 mol%).

As demonstrated in Fig. 10, at time periods exceeding 12 h, the degree of surface modification appeared to plateau as a result of the surface selectivity of FTIR spectroscopy in the ATR mode. Bulk modification was, however, visually evident upon prolonged reaction conditions by intensified colouration of the PVC films, corresponding to the formation of conjugated C=C double bonds during the dechlorination of PVC, as previously reported [5,20,21]. PVC should therefore be statically immersed in the reaction media for durations of less than 12 h to prevent loss of polymer mechanical integrity.

4. Conclusions

We herein present an optimised method for efficient surface functionalization of PVC with thiol moieties, determined through systematic investigation of the effect of variable reaction conditions, including solvent composition, sonication, and the presence of base and/or PTC, on mechanical integrity and degree of surface modification of PVC films. Sonication introduced surface irregularities, therefore samples should be statically immersed for reaction times of less than 12 h to maintain surface and bulk mechanical integrity of the polymer films. Detrimental effects on surface integrity were, in addition, demonstrated upon employment of potassium carbonate as the base, whereas control of the solvent composition

was important for maintenance of bulk mechanical integrity. Alternative solvent systems comprising THF/H$_2$O and DMF/H$_2$O resulted in dissolution and reduced ductility of the films respectively. Through this study, we can, importantly, conclude that optimal levels of surface modification approximating 150 μg cm^{-3}, with no loss of surface smoothness, were observed upon static immersion of PVC in the presence of the PTC, TBAB, with employment of caesium carbonate and DMSO as the base and solvent, respectively. This efficient method for thiol-functionalization of PVC will ultimately allow the performance of this widely used biomaterial to be enhanced through facilitation of a range of property-enhancing surface modifications.

Acknowledgements

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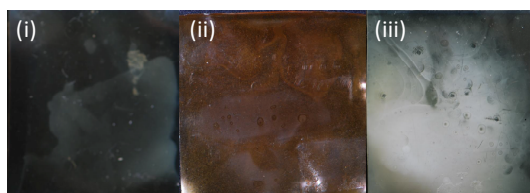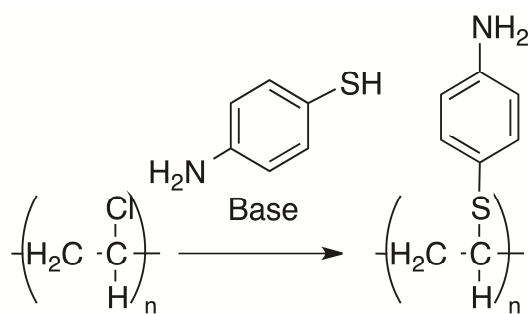
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Highlights

- PVC was herein surface functionalized with 4-aminothiophenol.
- A variety of reaction conditions were systematically investigated.
- Degrees of modification approximating 150 μg cm^{-3} were obtained under optimal conditions.
- This optimized method will facilitate an array of property-enhancing modifications.

Thiol functionalization of PVC in DMSO/H$_2$O with caesium carbonate and tetrabutylammonium bromide (0, 3.5 and 7 mol%), represented by (i), (ii) and (iii) respectively.