



Hydrophilic surface modification of poly(vinyl chloride) film and tubing using physisorbed free radical grafting technique

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ABSTRACT

The grafting of hydrophilic monomers from the surface of PVC films and complex geometries, such as tubing, was executed by a novel two-step process: physisorption of a hydrophobic free radical initiator onto a polymer surface followed by radical polymerization with hydrophilic monomers. The key step is creating a hydrophobic/hydrophilic diffusional barrier that promotes radical generation upon heating at the polymer surface. Transmission infrared spectroscopy, X-ray photoelectron spectroscopy, surface wettability and capillary rise, gravimetric analysis, UV–vis spectroscopy and gel permeation chromatography were utilized to prove successful covalent grafting of poly(hydroxyethylmethacrylate), poly(dimethylacrylamide), poly(hydroxyethylacrylate), poly(dimethylaminoethylmethacrylate), poly(acrylic acid), and poly(4-vinyl pyridine).

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1. Introduction

Poly(vinyl chloride) (PVC) is the second most commonly used polymer and accounts for an annual world-wide production of 26 million tons. Many applications are employed in the medical field, such as blood storage bags, endotracheal tubes, dialysis tubing, and intravenous catheters. The properties of PVC are drastically altered by the incorporation of plasticizer which induces flexibility by lowering the second order transition temperature. However, phthalate ester plasticizers typically used for PVC have been under public scrutiny as a potential carcinogens attributing to the pathogenesis of endocrine, pulmonary and hepatotoxicity [1–3]. Also, the poor biocompatibility of the hydrophobic PVC surface leads to unwanted protein adsorption and cell adhesion [4]. To solve these problems, considerable basic and applied research has been devoted to the surface modification. The polymer surface is the phase boundary that resides between the bulk polymer and the outer environment. By altering the properties of the boundary, the performance of the polymer can be modified.

Surface modifications of PVC have been developed by both chemical and physical processes to reduce plasticizer migration and increase the biocompatibility. Such techniques include surface coating [5–7], surface crosslinking with ultraviolet radiation or plasma treatment [8–11], and surface grafting with hydrophilic polymers [12]. Surface coating of antibacterial reagents, or hydrophilic polymers generally increases the biocompatibility of PVC

while surface crosslinking is intended to create a barrier to prevent interfacial mass transport of plasticizer.

Among these techniques, surface grafting has several advantages that include easy and controllable introduction of high density grafted chains accompanied by minor changes in the bulk properties. Covalent attachment of grafted chains onto a polymer surface avoids desorption and ensures long-term chemical stability unlike surface coating modifications. Plasma treatment can introduce active species on the surface of the polymer, followed by the polymerization of monomers. However, a limitation can be the expense of the technique. Irradiation treatments such as UV, gamma and microwave exposures are difficult processes to scale up. Also, irradiation can damage the polymer over prolonged exposure. Furthermore, all of the current modification techniques are incapable of easily modifying difficult sample geometries such as tubing or piping.

Grafting methods are generally divided into two classifications known as grafting-from and grafting-to [13]. The grafting-to process occurs when preformed polymer chains with reactive functional groups are covalently coupled to the surface. Grafting-from utilizes initiator species existing on the polymer surface to react with monomer. The monomer polymerizes to form a grafted chain from the surface. Hu and Brittain [14] reported a grafting-from technique in which hydrophilic polymers were created on the surface of poly(dimethyl siloxane) using a physisorbed free radical initiator. It was speculated that this method exploited the polarity disparity between the hydrophobic initiating species and the polar polymerization medium. In this report, we describe the extension of this technique to surface modification of PVC, including samples possessing complex geometries.

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2. Experimental section

2.1. Materials

Acrylic acid (AA) was passed through a column of neutral alumina oxide (Aldrich, 150 mesh). *N,N*-dimethyl acrylamide (DMA), 2-hydroxyethyl acrylate (HEA), *N,N*-dimethylaminoethyl methacrylate (DMAEMA) and 2-hydroxyethyl methacrylate (HEMA) were passed through a column of activated basic alumina (Aldrich, 150 mesh). 4-Vinylpyridine (4VP) was purified by distillation. Azobisisobutyronitrile (AIBN) was obtained from Aldrich and was recrystallized from methanol. PVC sheets were obtained from Universal Plastics. PVC tubing was obtained from VWR International.

2.2. Characterization methods

Transmission Fourier transform infrared (FT-IR) measurements were performed on a Nicolet model 730 FT-IR spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on a Perkin-Elmer instrument using Al $K\alpha$ radiation with a takeoff angle of 45° at the MATNET Surface Analysis Center at Case Western Reserve University. Before measurement, the samples were vacuum dried for 22 h. Ellipsometry was performed using a Gaertner model L116C ellipsometer with a He-Ne laser ($\lambda = 632.8$ nm) and a 70° fixed angle of incidence. Atomic force microscopy (AFM) was performed using a multimode scanning probe microscope (Digital Instruments, Nanoscope IIIA) in tapping mode with a silicon tip. The AFM images were obtained at room temperature in air. A scan rate of 1 Hz and a resolution of 512 × 512 pixel were selected to generate high-quality images. Digital pictures of the cross-sectioned tubing were taken using an Olympus BX51 Research Microscope with 5× magnification equipped with an Olympus DP70 Digital Camera. Elemental analysis was completed by Galbraith Laboratories. All ^1H NMR spectra were recorded on a Varian Mercury 300 spectrometer, using CDCl_3 as the solvent.

The construction of calibration curves for thickness determination by transmission FT-IR was based on spin-cast free polymer layers on silicon wafers (single side polished) and their relative absorbance and thickness values. An initial solution of free polymer was spin cast onto the wafer with the appropriate solvent: 5% poly(2-hydroxyethyl methacrylate) (PHEMA) (50:50 methanol/THF, w/w), 1% poly(2-hydroxyethyl acrylate) (PHEA) (methanol), 5% poly(dimethyl acrylamide) (PDMA) (30:70 methanol/THF, w/w), 5% poly(acrylic acid) (PAA) (75:25 methanol/ H_2O , w/w), 3% poly(4-vinylpyridine) (P4VP) (THF), 3% poly(dimethylaminoethyl methacrylate) (PDMAEMA) (toluene), and 2% PVC (THF). These solutions were diluted to spin cast polymer layers of reducing thickness. Each polymer layer was characterized by ellipsometry for thickness in nanometers and transmission IR for absorbance. The refractive index values used for film thickness determination are 1.53 for PAA and PDMA, 1.51 for PHEA and PHEMA, 1.52 for PDMAEMA and 1.47 for P4VP [15,16].

UV-vis measurements were made using a Hewlett Packard 8453 Diode Array UV-visible spectrophotometer equipped with tungsten and deuterium halogen lamps. The calibration curve for thickness determination by UV-Vis spectrophotometry was based on the absorbance values at 267 nm for solutions (free P4VP in DMF) of varying concentrations.

Contact angles were determined using a Rame Hart NRL-100 contact angle goniometer equipped with an environmental chamber and tilting base mounted on a vibrationless table (Newport Corp.). A 7.5 μL droplet of filtered, deionized distilled water was placed on the surface of the samples at room temperature. After 1 min the contact angles (advancing and receding) were measured using the tilting stage (35°) method. Each reported value is the average of five independent measurements.

Capillary rise measurements of the modified and unmodified PVC tubings were recorded using a traveling telescope cathetometer M912 from Gaertner Scientific. The probe fluid (water) rose for a few hours to equilibrate before measurements were made. The molecular weight for PVC was determined by gel permeation chromatography (GPC) in THF using a Waters 501 pump, Waters HR4 and HR2 styragel columns, a Waters 410 differential refractometer and a Viscotek 760A dual light scattering and viscosity detector. Other molecular weights were determined by GPC in DMF using a Waters 501 pump, two PLgel (Polymer Laboratories) mixed D columns (5 μm), and a Waters 410 differential refractometer. Molecular weights were calibrated by comparing narrow polydispersity poly(methyl methacrylate) standards ($200\text{--}1.0 \times 10^6$ g/mol) (Polymer Laboratories).

2.3. Grafting-from polymerization of hydrophilic monomers with physisorbed free radical initiator

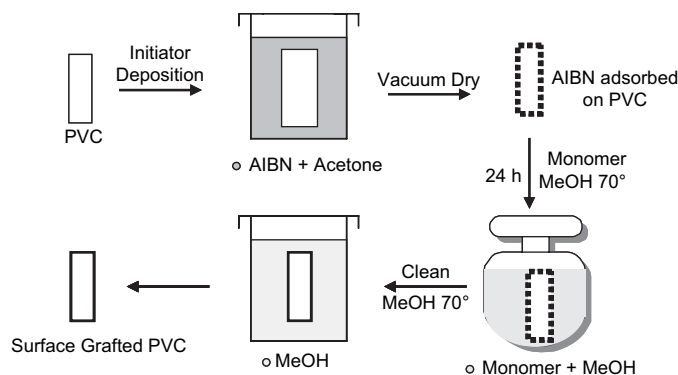
The PVC film (2 cm × 1 cm × 0.164 mm) was immersed into an acetone solution of 5% AIBN (w/w) for 15 min. The film was removed from solution and placed between two glass plates, where the percent swelling was measured. Percent swelling (S) was defined as: $S\% = ((A_f - A_i)/A_i) \times 100$, where A_i and A_f represent the area of the film before and after initiator deposition, respectively. The PVC film was then dried in a vacuum oven at room temperature for 24 h. The monomer solution (10% monomer in water or methanol, v/v) and the AIBN-adsorbed PVC film were transferred into a sealed glass vessel, purged with nitrogen for 1 h and heated at 70 °C for 24 h. The samples were then exhaustively treated with methanol for 2 h at 70 °C, sonicated for 2 h, and again immersed in solvent for 2 h at 70 °C to remove physisorbed monomer and polymer. The hydrophilic grafted PVC films were vacuum dried for 17 h *in vacuo*. Samples were kept under vacuum in a desiccator prior to characterization.

For polymerizations within PVC tubing, 2.5 ft sections were used. Initiator deposition was conducted by filling the tubing with a 5% AIBN/acetone (w/w) solution. After 15 min, the tube was vacuum dried for 3 h. For polymerization, the tubing was filled with a 10% monomer/methanol (w/w) solution and immersed in a water bath set for 75 °C. After 24 h, the tubing was removed from the water bath and cleaned by passing methanol (70 °C) several times through the tubing. Following sonication in methanol for several hours, the tubing was vacuum dried. The tubing was characterized by capillary rise and gravimetric analysis.

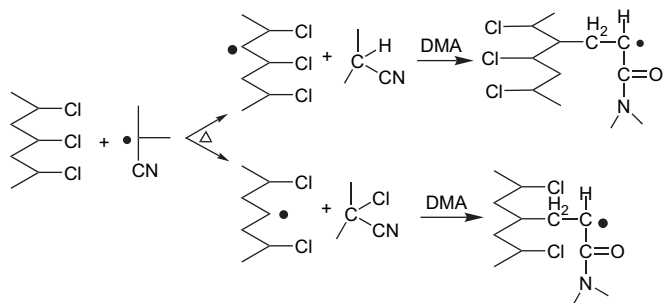
3. Results and discussion

3.1. Surface grafting onto PVC via physisorbed free radical initiation

The graft polymerization of hydrophilic monomers AA, PDMA, HEA, HEMA, PDMAEMA and P4VP from PVC was conducted using



Scheme 1. Simple two-step surface modification of PVC.



Scheme 2. Mechanism of hydrogen and chlorine abstractions.

a simple two-step process: (1) physisorption of a hydrophobic free radical initiator (AIBN) onto the surface of PVC, followed by (2) radical polymerization in hydrophilic media (Scheme 1). In step one, the hydrophobic PVC swells in a good solvent (acetone). We have determined that the PVC swells up to 142% of the original size. As the solvent evaporates, initiator remains on the surface and some may become entrapped in the subsurface of PVC. After the film is vacuum dried, it is placed into the polymerization media where a hydrophobic/hydrophilic diffusional barrier between the surface and the media promotes radical generation at the surface. The initiator decomposition can undergo three possible reactions: combination/disproportionation with another tertiary isobutyronitrile radical, polymerization with monomer in solution forming free polymer, or abstraction of a hydrogen or chlorine from the PVC backbone (Scheme 2). The surface PVC radicals formed from hydrogen or chlorine abstractions can react with hydrophilic monomer in solution forming grafted polymer chains. Energetically, the extraction of the chlorine or hydrogen is unfavorable. However, at the interphase of solid and liquid solution, the reaction of the hydrophobic radicals and PVC is enhanced by hindered diffusion of the initiator radicals into the aqueous environment. Also, there is a possibility of polymer chain transfer from the free polymer to the PVC; although we speculate that the majority of surface generated radicals arises from isobutyronitrile radical abstraction.

After polymerization, the polymer samples were exhaustively extracted by solvent (either water or methanol) and sonicated in solvent to remove the noncovalently attached free polymer. It was qualitatively observed that the modified PVC films became cloudy upon polymerization with all monomers. The films occasionally appeared opaque because the polymerization was run relatively close to the T_g of PVC, 81 °C, where there is possibility of long range segmental motion which induces crystallinity. Most experiments produced a more rigid and less flexible PVC film. We cannot disregard the possibility of radical-induced crosslinking as a cause for this change in bulk properties. The most probable answer is the loss of plasticizer during the initiator deposition stage. As the film swells in acetone, free volume increases allowing diffusion of the plasticizer. We anticipate that future work with reduced initiator deposition times and controlled emersion will reduce plasticizer migration during initiator deposition.

Table 1
Water contact angles for modified PVC substrates

Sample description	θ°_a	θ°_s	θ°_r
PVC	82 ± 2	74 ± 2	67 ± 2
PVC-g-PHEMA	61 ± 3	57 ± 3	47 ± 4
PVC-g-PHEA	61 ± 3	57 ± 4	45 ± 3
PVC-g-PDMAEMA	71 ± 2	66 ± 3	57 ± 2
PVC-g-PAA	62 ± 4	57 ± 4	49 ± 5
PVC-g-PDMA	46 ± 4	42 ± 3	34 ± 1
PVC-g-P4VP	67 ± 5	64 ± 4	56 ± 5

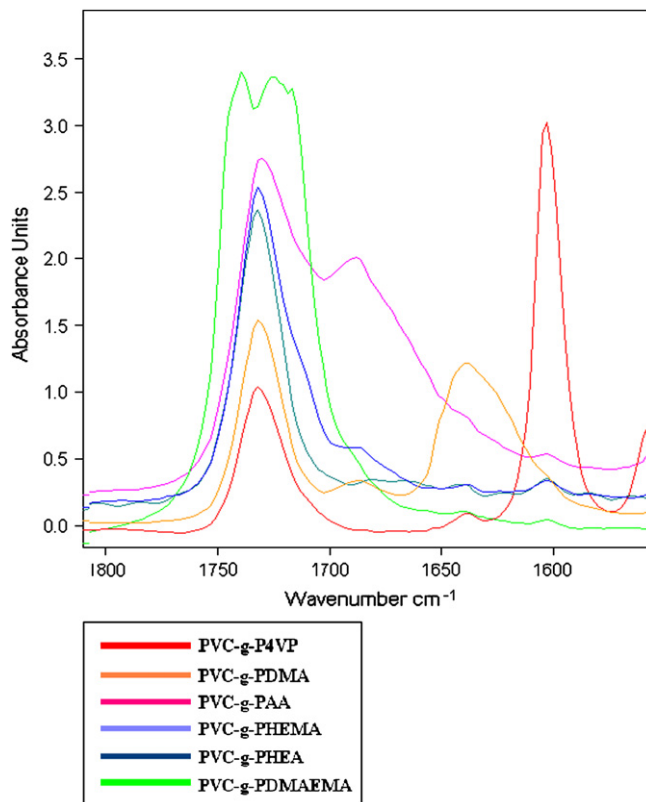


Fig. 1. Transmission IR spectra of modified PVC films.

3.2. Surface wettability of modified PVC

The modified PVC films were characterized by using water contact angles (Table 1). The advancing water contact angle of PVC is 82 ± 2°, the static angle is 74 ± 2° and the receding angle is 67 ± 2°. After surface modification the contact angles decreased significantly, consistent with the presence of a hydrophilic material on the surface. Literature values of the hydrophilic polymers verify that PHEMA (63°) [17], PHEA (69°) [18], PDMAEMA (65°) [19], PAA (45–50°) [20], PDMA (42°) [21] and P4VP (68°) [22] are present at the surface. For example, the PHEMA grafted film exhibits advancing and receding water contact angles of 61 ± 3° and 45 ± 4° which are similar to literature values.

3.3. Transmission IR spectroscopy

Surface characterization of the modified PVC films was carried out by transmission IR of the films. Fig. 1 shows the spectra of the modified PVC films in the carbonyl absorption region (1640–1800 cm⁻¹). Pure PVC is not typically known to have a carbonyl absorption. However, if the polymer has been partially oxidized during manufacturing or contains plasticizer, a carbonyl absorption is observed. Our starting PVC films display a carbonyl absorption at 1732 cm⁻¹ which we have assigned to a phthalate plasticizer. The

Table 2
XPS data of PVC modified and unmodified films

Sample description	C1s (%)	O1s (%)	Cl2p (%)	N1s (%)	C/O	C/N
PVC	71.0	22.6	6.4	0	3.1	N/A
PVC-g-PHEMA	68.1	23.9	6.8	1.2	2.8	56.8
PVC-g-PHEA	66.4	23.5	8.5	1.6	2.8	41.5
PVC-g-PDMAEMA	73.0	16.4	4.4	0.7	4.5	104
PVC-g-PDMA	66.9	25.2	4.6	3.3	2.7	20.3
PVC-g-PAA	66.1	31.6	1.9	0.4	2.1	165
PVC-g-P4VP	76.0	10.6	9.5	3.6	7.2	21.1

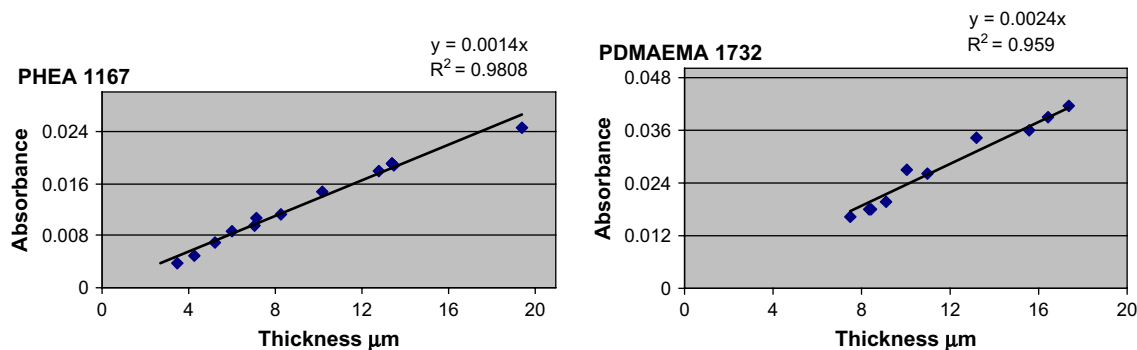


Fig. 2. Free PHEA and PDMAEMA absorbances vs. thickness calibration curves.

spectra of all modified films contain this absorption at 1732 cm^{-1} as well as additional carbonyl absorptions corresponding to the grafted polymer.

PVC-g-PHEMA, PVC-g-PHEA and PVC-g-PDMAEMA exhibit carbonyl absorptions that overlap with the plasticizer carbonyl absorption. PVC-g-PAA, PVC-g-PDMA and PVC-g-P4VP have additional absorptions at 1687 , 1640 and 1600 cm^{-1} , respectively. The peak at 1600 cm^{-1} is assigned to a C=N stretch. PVC-g-P4VP has the capability of possessing antimicrobial properties upon quaternization with various alkylating agents, which shifts the C=N stretch to 1640 cm^{-1} . These systems are currently under investigation and will be explained in a subsequent paper.

3.4. XPS analysis

Surface characterization with XPS probed the elemental composition roughly 5 nm beyond the film surface. Table 2 contains the percentage of oxygen, nitrogen, carbon and chlorine found at 530 , 400 , 285 and 200 binding electron volts, respectively. The neat PVC film was found to have the elements C, O and Cl at the surface. The presence of oxygen indicates the presence of plasticizer or oxidized PVC. The PHEMA and PHEA modified films exhibited absorptions for C, O, Cl and N, indicating that PVC was not completely or uniformly covered relative to the penetration depth of the XPS technique. The presence of nitrogen can be attributed to AIBN decomposition products. The percent oxygen present in the PAA modified sample increased to 31.6% and the percent chlorine decreased to 1.9% suggesting that the surface is more uniformly covered with modified polymer. The increase of percent nitrogen for the PDMA modified sample was expected. Although it is difficult to compare the experimental results with theoretical percent approximations due to the unknown concentration of plasticizer or defects, the results corroborate the successful attachment of hydrophilic monomers to PVC.

3.5. Measurement of grafted polymer thickness

Three methods were used to determine thickness: IR calibration, gravimetric analysis and UV-vis calibration.

Table 3
Thickness values for grafted layer on PVC as determined by FT-IR calibration curves

Sample description	Equation ^a (cm)	Thickness (μm)
PVC-g-PHEMA	$y = 0.0007x$	27.5
PVC-g-PHEA	$y = 0.0014x$	17.1
PVC-g-PDMAEMA	$y = 0.0024x$	6.7
PVC-g-PAA	$y = 0.0039x$	0.6
PVC-g-PDMA	$y = 0.0036x$	1.6
PVC-g-P4VP	$y = 0.0028x$	5.3

^a The equation was calculated with Microsoft excel by plotting thickness (x) vs. absorption (y) for all free polymers.

3.5.1. IR calibration curve

IR calibration curves were constructed via ellipsometry and transmission IR of free polymer films on silicon wafers. The Beer-Lambert law was utilized to plot absorbance vs. thickness for all free polymers as seen in Fig. 2. The absorbance value chosen for the hydrophilic polymer must be unique to the PVC spectrum, otherwise the thickness will also account for PVC (plasticizer). Therefore, the C–O stretch was used for polymers that had overlapping carbonyl absorptions with PVC unless a background subtraction of PVC was performed. The equations were used to calculate thickness of the grafted polymer layer when the absorbance (y) of the modified PVC film was known (Table 3). With this technique, grafted films were shown to have thickness values ranging from approximately 1 to $10\text{ }\mu\text{m}$ for PAA, PDMA, PDMAEMA and P4VP and 18 to $28\text{ }\mu\text{m}$ for PHEA and PHEMA.

It is important to point out that the absorbance values used for the thickness calculations exceeded values of 2 in some cases which may cause deviations in the use of the Beer-Lambert law. Also, thickness calculations were based on calibration curves for much thinner polymer films and thus we extrapolated the curves beyond the higher absorbance value of the calibration curve. The authors

Table 4
Thickness values for grafted layer to PVC as determined by gravimetric analysis

Sample description	Solvent ^a	Area ^b (cm^2)	Weight ^c (g)	Thickness ^d (μm)
PVC-g-PHEMA	THF or MEK	92.09	0.3438	16.2 ± 0.1
PVC-g-PHEA	MEK	63.57	0.1284	8.7 ± 0.1
PVC-g-PAA	MEK	78.47	0.0865	4.79 ± 0.07
PVC-g-PDMA	Cyclohexanone	75.83	0.4543	26.0 ± 0.2
PVC-g-P4VP	MEK	114.62	0.1682	6.38 ± 0.07

^a The solvent used for selective dissolution in gravimetric analysis.

^b The area of the modified film before gravimetric analysis.

^c The weight of the collected material upon selective dissolution.

^d Error calculated by propagation.

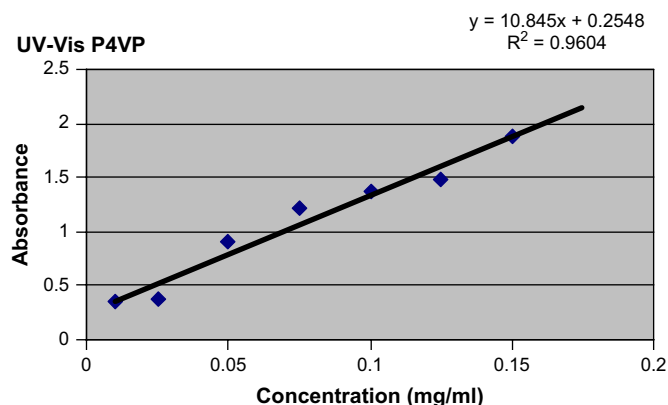


Fig. 3. UV-vis calibration curve for P4VP.

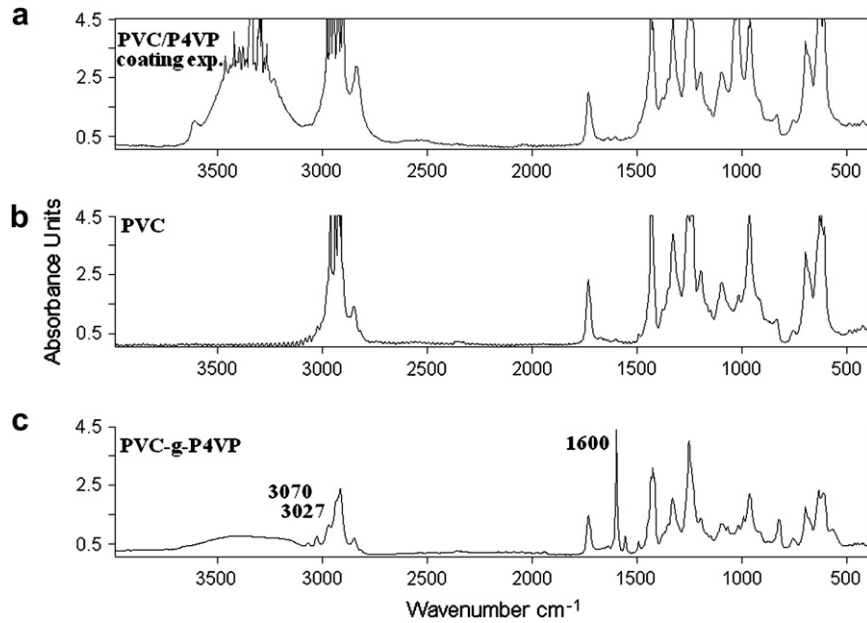


Fig. 4. IR spectra of (a) PVC after coating experiment with P4VP, (b) PVC and (c) PVC-g-P4VP.

recognize these inherent weaknesses in this thickness measurement method. However, as seen in the next section, there is a reasonable correspondence to thickness values determined by a gravimetric method so we ascribe value to this IR method.

3.5.2. Gravimetric analysis

A film of PVC (78.5 cm²) underwent the simple two-step grafting polymerization with HEMA. The modified film was weighed (1.954 g) and placed into 150 mL of THF where the PVC chains that were not covalently bonded to PHEMA dissolved while the PHEMA covalently grafted to PVC chains did not. The solids were collected upon centrifugation, dried and weighed (0.343 g). The thickness of the grafted PHEMA was then calculated from the following equation:

$$(W \times \rho^{-1} \times A^{-1})/2 = H$$

where W = weight of PVC chains grafted to hydrophilic polymer, ρ = density of polymer, A = area of film and H = thickness of hydrophilic graft.

The factor 1/2 is necessary because the weight is associated with the weight of grafted chains on both sides of the film. Table 4 identifies the solvent used for selective dissolution, the area of PVC modified, the weight of the grafted chains and the calculated thickness values. Even though the thickness value should be greater than the thickness value via IR (because this method includes the grafted PVC), they are comparable for the PHEMA, PHEA, PAA and P4VP systems. We were not able to use the gravimetric method for PVC-g-PDMAEMA because we could not find a selective solvent.

3.5.3. UV-vis calibration

The UV-vis spectrum for free P4VP in DMF exhibited an absorbance at 267 nm for the pyridine ring. Multiple solutions were made ranging in concentration from 0 to 0.15 mg/ml. Each solution gave a corresponding absorbance value at 267 nm that was used to construct the calibration curve shown in Fig. 3. The equation was used to determine the concentration (x) when there was a known absorbance for the PVC-g-P4VP film (0.163). The calculated thickness for the grafted P4VP is 18.5 μm . The thickness of other

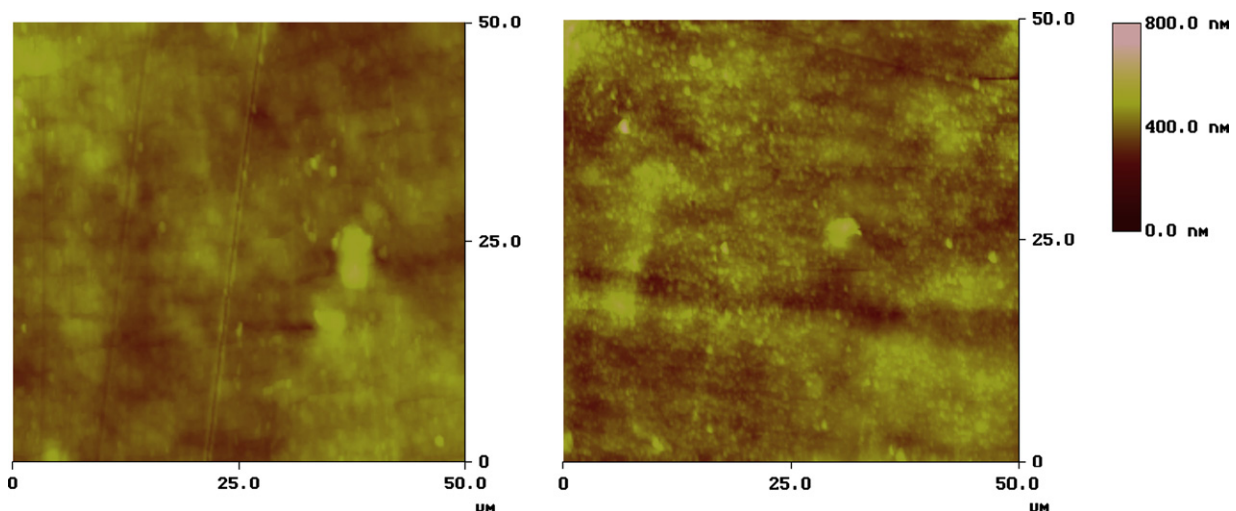


Fig. 5. AFM images of untreated PVC (left) and PVC-g-PHEA (right).

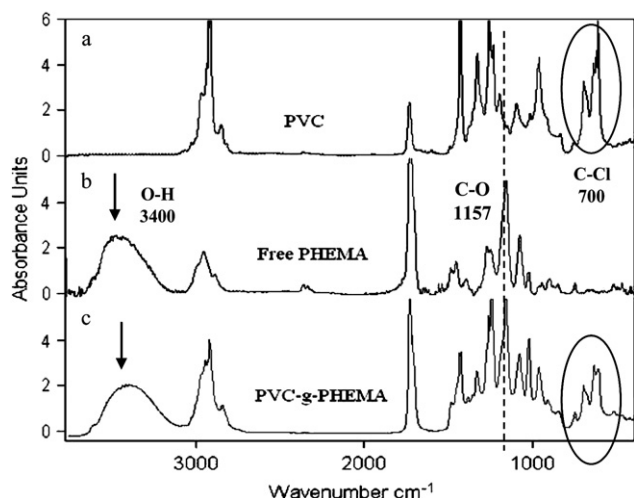


Fig. 6. IR spectra of PVC (a), free PHEMA (b) and PVC-g-PHEMA (c).

modified PVC films could not be determined by this technique because the hydrophilic polymers absorb in the same range as the solvent.

Determination of the thickness of the grafted layer on PVC was challenging. While agreement between the IR and gravimetric methods was good in all cases, the two methods indicate a typical grafted layer thickness is in the range of 1–30 μm . The layer thicknesses for the PVC tubing are in the range of 23–100 μm . Because the thickness is not in the typical nanometer range of grafted polymers, a coating experiment was performed to verify that no free polymer penetrated the surface of PVC accounting for the unexpected thickness results.

3.5.4. Coating of hydrophilic polymers to PVC

Both PHEMA and P4VP were added to a separate flask that contained a sample of PVC film and MeOH. The hydrophilic polymer was dissolved at 70 $^{\circ}\text{C}$ under nitrogen overnight. Samples were subsequently cleaned exhaustively by the same procedure as described before. Comparison of the IR spectra for the PVC film before and after the PHEMA coating experiment did show a discrepancy in the appearance of an O–H bend at 3300 cm^{-1} ; however, this is attributed to the exposure to MeOH and insufficient drying since there was no C–O peak present at 1078 cm^{-1} after coating. Similarly, the P4VP coating experiment showed no discrepancy at 1600 cm^{-1} or above 3000 cm^{-1} (aromatic C–H stretching) as seen in the comparison to IR spectra for PVC and

PVC-g-P4VP films (Fig. 4). The contact angle measurements after attempted coating with PHEMA are 76 ± 2 (s), 79 ± 2 (a) and 67 ± 4 (r), respectively. Measurements are consistent with a PVC hydrophobic surface and thus confirm that these hydrophilic polymers do not have tendency to absorb into PVC.

3.6. Surface roughness of PVC

Fig. 5 displays the comparison of the surface roughness between unmodified PVC and PVC-g-PHEA. We speculate that the small clusters are consistent with an increased roughness. We attribute these areas to grafted polymer. The rms roughness for the PVC-g-PHEA sample was 35 nm compared to 18 nm for untreated PVC. While the rms roughness only changed on the nanometer scale, local changes in thickness were much larger given the micron thick coatings. A rms roughness reflects an average over a larger area than individual chains.

3.7. Evidence for covalent attachment

Transmission IR was performed on the starting materials, free polymer and modified PVC films to substantiate covalent attachment by the presence of functional groups. GPC and elemental analyses were performed on the PVC-g-PHEMA sample collected during gravimetric analysis. For the PHEMA modified system, free PVC chains are soluble in THF while the PVC-g-PHEMA chains remain insoluble. The isolated PVC-g-PHEMA was used to prove covalent attachment via GPC and elemental analyses. Also a controlled experiment for radical generation verified radical generation at the surface of PVC.

3.7.1. Transmission IR

All modified PVC samples were exhaustively cleaned to remove any free polymer before transmission IR was performed. Fig. 6 compares the spectrum of PVC-g-PHEMA, starting PVC and free PHEMA. The occurrence of the broad O–H bend at 3400 cm^{-1} and the C–O stretch at 1157 cm^{-1} confirms the presence of PHEMA in the modified sample as well as the existence of PVC based on the C–Cl stretch at around 700 cm^{-1} .

3.7.2. Gel permeation chromatography

The chromatograms of starting material, free PHEMA and the PVC-g-PHEMA samples were obtained (Fig. 7). Fig. 7a shows the chromatogram for the PVC sample in THF, $M_n = 40,700$ g/mol. The PVC-g-PHEMA sample collected by selective dissolution was analyzed in DMF (b) and compared with free PHEMA (c). Both

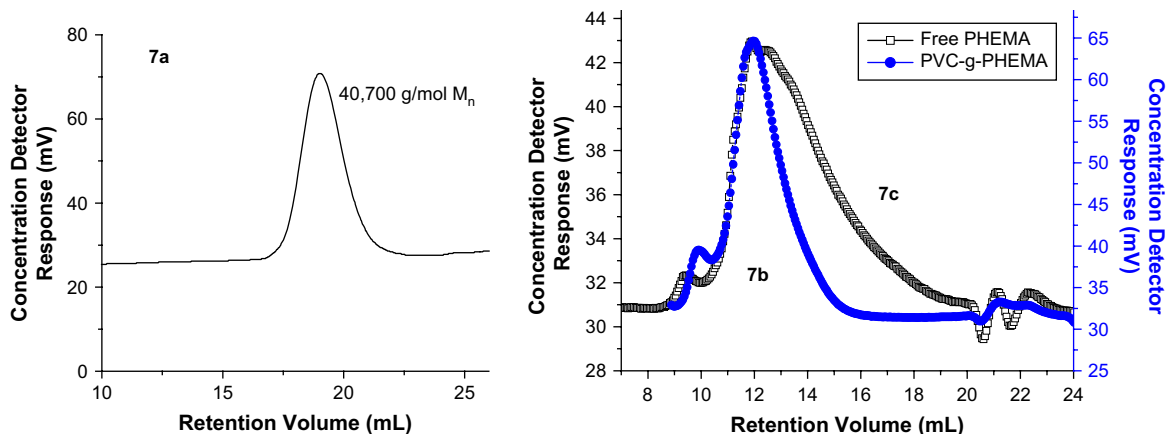


Fig. 7. GPC of PVC (left), free polymer and PVC-g-PHEMA.

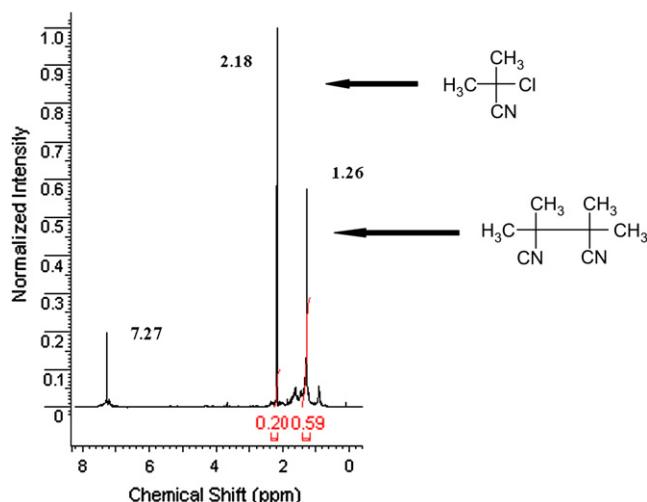


Fig. 8. ^1H NMR spectra of chlorine capped AIBN radicals (CDCl_3).

peaks have a broad distribution and a shoulder which is attributed to uncontrolled free radical polymerization. The M_n of free PHEMA was 23,000 g/mol while that of the PVC-g-PHEMA was 85,000 g/mol. The M_n of PVC-g-PHEMA should exceed the sum of the M_n for PVC and free PHEMA (63,700 g/mol), assuming that the molecular weight of free PHEMA is similar to that of the grafted PHEMA.

3.7.3. Elemental analysis

The elemental analysis of the PVC-g-PHEMA collected by selective dissolution revealed 57.83% carbon, 8.00% hydrogen, <0.5% nitrogen, 29.76% oxygen and 1.67% chlorine. If the sample was PHEMA alone, the expected percentages would be 54.95% carbon, 8.45% hydrogen and 36% oxygen. The increase in carbon and chlorine percentages in addition to the decrease in oxygen and hydrogen percentages confirms both vinyl chloride and HEMA units are present in the isolated material.

3.7.4. Control experiment for radical generation

A piece of initiated PVC film was placed into a round bottom flask with the same polymerization conditions, excluding the monomer. By excluding the monomer, it was possible to examine how the AIBN radicals would interact with the PVC surface. According to the proposed mechanism, the radicals should abstract either a chlorine or hydrogen from the PVC backbone. After the reaction ran overnight, the solution was evaporated into a weighing pan. The residue was analyzed by NMR (Fig. 8) and IR (Fig. 9) spectroscopies. Both characterization methods were consistent

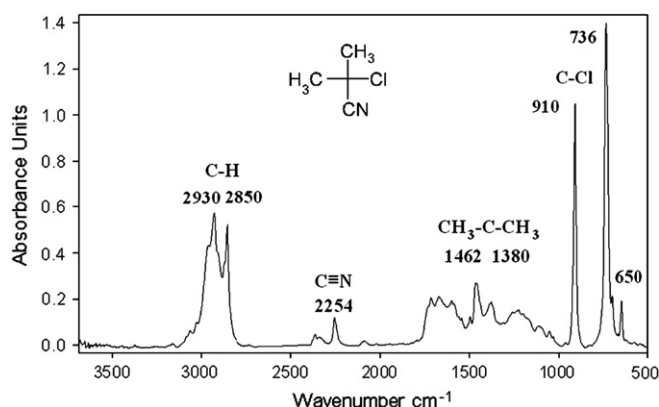


Fig. 9. Transmission IR of chlorine capped AIBN radical.

Table 5

Water contact angles and thickness values for modified PVC tubing

Sample description	Eluent ^a	h^b (cm)	θ^c	Thickness ^d (μm)
PVC-g-PHEMA	Deionized water	0.41	59	22 ± 1
PVC-g-PHEA	Ethylene glycol	N/A	N/A	36.6 ± 0.7
PVC-g-PAA	Ethylene glycol	0.68	52	58.6 ± 0.7
PVC-g-PDMA	Ethylene glycol	0.70	50	99.8 ± 0.7
PVC-g-P4VP	Ethylene glycol	0.80	43	59.4 ± 0.7
PVC	Ethylene glycol	0.13	83	N/A

^a The solvent used as an eluent with capillary rise experiments.

^b The height at which the eluent rose measured from the liquid vapor surface to the meniscus.

^c The angle at which the solvent met the wall, calculated via the Young–LaPlace equation.

^d Error calculated by propagation.

with preferential chlorine abstraction ($\Delta H_{\text{C-Cl}} = 81$ kcal/mol) over hydrogen ($\Delta H_{\text{C-H}} = 98$ kcal/mol) [23]. The NMR exhibits two singlets at 2.18 and 1.26 ppm indicative of the methyl hydrogens of the chlorine capped product and the combination byproduct, respectively. The integration of peaks is 1:3. If the hydrogen capped product was present, there would be two peaks at 2.8 and 1.3 ppm with integration 1:6. The transmission IR also confirms the presence of the chlorine capped AIBN radical. Absorptions at 2254, 1380 and 736 cm^{-1} are indicative of the nitrile, gem-dimethyl and C–Cl absorptions, respectively.

3.8. Grafting inside PVC tubing

PHEMA, PHEA, PAA, PDMA and P4VP were grafted on the interior of PVC tubing. The modified PVC tubing was characterized by capillary rise and gravimetric analysis.

3.8.1. Capillary rise

The Young–LaPlace equation describes the phenomenon of capillary rise.



Fig. 10. Picture of PVC-g-PHEMA tube in THF. The inside of the tube appears white because the PHEMA that is grafted to the interior chains is not soluble in THF.

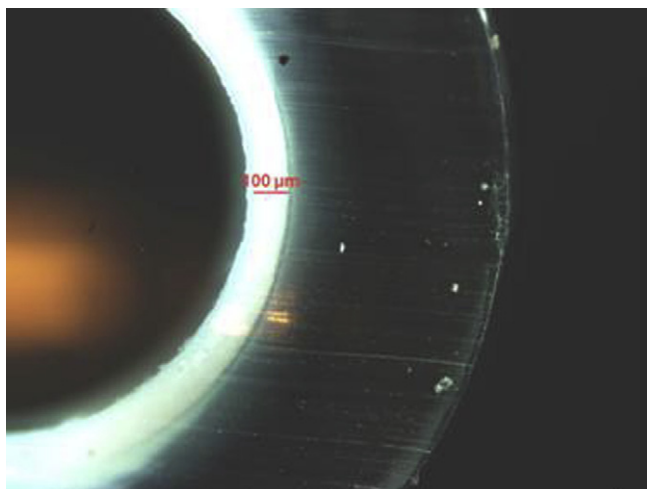


Fig. 11. Digital microscopic image of PVC-g-PDMA in air. The inner white layer represents PDMA grafted chains approximately 100 μm thick.

$$\gamma = \Delta\rho ghr / 2\cos\theta,$$

where θ is the contact angle, $\Delta\rho$ (g cm^{-3}) is the density difference of the liquid and air, g (cm s^{-2}) is the acceleration of gravity, h (cm) is the rise of the liquid, r (cm) is the radius of the tube and γ (g s^{-2}) is the air–liquid surface tension. Ethylene glycol was used for unmodified PVC and modified PDMA, P4VP and PAA tubings. Water was used for PHEMA modified PVC tubing. The decrease in contact angle (Table 5) of all modified PVC tubings relative to PVC indicates increased surface wettability that is comparable to modified flat film contact angles. For example, the water contact angle of 59° for PVC-g-PHEMA tubing is relatively close to the film contact angle of 57° .

3.8.2. Gravimetric analysis

Similar to the procedure of film gravimetric analysis, a piece of modified tubing was immersed in a specific solvent for selective dissolution of unmodified PVC chains. The PVC chains that are covalently attached to the grafted polymer were collected by centrifugation, dried and weighed. The weight can be converted to volume and the volume of the grafted hydrophilic polymer is equivalent to:

$$V = \pi h [(r_{\text{outer}})^2 - (r_{\text{inner}})^2],$$

where r_{inner} is the radius of the modified PVC tube and r_{outer} is the radius of the initial unmodified PVC tube. Upon dissolving the PVC-g-PHEMA tube into THF, the free PVC chains went into solution while the PHEMA covalently bound to PVC chains did not, depicted in Fig. 10. The free PVC chains are visible and transparent because the picture was taken immediately after immersion into THF. After 5 min, the only visible matter was the grafted chains. This sample was collected upon centrifugation, dried and weighed (0.213 g). All modified film thickness values are listed in Table 5.

The PVC-g-PDMA tubing gave a gravimetric thickness result for the grafted chains that was analogous to digital microscopic

measurements. Without solvent, the PDMA graft appeared opaque in visible light, while the PVC tubing remained transparent. Fig. 11 displays the same phenomenon of two distinct layers with different refractive indices for PVC-g-PDMA. The inner grafted layer (white) is slightly less than the scale bar measurement of 100 μm, similar to gravimetric measurement of 99.82 μm.

4. Conclusions

Analogous to the surface modification of PDMS [14], we have covalently attached hydrophilic monomers onto the hydrophobic PVC polymer surface by an experimentally simple polymerization design which involves the following steps: (1) physisorbed attachment of AIBN onto the surface of PVC, followed by (2) radical graft polymerization of the hydrophilic monomers onto the polymer surfaces. The thickness, roughness and chemical composition of the grafted layers were determined. Our method offers the possibility of modifying complex geometries of PVC.

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