

Review

Recent Progress in Surface Modification of Polyvinyl Chloride

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Abstract: Surface modification of polymers has become a vibrant field of research on account of a myriad of rationales which stimulated numerous efforts. The current paper serves as a condensed survey of the advances made through different approaches adopted for tuning the surface properties of polyvinyl chloride as a homopolymer extensively used on a large scale. Though it does not address all challenges involved, this paper communicates and highlights, through concise discussion, the findings of the efforts undertaken in recent decades. It is ultimately concluded with a perspective of the huge capacities and promising future directions.

Keywords: polyvinyl chloride; surface modification; surface treatment

1. Introduction

Many interactions among different materials in contact take place at surfaces/interfaces. Besides the ambient factors such as pressure, pH and temperature, the interactions are largely controlled by interplay of surface hydrophilicity, topography, and chemical composition. This implies that manipulating the surface characteristics in terms of physicochemical aspects may guide the

interactions to a sought-after direction. A broad spectrum of applications are met spanning from simple coatings to complicated biological adsorptions [1,2].

Polyvinyl chloride (PVC) faces many challenges due to the hydrophobic nature of the polymer surface. The current opinion is that the surface hydrophobicity may bring forth severely adverse consequences, in particular when such materials are exposed to biological systems. This has motivated extensive research during recent decades seeking efficient means to figure out the problem [3]. A clear consensus of the findings points to exploiting the surface modification techniques as a straightforward solution for the issue which does not impair bulk properties [4,5].

PVC is the second most widely used polymer in terms of consumption volume accounting for a global production of over 25 million tons per annum. It has mostly found applications in the medical field where it covers around 28% of total plastics use, ranked after polyethylene and before polystyrene [6]. The phthalate ester plasticizers typically used to soften PVC are considered as potential carcinogens and are inclined to leach away and diffuse into the environment [7,8]. Besides intimate hydrophobicity and low surface free energy, PVC suffers from poor biocompatibility, unwanted protein adsorption, and bacterial adhesion [9]. To alleviate the severity of these problems, different approaches have been adopted. Of particular significance are those strategies based on surface treatment, whereby great advances have been made within the last three decades to fine-tune the surface properties and decrease the plasticizer migration. The focus of the current report is to present concisely the existing knowledge in the available literature surrounding the efforts made on the surface modification of PVC in terms of surface physics and chemistry followed by the intended applications.

2. Strategies for PVC Surface Treatment

Several strategies for PVC surface treatment are available. In some cases, it is necessary to utilize two or more techniques consecutively to gain the desired modification level. Nonetheless, all various methods for surface modification have more or less common interests from chemical and physical viewpoints. The methods engineer the surface by introducing superficial functionalities, by which many surface characteristics such as hydrophilicity, roughness, *etc.* can be regulated to a great extent. This often makes the controlled modification of the surface intended for a certain application a demanding project. In the following paragraphs, a short background is given on different techniques employed for the surface modification purpose. More comprehensive information can be found in notable reviews [4,5,10–20].

Plasma treatment is an extensively used technique of enormous potential for surface modification. Plasma is defined as a partially ionized gas containing free electrons, ions, and radicals, as well as neutral particles. It is an active environment where several different interactions between energetic particles and the surface may occur. The interactions are classified as plasma polymerization, plasma functionalization, and plasma etching/ablation. In plasma polymerization, an organic monomer in solution or vapor phase is polymerized, that is, grown while attached onto the substrate by one end, and developed into a coating. In plasma functionalization, depending on the medium identity, various chemical groups are attached to the surface. The last interaction involves removal of the surface entities through strong collision with plasma particles [21–23].

High energy irradiation category includes γ -radiation, β -irradiation (electron beam), and ion radiation. The latter is widely used to achieve either ion implantation at the top surface layer or to deposit coatings. For this purpose, several ions like hydrogen, noble gases, gold, *etc.* are employed. High energy photons can deliver surface radicals which act as initiating sites for subsequent functionalization. For the treatment of polymers, additional simultaneous chemical effects are also probable, e.g., free radical recombination and crosslinking, as well as chain scission [24–26].

Ultra violet (UV) treatment is widely applied as a surface modification technique usually in the presence of a photoinitiator/photosensitizer and induces a combination of functionalization and ablation reactions. UV can be put to use in various environments with different physical states. Surface grafting of polymers can be performed easily via this technique. The extent of surface modification may be well controlled by fine-tuning the irradiation time, monomer concentration, photoinitiator, and solvent. The solvent selection is very critical in this context, to avoid which the treatment can be run in vapor phase [27–29].

Exposure of the material surface to ozone gives rise to surface oxidization as a consequence of O_3 formation-decomposition combined reactions. This can be carried out also along with UV irradiation to favorably guide the reaction kinetics. However, degradation is an unwanted phenomenon which may arise after ozone treatment and can be controlled somewhat by adjusting the exposure time. The technique is usually employed as pre-treatment after which grafting of certain chemical entities can be accomplished [30–32].

A classic method of current use includes the wet chemical means, where chemical reactions are allowed to take place between a compound dissolved in an organic solution and polymer surface. Aminolysis and alkaline or acidic hydrolysis represent typical instances. Oxidation of the surface by hydrogen peroxide is regarded as a wet chemical method as well, where the introduced hydroperoxide entities serve as initiation sites for subsequent functionalization steps. Hydroxyl and carboxyl terminals are generated when the functionalities are hydrolyzed through bond scission [33].

A recent technique of attraction is surface-initiated polymerization mostly fulfilled through wet chemical methods giving rise to brush-like structures. By this technique, grafting polymers onto solid substrates is feasible leading to the formation of high density, end-tethered polymer brushes. In usual cases, a surface-confined initiator is exploited for graft polymerization, provided that the reaction proceeds via state-of-the-art mechanisms like atom transfer radical polymerization (ATRP), a precision surface modification is then possible [34–38]. Polymer brushes can be prepared via the grating-to approach as well; however it usually yields low grafting density [16,39].

The direct immobilization of natural entities such as biotin, heparin, insulin, and amino acids has also been carried out extensively in order to impart various biological applications. In this context, numerous bioconjugation techniques have been developed to facilitate the immobilization, among which carbodiimide coupling of carboxylic groups with primary amines is of paramount importance. Indeed, many attempts have focused on introduction of carboxylic groups onto the surface and then their activation in order to employ this coupling method [40,41]. Last but not least, a state-of-the-art approach for surface modification is self-assembly. It is described as a process by which a disordered system of preformed components develops an organized structure or pattern by virtue of specific, local interactions among the components themselves without external direction. As regards the surface, self-assembled monolayers can be constituted on the surface via hydrophobic interactions in this way.

In order for this method to be applicable on polymers, a block copolymer with an amphiphilic tendency is needed as an intermediate [19,20].

3. Research Highlights of PVC Surface Treatment

The attributes of polymer surfaces are strongly correlated with respective physicochemical factors. It goes without saying that any surface treatment targets the properties in terms of two critical aspects, surface chemistry and physics, which also governs bioactivity, dielectric, optical, and mechanical properties. The current overview addresses the PVC surface modification reports from these two fundamental standpoints.

3.1. Surface Chemistry

Surface chemistry is the principal factor determining the majority of the polymer surface properties. It fundamentally refers to the molecular structure and organization at the surface which is also a measure of the propensity of the substance to undergo surface reactions [42]. The surface of virgin, pure PVC is mostly rich in C–C, C–H, and C–Cl moieties and is thus hydrophobic. The minimal defects which occur upon manufacturing cause oxidation (C–O), unsaturation (C=C), and branching. Surface chemistry can be altered via physicochemical interactions after almost any strategies mentioned above to make the PVC tailored for a specific application. It is noteworthy that plasticized grades of PVC also contain a considerable amount of single and carbonyl bonds which affect the surface polarity and might bring out some confusion when interpreting the chemical data after surface modification.

The major research in this field has been conducted on the influence of plasma treatment under different working environments on PVC surface chemistry [43–66]. This may be because of the solvent-free basis of the method which is of importance from an environmental viewpoint. However, it lacks precision control on the surface chemistry and is usually expensive. It was seen that treating PVC surface in plasma led to the C–C, C–Cl, and C–H bonds scission since the induced energy exceeded the bonds dissociation energy [43–53]. Plasma exposure in an inert gas gave rise to the generation of metastable species, that is, carbon radicals (Figure 1) on PVC surfaces which could either form a crosslinked network or be oxidized to give new functionalities, in case the treated surface was exposed to air [43–58]. Provided oxygen or air was operated as the working gas, carbonyl, carboxyl, peroxide, and ester groups were most probable to form [59]. This is why the treated surface was found to be predominantly negatively charged, as demonstrated in Figure 2 [60]. It was observed that the level of the surface chemical changes directly depended on the plasma discharge voltage and inversely on the working pressure [44]. The sample position from the plasma source could affect the surface modification extent (Table 1). The researchers reported that plasma treatment in remote configuration could enhance radical reactions and hinder electrons and ion ablation interactions and found it more effective than direct plasma treatment when it came to the dechlorination of PVC films [61,62].

Figure 1. Electron spin resonance spectra of pristine and plasma-treated PVC surfaces (Reprinted with permission from [45]. Copyright 2008 Elsevier).

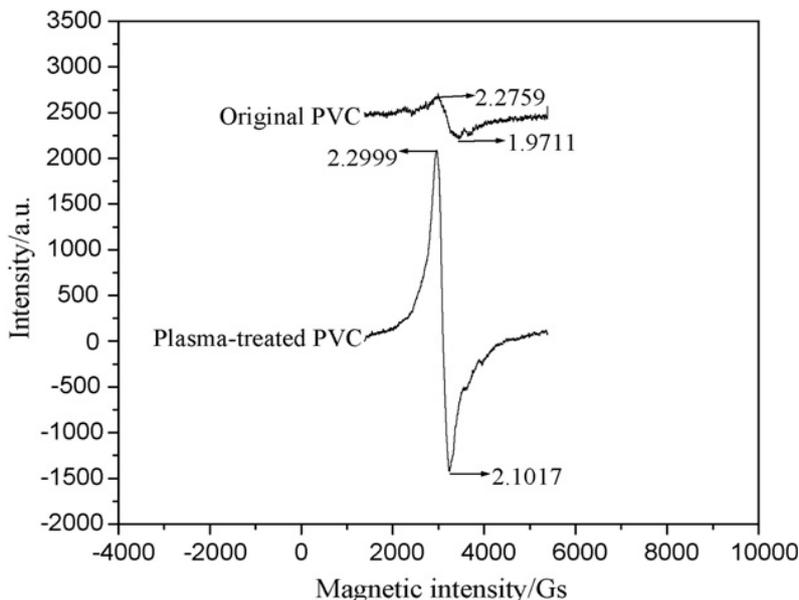


Figure 2. Zeta potential values of (1) untreated PVC; (2) plasma-treated PVC; and (3) 24 h after plasma treatment. The last sample is indicative of recovery (Reprinted with permission from [60]. Copyright 2007 Elsevier).

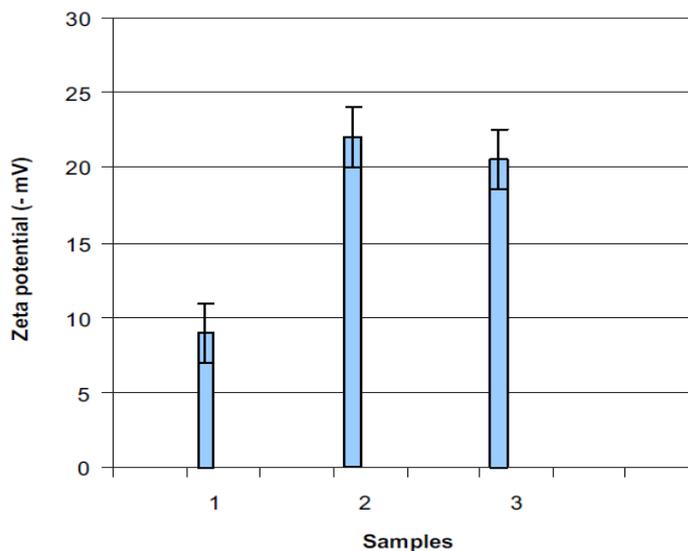
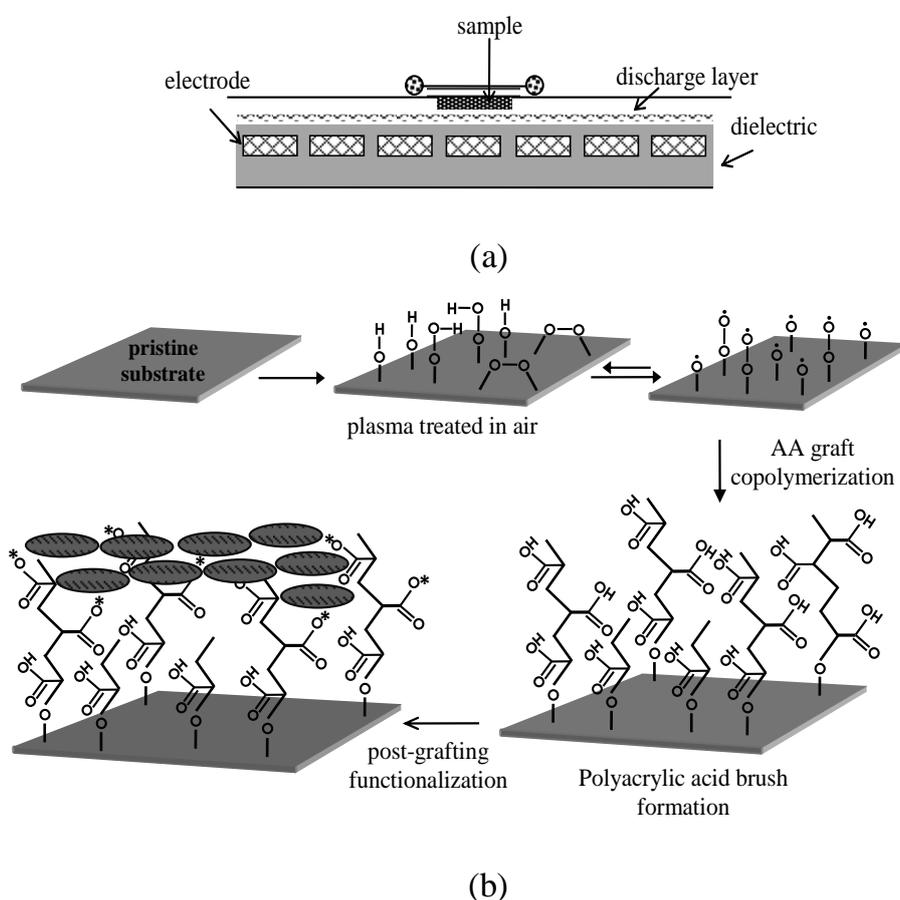


Table 1. X-ray photoelectron spectroscopy atomic composition of remote and direct argon plasma treated PVC at 60 W for 3 min (Adapted from Ru *et al.* [62]).

Plasma type	C1s Component (%)			O1s Component (%)		Atomic ratio	
	C-H	O-C C-Cl	C=O O-C=O	O=C	O-C	O/C	Cl/C
Untreated	83	15	2	–	~100	0.06	0.14
Direct treatment	67	19	14	40	60	0.15	0.03
Remote treatment	73	18	9	53	47	0.018	0.01

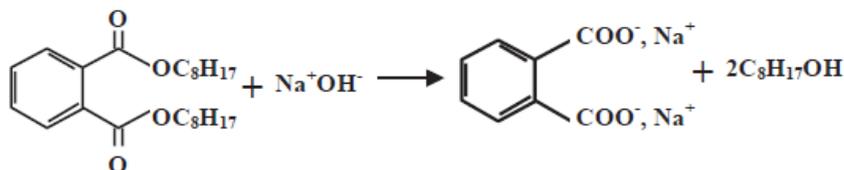
Post-plasma grafting and immobilization have been extensively carried out for subsequent PVC surface treatment [48–50,53,63–65]. Asadinezhad *et al.* [48–50] used diffuse coplanar surface barrier discharge (DCSBD) plasma to polymerize acrylic acid (AA) groups onto PVC surface in high density. The plasma generated surface radicals acted as the initiators for the acrylic acid radical graft polymerization in room temperature. The carboxyl groups of the polyacrylic acid brush were then exploited for further functionalization (Figure 3). Zhang *et al.* [53] coated PVC surface with bronopol and triclosan after argon plasma treatment and found that bronopol and triclosan were well attached to the activated surface while retaining their structure. Hu *et al.* [63] successfully immobilized benzyltrimethylammonium cationic groups onto PVC using low pressure argon plasma grafting, quarterization, and alkalization. Liu *et al.* [64] treated PVC under SO_2/O_2 gas plasma and found that sulfonic acid groups were selectively introduced onto the surface. Balazs *et al.* [65] effectively modified PVC films by monovalent silver through oxygen glow discharge plasma, followed by a two-step post-plasma treatment in sodium hydroxide and silver nitrate solutions (Scheme 1). The saponification with sodium hydroxide of esters produced sodium carboxylate and sodium phthalate salts. In some contrast to the foregoing reports, Anuradha *et al.* [66] could not find significant changes in surface chemistry of PVC after modifying by plasma glow discharge in vacuum. Although, when the polymer was exposed to plasma, it could expand and produce free volume among the chains; hence, the surface ions or segments could move into the free volume.

Figure 3. A schematic graph of (a) DCSBD plasma device; (b) multistep approach pursued to modify PVC surface (Reproduced with permission from [50]. Copyright 2010 MDPI).

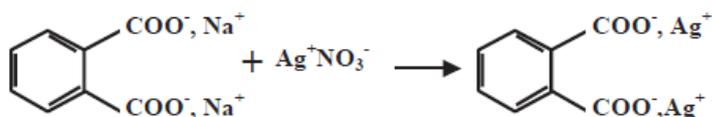


Scheme 1. Chemical modification of PVC through sodium hydroxide and silver nitrate wet treatments (Reprinted with permission from [65]. Copyright 2004 Elsevier).

Step 1 - Creation of sodium phthalate



Step 2 - Trapping of silver ions



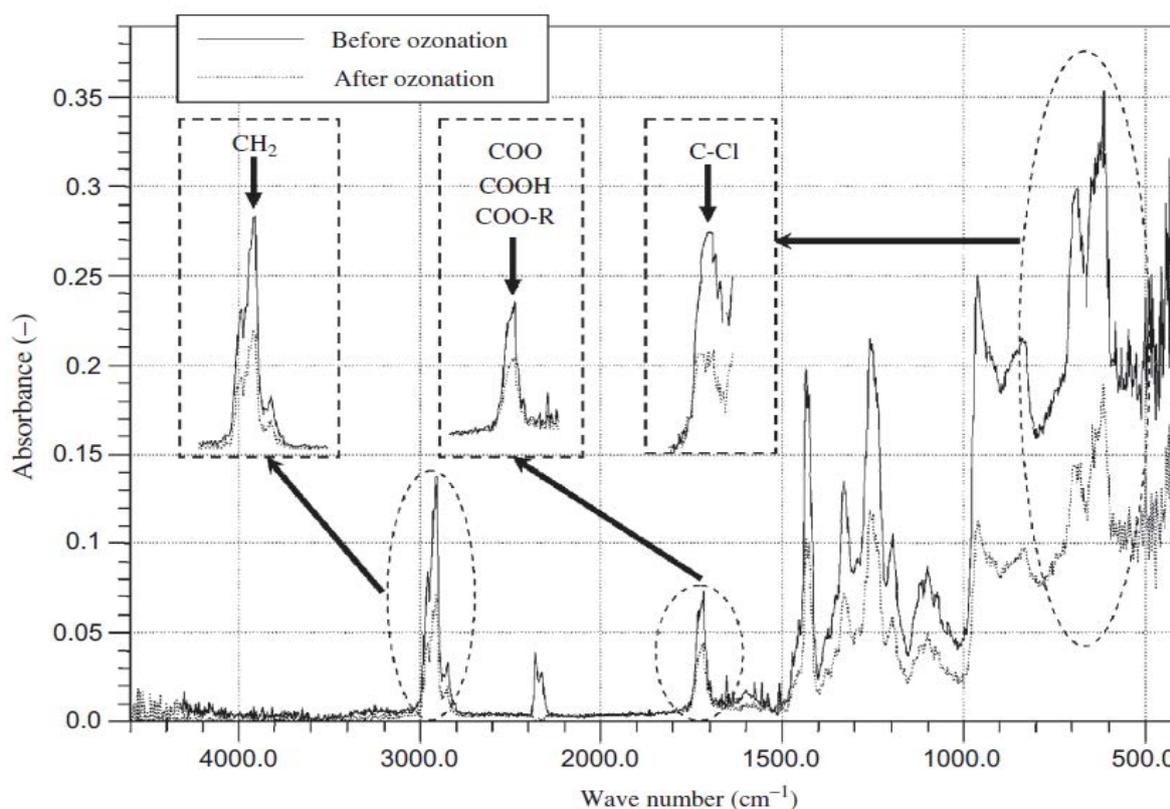
As an alternative to plasma exposure, high energy irradiation (electron, gamma, and UV radiation) has been utilized to alter the PVC surface in terms of chemistry meant for various intents [67–73]. Such methods, despite requiring rather expensive equipment, are also safe in terms of hazardous materials exposed to the living environment. Jung *et al.* [67] modified the PVC surface using ion irradiation by H^+ ions to create surface patterning. They observed that severe chemical changes occurred due to dehydrochlorination and oxidation (Table 2). Elsewhere, Cota *et al.* [68,69] exposed PVC films to argon ion sputtering and observed a non-stoichiometric chloride concentration profile implying the evolution of chlorine and explained that the electron beam-induced dissociation of the polymer surface accounted for this effect. Manfredini *et al.* [70] found that after electron irradiation, some hydrogen chloride gas was evolved from the surface of the plasticized PVC and polymer degradation took place faster. Sinha *et al.* [71] investigated the effect of gamma irradiation on PVC films and realized that the thermal stability of the PVC samples reduced because of C–Cl bonds scission. de queiroz *et al.* [72] could graft acrylic acid units on gamma-irradiated PVC surface. The gamma irradiation generated active radicals which could initiate acrylic acid chain polymerization in a surface-confined fashion. A similar procedure was attempted by another group of researchers to graft and copolymerize sucrose acrylate with benzophenone sensitizer activated with UV irradiation where the grafting was found to increase with time [73].

Table 2. X-ray photoelectron spectroscopy data on surface composition of ion beam irradiated PVC at different intensities (Adapted from Jung *et al.* [67]).

Ion beam intensity (ions/cm ²)	0	1×10^{14}	1×10^{15}	1×10^{16}
C 1s component (%)	64.79	65.23	76.44	82.80
C–C/C–H	49.70	50.04	57.34	68.79
C–Cl/C–O	12.18	12.16	11.16	10.20
C=O	–	–	3.77	–
C=O–O	2.91	3.03	4.17	3.81
O 1s component (%)	9.03	10.71	20.16	16.22
Cl 2p component (%)	26.18	24.05	3.40	0.98
[O]/[C] ratio	0.13	0.16	0.26	0.20
[Cl]/[C] ratio	0.40	0.37	0.04	0.01

Ozone treatment has been tried successfully for PVC surface modification [74,75]. Ozone (O_3) was either thermally or by irradiation decomposed to O_2 and O radical which began the functionalization upon colliding with the surface molecules. Kurose *et al.* [74] reported that the selective hydrophilization by ozonation was achieved for those polymers having chlorides in their structures. A similar finding was also published by Okuda *et al.* [75] where they showed aliphatic and chlorine characteristic peaks were reduced in intensity after ozonation and found a significant amount of the chlorine ion released implying an oxidative degradation (Figure 4).

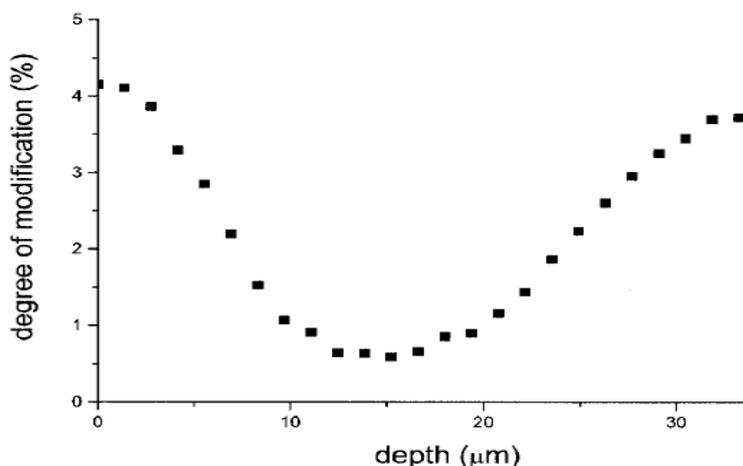
Figure 4. Fourier transform infrared spectra of the PVC sample before and after ozonation (Reprinted with permission from [75]. Copyright 2007 Taylor & Francis).



Wet chemical means have been widely employed to alter the surface chemistry of PVC [76–88] due to the flexibility in terms of methodology and inexpensiveness. Nonetheless, they are risky to the living environment since hazardous chemicals are often needed as solvents, catalysts, *etc.* It was generally observed that the surface selectivity and overall degree of modification depended essentially on the solvent quality, reaction time, and temperature [76–85]. Kurian *et al.* [76] carried out the surface modification of PVC from various sources with the ionic bonding of polyelectrolyte by exposing the polymer sheets to dilute zephiran chloride followed by immersing in polyelectrolyte solutions. Reyes-Labarta *et al.* [77] studied the chemical modification of PVC films with 4-aminothiophenol (4-ATP) in dimethylformamide (DMF) aqueous solution and observed a concentration gradient of the modifier across the films. Also, a partial extraction of the plasticizer was detected. McGinty *et al.* [78] prepared hydrophilic PVC surface using physisorption of azobisisobutyronitrile onto the surface followed by radical graft polymerization of a number of hydrophilic monomers. Sacristan *et al.* [79–81] examined the appropriate reaction conditions for the

selective surface modification of PVC films with sodium azide and 4-ATP and found that high surface selectivity was correlated with short reaction time, low temperature, and low solvent quality, while using a good solvent, higher overall degrees of modification with lower surface selectivity were achieved. Moreover, the modification degree was learned to be correlated with the depth as indicated in Figure 5.

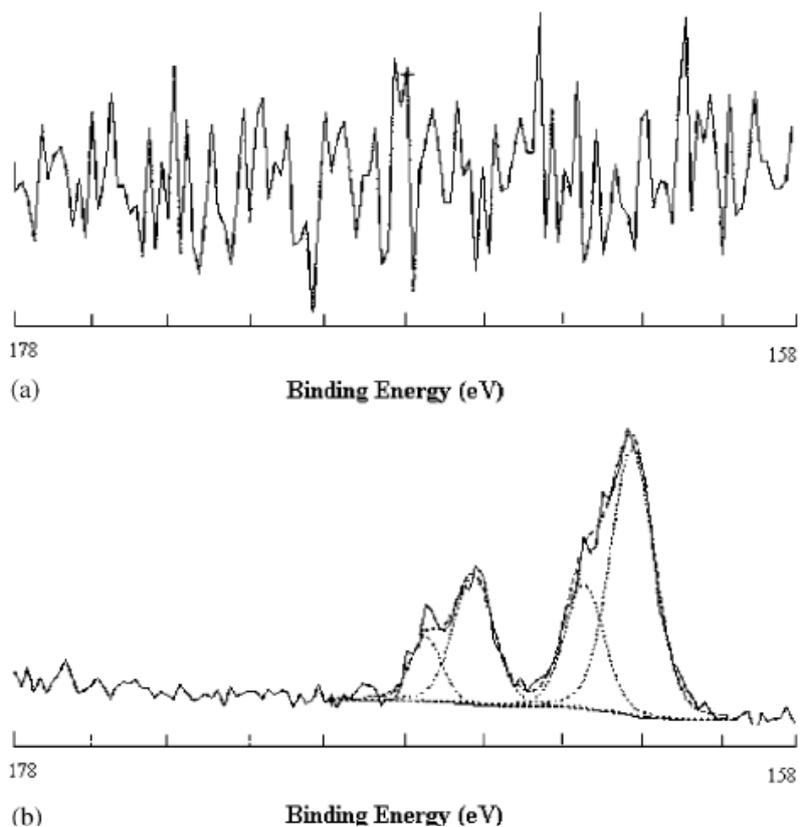
Figure 5. Depth profile of the modification degree obtained from Raman spectroscopy for PVC film treated with 4-ATP in DMF at 30 °C (Reprinted with permission from [80]. Copyright 2000 American Chemical Society).



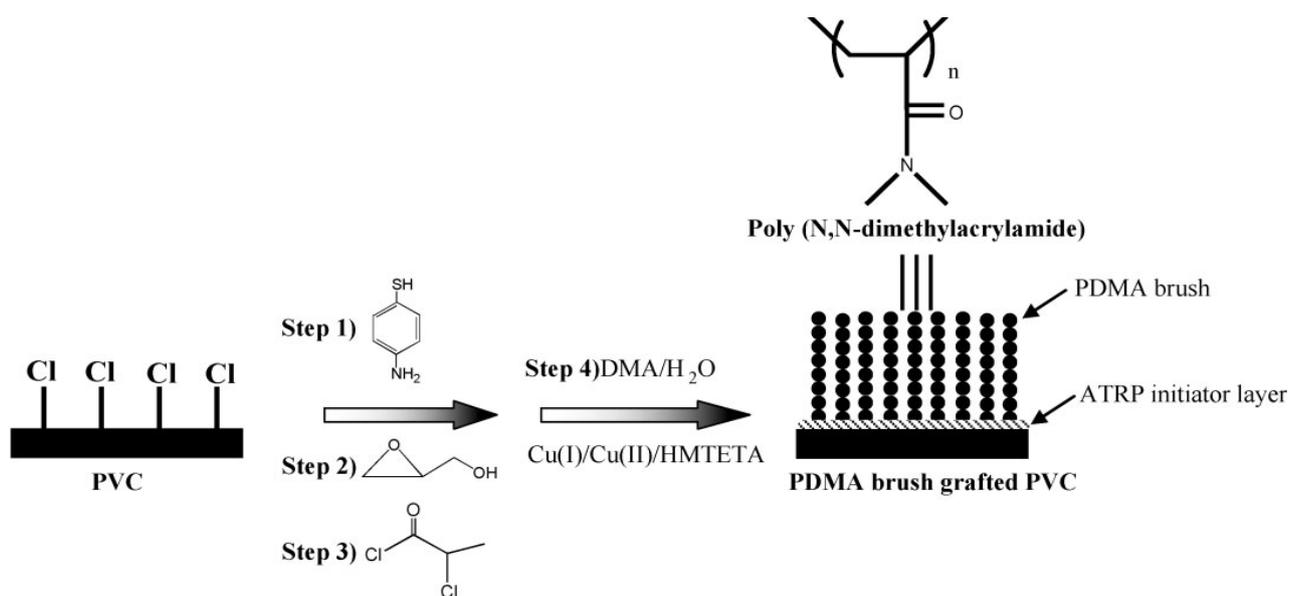
Elsewhere, Lakshmi *et al.* [82] immobilized thiosulphate groups onto PVC films using a phase transfer catalyst in aqueous media which led to the nucleophilic substitution of chlorine atoms by thiosulphate moieties (Figure 6). Also, the plasticizer leaching was detected when the PVC samples were exposed to the modifier. Likewise, James *et al.* [83] covalently bound thiocyanate groups onto PVC films using sodium thiocyanate which led to the nucleophilic substitution of chlorine by thiocyanate groups.

More efficient modifications have been attained using controlled chemistry via precision mechanisms such as ATRP [84–86]. Zou *et al.* [85,86] prepared poly(N,N-dimethylacrylamide) brushes on PVC sheets. To this end, primary amine groups were first introduced onto PVC surface by wet chemical modification with 4-ATP, followed by coupling of hydroxyl groups by a ring opening reaction of amine groups with glycidol. The ATRP initiator was then covalently coupled to the surface by an ester linkage, after which the surface-initiated ATRP of dimethylacrylamide was carried out (Scheme 2). Their studies showed that the surface initiation was a slow process and graft density gradually increased over time, so did the brush uniformity. They also found that both monomer concentration and reaction time were important for controlling the molecular weight and graft density. Self-assembly based on wet chemistry has also been used to modify the PVC surface by thin films formation on the polymer, where Zha *et al.* [87] produced multilayer coatings on PVC film using alternating deposition of iron and polysaccharides after immersing the films in cetyltrimethylammonium bromide. The multilayers were reported to be stable because of the electrostatic interactions.

Figure 6. High resolution spectra of S2p signal recorded by X-ray photoelectron spectroscopy from unmodified (a) and thiosulphate-substituted plasticized PVC sheet (b) (Reprinted with permission from [82]. Copyright 2002 Elsevier).



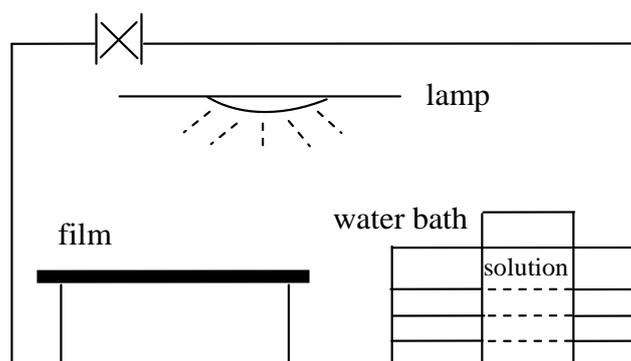
Scheme 2. Incorporation of ATRP initiators and surface initiated ATRP on PVC substrate in four steps (HMTETA: hexamethyl triethylene tetramine; PDMA: poly (dimethylacrylamide) (Reprinted with permission from [86]. Copyright 2010 Wiley).



Surface modification in the phases other than liquid has been performed, as well [88–90]. D'yakova *et al.* [88] modified the surfaces of PVC films with vanadium and phosphorus-containing

groups via chemical gas modification in a flow-type reactor. Xie *et al.* [89] grafted bifunctional glycidyl methacrylate (GMA) monomer onto the surface of PVC after polymerization in a gas phase photografting reactor (Figure 7); heparin was then immobilized onto the poly (glycidyl methacrylate) segments. Zimmermann *et al.* [90] chemically tethered a thiol-substituted hydroxybenzophenone to PVC films in a solid-state reaction carried out at a temperature below the glass transition. It was observed that the chlorine atoms on the PVC backbone were substituted using a potassium thiolate of thiol-substituted hydroxybenzophenone.

Figure 7. Schematic representation of gas-phase photografting reactor design (Reproduced with permission from [89]. Copyright 2002 Wiley).



3.2. Surface Physics

Surface physics is principally associated with the physical state of the surface, free energy, crystallinity, dynamics, and the topographical changes. Among them, morphology of the surface layers, as well as the free energy, stands out as two critical properties often analyzed [42]. As for virgin PVC, low surface free energy and usually smooth morphology have been unanimously evidenced as drawbacks for many applications and can be well tuned through appropriate surface modification routes.

Almost the entire research works contributed to this area reported that the polar component of the surface free energy of PVC increased after the modification (Table 3) [91,92]. This increase was in principle attributed to surface chemical changes due to the introduction of functional groups and on the other hand was finely associated with topographical changes because of the ablation/etching.

Table 3. The influence of air-plasma treatment for different periods on polar and dispersive components of the surface free energy for PVC films calculated based on various models and reported as an average (Adapted from Kaczmarek *et al.* [92]).

Plasma duration (s)	γ^d (dispersive part) (mN/m)	γ^p (polar part) (mN/m)
0	48.02	0.59
2	21.99	42.71
4	25.81	36.03
7	25.90	43.23
10	26.89	42.85

Plasma treatment has been established to strongly affect the PVC surface properties in terms of physical aspects [43–51,57–60,92]. Exposure to Plasma has been found to slow down the plasticizer leaching away from the PVC bulk. Wen *et al.* [44] learned that the migration rate was dependent on plasma treatment time and working pressure. It was inferred that crosslinking of the surface layer led to the plasticizer migration hindrance. Kucherenko *et al.* [46,47] treated the PVC surface via corona discharge in air as well as plasma in an oxygen-nitrogen mixture and found a transition in surface morphology from crystalline to amorphous state. The observed changes in the morphology of the PVC film surface were attributed to its amorphization and oxidation, simultaneous with partial degradation on the polymer surface. Elsewhere, Anuradha *et al.* [66] found out that the PVC crystallinity was reduced upon exposing PVC surface to plasma treatment *in vacuo*. Also, the predominant increase in the grain size of the specimen after plasma treatment was attributed to the coalescence of the neighboring grains after plasma treatment.

It was almost unanimously accepted that hydrophilicity (wettability) increased after plasma treatment (Figure 8) which could be translated as an increase in surface free energy, so did the roughness (Figure 9) [48–50,56–58,61]. This was more obvious at longer treatment time, higher plasma discharge power, and lower working pressure. However, part of the modification was restored after treatment due to the thermodynamic recovery [44].

The extent of wettability enhancement and also thermodynamic recovery have been established to be dependent on plasma power and modification time, as well as the post-plasma storage temperature [12]. This can be seen in Figure 10. Liu *et al.* [64] modified PVC surface by doing plasma treatment in a gas mixture of oxygen and sulfur dioxide and found that the water contact angle sharply reduced because of the sulfonic acid introduction. The maximum wettability was found when an equal volume of the gases was used.

Figure 8. Water contact angle data (a) as well as roughness values (b) as a function of the plasma power (Reprinted with permission from [58]. Copyright 2011 Elsevier).

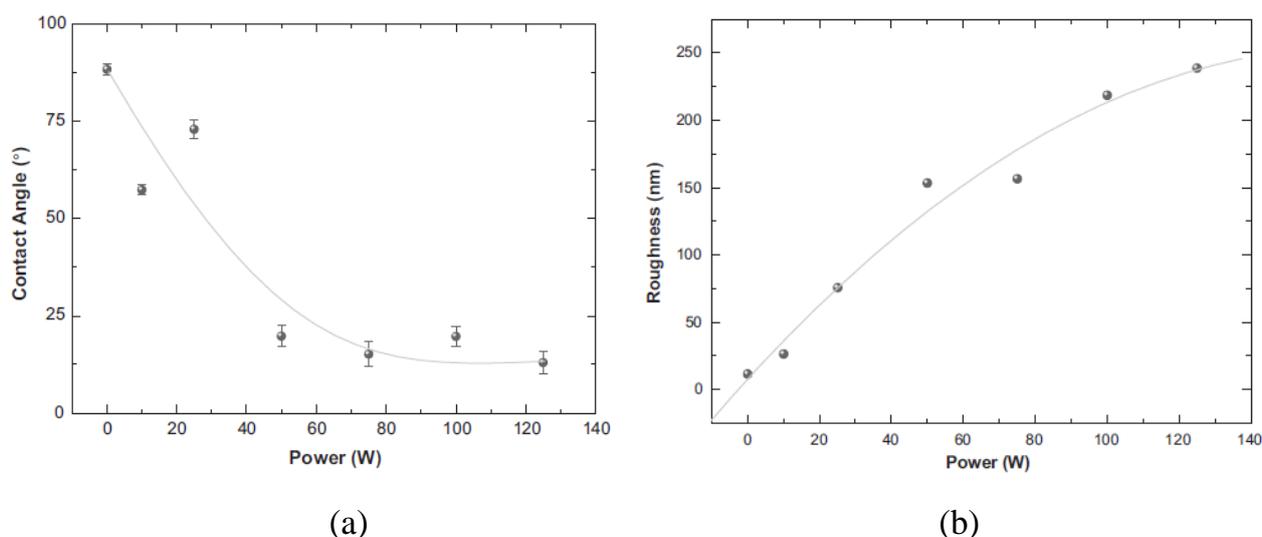


Figure 9. Surface morphology of untreated (a) and plasma-treated PVC (b) obtained from scanning electron microscopy (Reproduced with permission from [50]. Copyright 2010 MDPI).

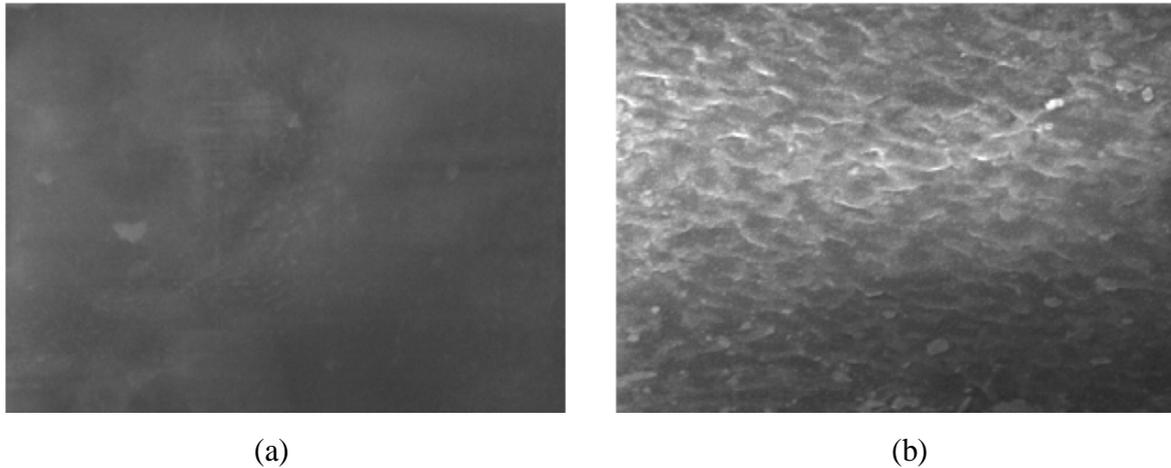
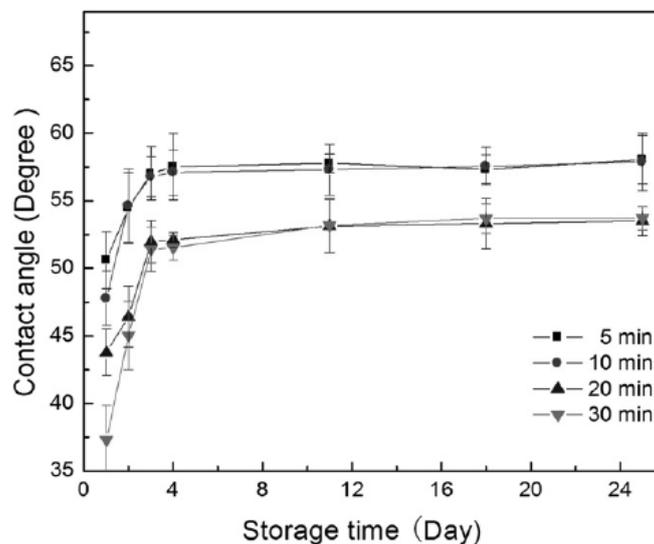


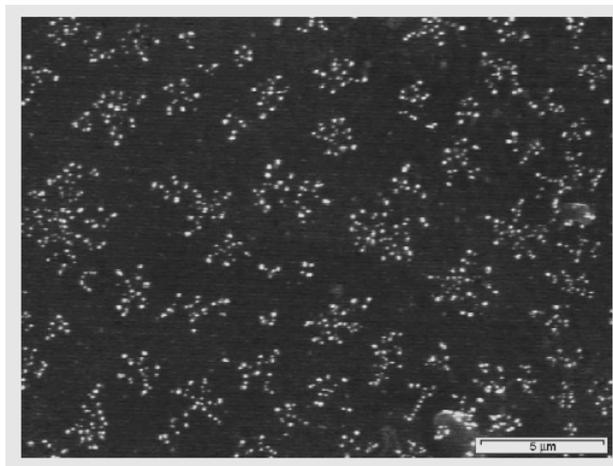
Figure 10. Thermodynamic recovery of the treated surface over storage time after modification (Reprinted with permission from [44]. Copyright 2011 IEEE).



Zhang *et al.* [53,59] used plasma immersion ion implantation in argon to modify PVC surface. They found enhanced hydrophilicity but not a very different morphology. This was attributed to the crystallization of triclosan and bronopol used as the antibacterial agents leading to a coarse morphology. The sample position in plasma chamber has been found effective as well. Ru *et al.* [61] examined the effects of long-distance and direct argon radio frequency plasma surface treatment on PVC films in terms of wettability. They reported that both configurations were able to increase surface roughness and hydrophilicity; nonetheless, the effect of the long-distance argon plasma was more notable as was emphasized in the former section. Khorasani *et al.* [60] treated PVC surface with oxygen plasma at low pressure and found fractal morphology after plasma treatment and explained that since the plasticizer had lower resistance to oxygen plasma treatment than PVC matrix, the

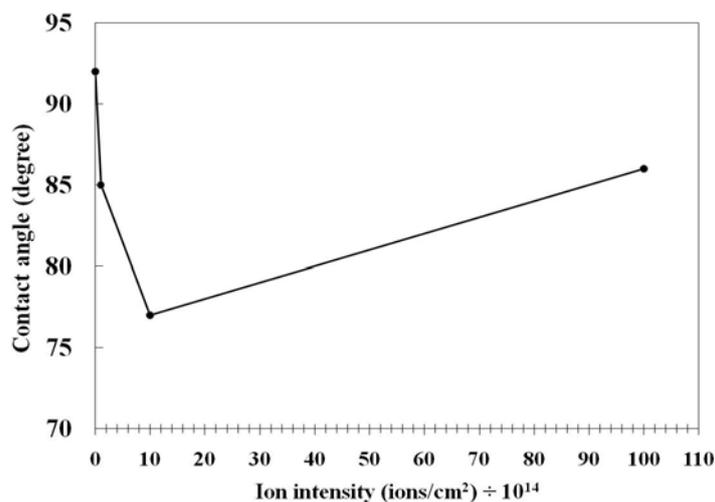
heterogeneity on morphology structure of untreated PVC caused separation of polymer and plasticizer moieties resulting in fractal morphology after plasma treatment (Figure 11).

Figure 11. Fractal morphology of oxygen plasma-treated PVC (Reprinted with permission from [60]. Copyright 2007 Elsevier).



In connection with the other surface treatment strategies, Jung *et al.* [67] used ion irradiation to enhance cell patterning on PVC surface and found that in low to medium ion flux, the wettability increased while at higher ion flux, due to excessive carbonization, the wettability reduced (Figure 12).

Figure 12. The effect of ion beam fluence on water contact angle values of the treated PVC (Reproduced with permission from [67]. Copyright 2010 Wiley).



McGinty *et al.* [78] showed reduced plasticizer migration by grafting hydrophilic polymers. Kurose *et al.* [74] carried out the surface treatment of PVC by ozone and found an increase in selective hydrophilicity due to the replacement of chlorine with oxygen-containing groups. It was interesting that they found a decreased roughness upon ozonation which was described as the factor which led to increase the hydrophilicity. Okuda *et al.* [75] used this approach to separate PVC from other plastics of almost equal density based on the froth flotation technique. The researchers who took advantage of the wet chemical methods to modify PVC surface reported that the wettability and topography of the

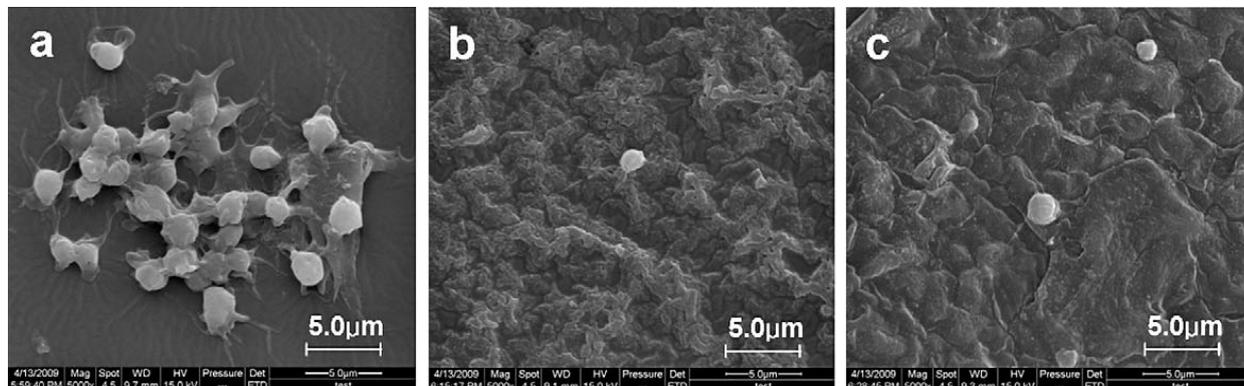
surface were effectively altered. D'yakova *et al.* [88] found that modification of the surfaces of PVC films via chemical gas modification with vanadium and phosphorus-containing groups made the surface layer of the polymers more hydrophilic, whereas silicon- and titanium-containing structures rendered more hydrophobicity.

3.3. Applications of PVC Surface Treatment

Surface modification of PVC is principally intended for various applications. Thus far, it has been practiced to impart biological activity, ink printability, and ion permeability to PVC. Sowe *et al.* [54,55] treated PVC films by DCSBD plasma in air and found enhanced ink printability due to the new functionalities generated on the surface. This finding was deemed to be beneficial for packaging industries. For a different purpose, Hu *et al.* [63] prepared ion exchange membranes for application in alkaline directly alcohol fuel cells based on PVC powder. They successfully immobilized benzyl trimethylammonium cationic groups onto PVC matrix using low pressure argon plasma grafting, quaternization and alkalization. The plasma-grafted alkaline anion-exchange membrane exhibited good ionic exchange capacity, ionic conductivity, and methanol permeability.

Biocompatibility towards cell and blood as well as biocide activity are all considered most important characteristics which can be granted to PVC via surface modification. Zou *et al.* [85,86] grew poly(*N,N*-dimethylacrylamide) on PVC by well-controlled ATRP and saw that the graft densities of the brushes played an important role in controlling interfacial properties. They found that the blood platelet activation was reduced compared to unmodified PVC especially in higher molecular weights. Liu *et al.* [64] treated PVC surface via SO₂/O₂ gas plasma treatment and found that the blood platelets were effectively suppressed on surface sulfonation of PVC film. de Queiroz *et al.* [72] evaluated the thrombogenic behavior of PVC films modified by gamma rays irradiation followed by AA grafting and bovine serum albumin immobilization. They found that the adopted modification was very effective in suppressing the adhesion and activation of platelets when contacted to blood. Yoshizaki *et al.* [84] coated PVC surface with poly (2-methoxyethylacrylate). The hemocompatibility from this polymer was compared with the covalent-bound heparin over a short period of blood circulation. Both circuits showed a similar character in hemocompatibility. Zha *et al.* [87] tried to produce hemocompatible coatings on PVC films by consecutive alternating adsorption of iron and two kinds of polysaccharides, heparin and dextran sulfate via electrostatic interaction. Also, iron-polysaccharide multilayer coating gave a marked reduction in adherence degree of platelets (Figure 13). The multilayer coating involving both heparin and dextran sulfate was shown to lower non-specific protein adsorption in comparison with when only one agent was used. Xie *et al.* [89] attempted a procedure of heparinization on the surface of PVC for antithrombogenicity utilization. A bifunctional monomer, GMA, was grafted onto the surface of PVC by gas-phase photografting polymerization, then heparin was immobilized onto the poly (glycidyl methacrylate) segments. Their results indicated that the blood compatibility of the product was improved greatly. Lamba *et al.* [93] examined the interactions of blood with PVC and found that PVC led to blood coagulation which could be reduced upon using heparin.

Figure 13. Scanning electron micrographs of PVC surface after being contacted with fresh platelet enriched plasma for (a) control PVC; (b) heparin/iron coated; and (c) dextran sulfate/heparin/iron coated samples (Reprinted with permission from [87]. Copyright 2009 Elsevier).



Asadinezhad *et al.* [48–50] improved the antibacterial properties of PVC against two bacterial strains. DCSBD plasma was used for this purpose, followed by AA grafting and antibacterial agents coating. They found that plasma treatment and acrylic acid grafting were effective in suppressing the bacterial adhesion. The approach was effective in reducing the adhesion of bacteria for antimicrobial agents like triclosan, chitosan, chitosan/pectin multilayer, benzalkonium chloride, bronopol, and chlorhexidine. Zhang *et al.* [53] used plasma immersion ion implantation to bind triclosan and bronopol molecules to enhance the antibacterial properties of PVC films. They found that the plasma-modified PVC with bronopol exhibited good antibacterial properties. However, triclosan-coated sample acted showed superior activity against gram negative bacteria. Triandafillu *et al.* [91] studied the bacterial adhesion on native and chemically modified PVC surfaces. The oxygen plasma treatment of the PVC films reduced the number of adhering bacteria (Figure 14). It was demonstrated that the surface modification of the PVC using oxygen-plasma treatment was just successful in decreasing the initial adhesion of the bacteria not in preventing the bacterial biofilm formation. Rad *et al.* [94] examined the adhesion of five different bacterial strains to PVC catheters and found that the bacterial attachment to the hydrophobic sample was high. In contrast, plasma treated catheter showed a remarkable reduction in number of bacteria adhered onto the surface. The reduction of bacteria was more evident for plasma treatment carried out in AA vapor. McGinty *et al.* [78] using physisorbed free radical initiation reduced the plasticizer migration which was beneficial for medical uses and also enhanced the antimicrobial properties of PVC. They reported that PVC films treated with poly (vinyl pyridine) and quaternized with various bromoalkanes were effective in killing bacteria.

Khorasani *et al.* [60] investigated the effect of wettability and surface charge of PVC surfaces on fibroblast cells attachment. They reported that the differences in surface charge probably influenced the cell adhesion. Their results indicated a trend of less cell attachment and proliferation for treated PVC. They also reported the dependence of zeta potential of treated PVC (more negatively charged) compared to virgin PVC on cells attachment and growth. Jung *et al.* [67] studied the creation of micro-patterns of cells on PVC films using ion irradiation. A PVC film was irradiated with H^+ ions through a pattern mask in order to create patterns of the hydrophilic/hydrophobic regions on the PVC surface. Their results revealed that selective adhesion and proliferation of the cells on the ion-irradiated

regions were observed (Figure 15). They believed that this method based on ion irradiation could be applicable to the fabrication of cell-based sensing devices and tissue engineering.

Figure 14. Adhesion effectiveness of a subset of *Pseudomonas aeruginosa* strains to oxygen plasma-treated PVC as compared to untreated PVC (Reprinted with permission from [91]. Copyright 2003 Elsevier).

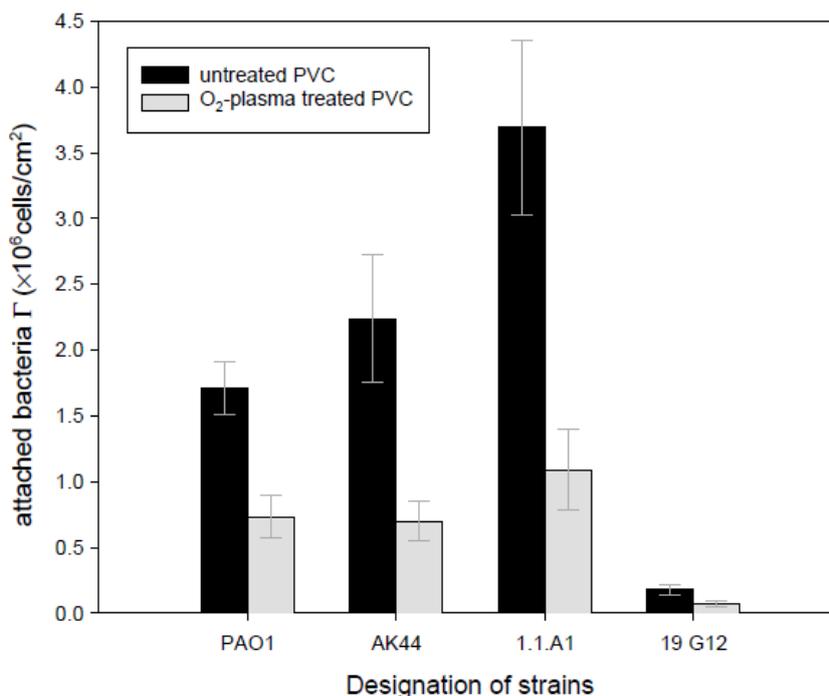
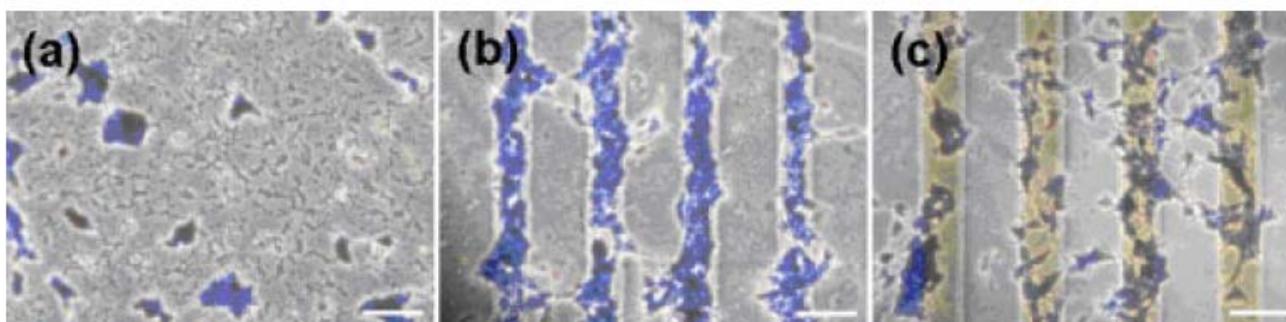


Figure 15. Optical microscope images of the cell patterns on PVC surfaces irradiated with ion beam at (a) 1×10^{14} ; (b) 1×10^{15} ; and (c) 1×10^{16} ions/cm². Each scale bar represents 100 nm (Reprinted with permission from [67]. Copyright 2010 Wiley).



As for biodegradability, Rios *et al.* [73] studied the graft copolymerization of sucrose acrylate onto thin films PVC with benzophenone sensitizer initiated with UV irradiation. It was found through microbiological assays that the microorganisms present in the soil were able to utilize the modified PVC as a source of carbon indicating biodegradation. It was concluded that the copolymerization of synthetic backbones with natural side chains could be considered as a way of producing compounds more sensitive to degradation in a natural environment.

4. Concluding Remarks

In this brief review, various approaches within the last three decades taken to engineer the PVC surface along with the respective highlights have been sketched. It has been established that the PVC surface can be turned into a hydrophilic surface of high free energy with an enhanced bonding strength and minimized biofouling without affecting the bulk properties. Also, cell and blood compatibility have been observed to increase as a result of appropriate surface modification. The modified PVC exhibited less plasticizer migration, as well. It seems necessary here to describe some general perspectives on this issue. As per the number of publications, it can be claimed that the subject of polymer surface engineering itself is developing quite rapidly. Concerning PVC in particular, a sharp increase is evident over the last decade in the amount of the relevant research. Among various strategies pursued, the solvent-free techniques—especially plasma treatment—are increasingly becoming attractive. Also, wet chemical methods based on the state-of-the-art controlled chemistry are at the center of intense focus. The achievement of enhanced control over the modified surface can also be mentioned as another trend. This concise overview also makes it clear that there are complex phenomena occurring at the surface once the PVC surface is exposed to external bodies. As better understanding of the complex phenomena and aging effects due to the interactions between polymer surface and surroundings is gained, new possibilities of enhanced control over surface properties emerge. Accordingly, a new generation of biomaterials based on PVC is being created to enable the design and production of superior medical devices. In addition to what has already been mentioned, to reach the optimal PVC surface, fine-tuning and the avoidance of overdevelopment, as well as effective, interdisciplinary collaboration among materials scientists, chemists, biologists, and bioengineers will be necessary.

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