

Graft-Polymerization Of N-Vinyl-2-Pyrrolidone, Allylamine And Acrylic Acid Onto PVC Film By Plasma Treatments

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Abstract—In this study, PVC films were modified by graft polymerization of N-vinyl-2-pyrrolidone (NVP), allylamine (AM) and acrylic acid to improve hydrophilicity for medical applications such as catheters, urological products and flexible tubes. The PVC films were immersed hydrophilic monomers and then were treated with NVP and AM plasma. Wettability of PVC films was investigated using contact angle measurement. Experimental results showed that the water contact angle values decreased from 116.4° for the uncoated PVC film to the lowest value 0° for the coated PVC film. Graft-polymerization by plasma treatment can be used to enhance hydrophilicity of PVC surfaces.

Keywords—Plasma modification, graft polymerization, PVC film, hydrophilicity

1. Introduction

Polymers are commonly used in industry because of their excellent bulk properties, such as strength and good resistance to chemicals. Their surface properties are for most application inadequate due to their low surface energy. A surface modification is often needed, and plasma surface modification is used with success the past decades [1].

Surface modification techniques based on plasma processes allow to tune surface composition, morphology and properties of materials in several applications. Plasma processes are widely used for modifying the surface of materials in several fields, including that of biomaterials, being versatile tools to tailor smartly chemical and physical properties of material surfaces at room temperature, without altering their bulk. High versatility, adaptability to various substrates, minimum consumption of reagents, no use of solvents, up-scalability and high/easy integration in industrial processes are other advantages of the technique. The intrinsic sterilization of materials exposed to the highly energetic plasma environment is a feature that obviously attracts biomedical operators [2].

Plasma polymerization is a deposition technique where a gaseous or liquid monomer is introduced in the plasma discharge and converted into reactive fragments [3–6]. These can react with the surface to

form a so-called plasma polymer coating, that has unique physical and chemical properties. These coatings are pinhole-free, highly cross-linked and are therefore insoluble, thermally stable, chemically inert and mechanically tough. Often these films are highly coherent and adherent to a variety of substrates including conventional polymer, glass and metal surfaces [7].

In addition, plasma-graft polymerization has been frequently applied for hydrophilic surface modification of polymers. In plasma-graft polymerization involve two step. First step, a polymer is exposed to an adequate plasma such as argon plasma, nitrogen plasma or oxygen plasma for a very short time and then second step comes into contact with the vapor of a monomer or becomes immersed in the aqueous solution of a monomer at an elevated temperature [8]. At the previous works, vinyl monomers with hydrophilic groups like acrylic acid and acrylamide were used as monomers for plasma-graft polymerization [9-13]. These works showed that plasma-graft polymerization with vinyl monomers were enhanced the hydrophilicity of surfaces.

In recent years, plasma surface modification for biomedical polymers has been investigated. For biomedical polymers, the surface properties need to be altered to promote a good cell adhesion, growth and proliferation and to make them suitable for implants and tissue engineering scaffolds [1,14]. Modification of polymer surfaces can be rapidly and cleanly achieved by plasma treatment due to the possibility of the formation of various active species on the surface of polyethylene (PE), poly(3-hydroxybutyrate), polycaprolactone, polypropylene (PP), and polytetrafluoroethylene (PTFE), although plasma treatment is generally slow and expensive in fiber applications and has found only limited applications. Plasma treatment also results in deposition of a macromolecular structure, graft polymerization, functionalization, etching, roughening, and cross-linking. It has been used to enhance wettability of surfaces [15-23].

In this study, poly(vinyl chloride) (PVC) films were used as a substrate since PVC is employed in applications including generally preferred for medical devices such as catheters, urological products and

flexible tubes. Hydrophilicity which is an important consideration for polymers and materials are generally preferred for medical devices such as catheters [24-27]. Firstly, PVC films were immersed in monomer of allylamine, N-vinyl-2-pyrrolidone, and acrylic acid (AAc) then immediately films were treated with allylamine and NVP plasma at constant plasma power (180 W) and constant plasma treatment time (15 minute). The effect of plasma treatment on wetting behaviour of the PVC films was characterized by using contact angle measurements. Surface free energy of coated and uncoated PVC films were calculated with acid-base approaches. The changes in surface morphology were also examined using Atomic Force Microscopy (AFM). The thermal behaviour of PVC films were performed by thermogravimetric analyzer (TGA).

II. Experimental

A. Materials

PVC films were supplied by Super Film Packing Co. PVC films were cut into pieces of dimensions 12 cm x 7 cm for every plasma treatment. The monomer allylamine (C₃H₇N), N-vinyl-2-pyrrolidone (C₆H₉ON) and acrylic acid (C₃H₄O₂) were purchased from Aldrich. PVC films were treated with plasma-graft polymerization as described in Table 1.

B. Plasma-graft polymerization

A radio frequency (RF) with an electrical power ranging between 0 and 300 W plasma generator was used in this study. Plasma reactor has three shelf and volume of reactor is 50 L. A combination of cold trap and vacuum pump was used to maintain the pressure range in the reactor between 0.1 and 1 mbar. In the absence of the monomer vapor, the pressure of the reactor was decreased to about 0.1 mbar.

Table 1. Code of materials used in this study

Specimen code	Description
PVC	Uncoated poly (vinyl chloride) film
PVC-NVP180W15M	At 180W and for 15 minute N-vinyl-2-pyrrolidone plasma treated PVC film
(PVC+AM)-NVP180W15M	Firstly immersed in allylamine monomer for 1 minute then at 180W and for 15 minute N-vinyl-2-pyrrolidone plasma treated PVC film
PVC-AM180W15M	At 180W and for 15 minute allylamine plasma treated PVC film
(PVC+NVP)-AM180W15M	Firstly immersed in N-vinyl-2-pyrrolidone monomer for 1 minute then at 180W and for 15 minute allylamine plasma treated PVC film
(PVC+AAc)-AM180W15M	Firstly immersed in acrylic acid monomer for 1 minute then at 180W and for 15 minute allylamine plasma treated PVC film

When the monomer vapor was fed into the reactor by a needle valve, the pressure was obtained between 0.26 – 0.30 mbar and was kept at that level during the plasma operation. Firstly, PVC films were

immersed in monomer of allylamine (AM), N-vinyl-2-pyrrolidone (NVP) and acrylic acid (AAc) during 1 minute. Then immediately films were treated with allylamine and NVP plasma at constant plasma power (180 W) and constant plasma treatment time (15 minute).

C. Characterization of plasma surface modified PVC films

The surface wettability of uncoated and coated PVC films were characterized using the surface contact angle of water. Water contact angle of PVC film surfaces were measured with Kruss DSA 100 equipment with a fast CCD camera. The static contact angles on the film surface were determined the by sessile drop method at room temperature. All measurements were made using deionised water. A water droplet of 10 µL was placed on the film surface. The surface topography and roughness of PVC films were analyzed with Atomic Force Microscopy (AFM) operated in tapping mode on Park System XE 70 AFM Instrument. The thermal behaviour of PVC films were performed by Thermogravimetric Analyser (Setaram SetSys Evolution 1750 TGA-DSC) in nitrogen atmosphere at a scan rate of 10 °C/min from 25 °C to 700 °C. The amount of sample used on TGA studies were about 10 mg.

D. Calculation of surface free energy Lifshitz-van der Waals/Lewis acid-base (LW/AB) approach

Several theoretical approaches have been developed to assess determination the surface free energy. This approach was proposed by Van Oss, Good and Chaudhury [28]. The acid-base character of the surfaces is determined with using contact angle measurements [29]. According to this approach, the surface free energy of a solid as the sum of two components, Lifshitz-van der Waals interactions (γ_s^{LW}) and Lewis acid-base interactions (γ_s^{AB}) [30,31].

$$\gamma_s^{Tot} = \gamma_s^{LW} + \gamma_s^{AB} \quad (1)$$

The component of γ_s^{AB} is a combination of the electron-acceptor (γ_s^+) and the electron-donor (γ_s^-) parameter of the surface free energy.

$$\gamma_s^{AB} = 2\sqrt{\gamma_s^+ \gamma_s^-} \quad (2)$$

The relationship between the equilibrium contact angle θ and the surface tension components of liquids and solids is given by a modified Young-Dupre equation.

$$\gamma_l^{Tot} (1 + \cos \theta) = 2 \left\{ \sqrt{\gamma_s^{LW} \gamma_l^{LW}} + \sqrt{\gamma_s^+ \gamma_l^-} + \sqrt{\gamma_s^- \gamma_l^+} \right\} \quad (3)$$

l and s are symbolized the liquid and solid surfaces. From contact angle measurements and surface energy parameters of three polar and one apolar

liquids, the solid surface energy can be calculated. We used double distilled water, formamide, ethyleneglycol as polar liquids and diiodomethane as apolar liquid for contact angle measurements. In Table 2, literature values (mN/m) for Lifshitz-van der Waals, electron-acceptor and electron-donor components of standart liquids used for the determination of surface free energy components are given.

Table 2. Literature values (mN/m) for Lifshitz–van der Waals, electron-acceptor, and electron-donor, components of standard liquids (γ_i) used for the determination of surface free energy components [17]

	γ_1^{Tot}	γ_1^{LW}	γ_1^+	γ_1^-
Water	72.8	21.8	25.5	25.5
Diiodomethane	50.8	50.8	0	0
Ethyleneglycol	48.0	29.0	1.92	47.0
Formamide	58.0	39.0	2.38	39.6

III. Result and Discussion

A. Contact Angle

Contact angle measurements are one of the simplest available methods for determining the hydrophobic or hydrophilic nature of a surface. Wettability of uncoated and coated PVC films were characterized by measuring water drop contact angles. Figure 1 shows the contact angles of the samples. The water contact angles of PVC film surfaces were decreased with NVP and AM plasma treatment from 116.4° to 63.9° and 40.7°, respectively. These values were markedly decreased with plasma-graft polymerization. Especially AM plasma treatment after immersing monomers, the water contact angles values of PVC film surfaces became 5.7°, 0°. In other words, the PVC film surface became very hydrophilic.

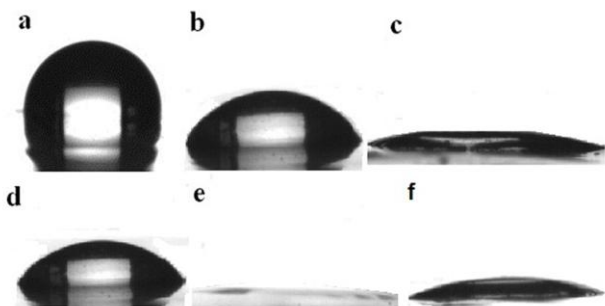


Figure 1. Contact angle pictures, a)uncoated PVC, b)PVC-NVP180W15M, c)(PVC+AM)-NVP180W15M, d)PVC-AM180W15M, e)(PVC+NVP)-AM180W15M, f)(PVC+AAc)-AM180W15M

Figure 2 shows the variation of contact angles of samples after one month. It was seen that after 15 days, contact angles of plasma treatment samples increased. After 30 days, the contact angle values continued to increase. We accept that, after plasma treatment functional groups were produced onto PVC

surface. These groups are hydrophilic and consequently contact angle decreased. But during storage time, films contacted with non-polar environments (air) and contaminated.

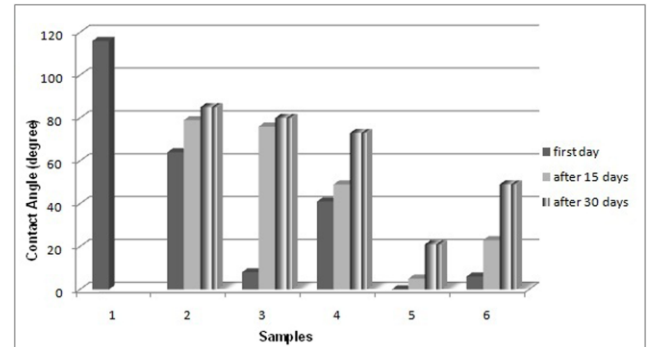


Figure 2. The effect of storage time on the contact angle of the PVC films, 1)uncoated PVC, 2)PVC-NVP180W15M, 3)(PVC+AM)-NVP180W15M, 4)PVC-AM180W15M, 5)(PVC+NVP)-AM180W15M, 6)(PVC+AAc)-AM180W15M

B. Surface Free Energy

From Equation (1), (2), (3), contact angle measurements of double distilled water (W), formamide (F), ethyleneglycol (EG), diiodomethane (DM) and surface energy parameters of these liquids, dispersion and polar components of uncoated PVC and coated PVC surfaces were calculated, and thus the change in surface energy was investigated. Table 3 shows the contact angle values of PVC films with these liquids before and after surface modification.

Table 3. Contact angle values of uncoated and coated PVC films with different liquids

Sample	W (deg)	F (deg)	EG (deg)	DM (deg)
PVC	116.4	87.7	73.1	60.4
PVC-NVP180W15M	63.9	57.9	49.6	69.9
(PVC+AM)-NVP180W15M	8.2	15.3	27.8	45.6
PVC-AM180W15M	40.7	2.7	32.7	39.1
(PVC+NVP)-AM180W15M	0.0	0.0	0.0	45.8
(PVC+AAc)-AM180W15M	5.7	0.0	35.1	55.2

The results of surface energy parameters of PVC samples are given in Table 4. It is clear from the table that after surface modification of the PVC films, total surface free energy (γ_s^{Tot}) increased from 28.4 to 53.6 and the basic component (γ_s) of the surface energy of the PVC films increased from 0.0 to 67.9. We accept that, after the surface treatments, the hydrophilic and polar functional groups were formed on the PVC surfaces, and increased the polar component in surface energy of PVC surfaces.

Table 4. Surface energy parameters of PVC films before and after surface modification

Sample	contact angle (with water)	γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{Tot}
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	(deg)				
PVC	116.4	28.4	0.23	0.0	28.4
PVC-NVP180W15M	63.9	22.9	1.17	23.8	33.5
(PVC+AM)-NVP180W15M	8.2	36.7	0.77	65.7	50.9
PVC-AM180W15M	40.7	32.3	1.66	64.1	52.9
(PVC+NVP)-AM180W15M	0.0	36.6	1.21	61.3	53.8
(PVC+AAc)-AM180W15M	5.7	31.3	1.83	67.9	53.6

C. TGA results

The thermal degradation behaviors of uncoated PVC film and PVC that firstly immersed in NVP monomer then was applied AM plasma treatment for 15 minute plasma time at a heating rate 10 °C/min from 25 °C to 700 °C under nitrogen atmosphere ((PVC+NVP)-AM180W(RF)15M) were investigated by TGA. Figure 3. shows the thermograms of samples uncoated PVC and (PVC+NVP)-AM180W(RF)15M. Uncoated PVC film started to decompose at about 275 °C until 470 °C the total weight loss was %100 from the beginning. It is observed that decomposition of coated PVC started at about 350 °C until at 500 °C, total weight loss was about %100. It was seen that thermal stability of the PVC film was altered by the plasma treatment.

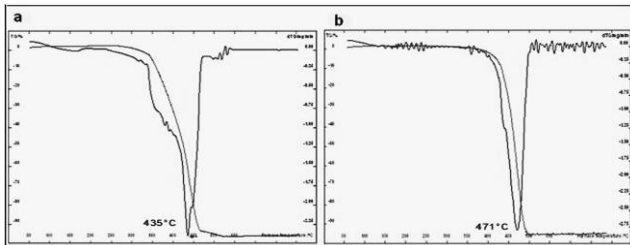


Figure 3. TGA thermograms of PVC film, a)uncoated PVC, b)(PVC+NVP)-AM180W(RF)15M

D. AFM surface analysis

The surface morphology and roughness of the samples were obtained by Atomic Force Microscopy (AFM). PVC surfaces were scanned in an area of 10x10 μm². The images were collected while the tip was operated at Tapping Mode. Three-dimensional z images and two-dimensional phi images of both uncoated and coated PVC films are shown in Figure 4 and Figure 5. Also, surface roughness values of samples are given in Table 5.

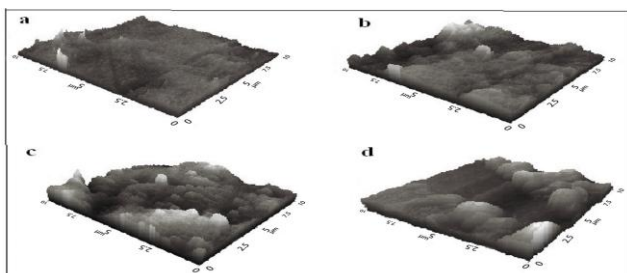


Figure 4. Three-dimensional z images (10X10μm²) of uncoated and coated PVC films, a)uncoated PVC, b)(PVC+AM)-NVP180W15M, c)(PVC+NVP)-AM180W15M, d)(PVC+AAc)-AM180W15M

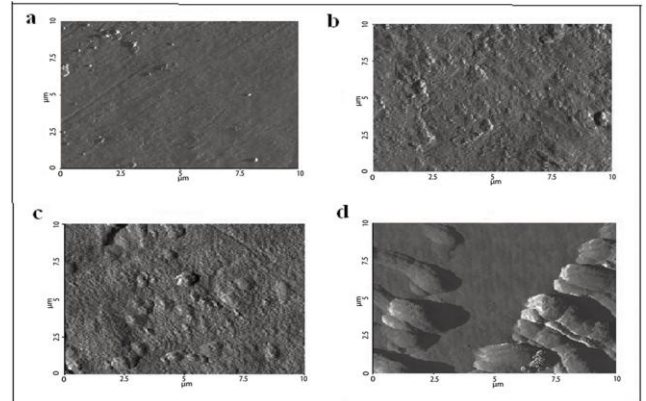


Figure 5. Two-dimensional phi images (10X10μm²) of uncoated and coated PVC films, a)uncoated PVC, b)(PVC+AM)-NVP180W15M, c)(PVC+NVP)-AM180W15M, d)(PVC+AAc)-AM180W15M

Table 5. Surface roughness values of uncoated and coated PVC films

Sample code	Surface roughness 10x10 μm ²
PVC	10.1
(PVC+AM)-NVP180W15M	18.5
(PVC+NVP)-AM180W15M	26.8
(PVC+AAc)-AM180W15M	41.8

According to Figure 4, Figure 5 and Table 5, it was seen that the distinct changes were observed in topography images and roughness values between uncoated and coated PVC surfaces. The uncoated PVC surface had an average surface roughness value Ra of about 10.1 nm. After coating, Ra values increased at 18.5 nm for (PVC+AM)-NVP180W15M, 26.8 nm for (PVC+NVP)-AM180W15M and 41.8 nm for (PVC+AAc)-AM180W15M. The uncoated PVC film have a relatively smooth and uniform surface. A significant roughness and an altered morphology can be observed on the coated PVC films.

IV. Conclusion

Surface modification of the PVC film with plasma treatment and graft plasma polymerization has been investigated. Plasma treatment with NVP and AM improved the surface wettability of PVC films and PVC films became highly hydrophilic. The surface free energy of PVC surfaces has been calculated using asid-base approach. Both the basic components and the total surface energy of coated PVC films increased. These results shows that surface free energy depends on hydrophilicity. It was seen that with grafting plasma polymerization, maximum degradation temperature and thermal stability of films were increased. The results showed that NVP and AM plasma treatment improved the wettability and surface roughness of the PVC films.

Also it was seen that hydrophilicity of PVC films decreased from 116.4° to 0° with plasma graft polymerization.

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