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The Influence of DC Glow Discharge Plasma on the Hydrophilic Properties of Polyvinyl Chloride Films

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ABSTRACT

In the present study, polyvinyl chloride (PVC) films were treated by DC argon glow discharge plasma to improve the hydrophilic properties of the films. The influence of plasma treatment on hydrophilic properties of the films was examined by the water contact angle and surface free energy (SFE) measurements. Also, the influence of treatment conditions (exposure time, applied power and working pressure) on water contact angle and surface free energy (SFE) of PVC surface was examined. The results showed that the water contact angle decreased from 85° for pristine sample to 35° after treatment time 60 min. The SFE were increased significantly with increasing exposure time, applied power and working pressure. The influence of aging on wettability of the plasma treated samples was also examined. The water contact angle of the stored samples increases rabidly and reaches a plateau value after 5 days which is still lower than that for the pristine sample.

Keywords: Ar-plasma, Surface modification, PVC, Contact angle, SFE, Hydrophilicity

INTRODUCTION

Poly (Vinyl Chloride) PVC is one of the most widely used polymer today, has wide range of applications such as health care instruments, packaging, toys, electrical wire insulation, clothes, furniture, building materials and the industry of the cars [1,2]. The PVC has several advantages such as relatively low cost, chemical inertness, flexibility, durability and high transparency [3]. Despite these excellent characteristics, PVC is hydrophobic and rigid polymer [4]. This limits the uses of PVC in different applications. To overcome these disadvantages, the surface modifications have been used in the last decades [5].

There are various surface modification techniques such as flame, corona treatment, UV, gamma ray, electron beam irradiations, ion beam, plasma treatment and laser treatments [6-9]. Among them, plasma treatment is considered to be the most promising and up-to-date method for modifying the surface properties of polymeric materials [10]. The using of plasma treatment have distinct advantages such as it changes the properties of the material only a thin near-surface layer typically with depth 0.005 to 0.05 μm [11]. In addition, it is a rapid and environmentally friendly process [12].

Plasma can be defined as "an ionized gas consisting of charged and neutral particles, such as electrons, ions, atoms, molecules and radicals". Depending on the gas composition and treatment conditions, the active plasma species (electrons, ions, fast atoms, free radicals and UV photon) participate in polymer surface treatment, resulting in etching, activation and cross-linking processes [5].

In the present paper, we study the effect of DC Ar plasma treatment on hydrophilicity and surface free energy of PVC films. Improvement in the hydrophilic properties of PVC surface was studied by measuring the water and glycerol contact angles. The effect of treatment conditions (exposure time, applied power and working pressure) on contact angle and surface free energy of PVC surface were investigated.

MATERIALS AND METHODS

Samples preparation and plasma treatment

Polyvinyl chloride (PVC) films were prepared by the casting method. PVC powder of molecular weight 85000 supplied by Sigma-Aldrich Company. PVC was dissolved in Tetra Hydro Furan (THF) with purity 99.99%; the complete dissolution was obtained using a magnetic stirrer at room temperature for 3 h until homogenous solution was obtained. The solutions were then cast into a different clean glass Petri dish. The whole assembly was placed in a dust free chamber and allowed to evaporate the solvent slowly in air at room temperature for one week. The prepared PVC films with thickness in the range of 0.22-0.25 mm. Subsequently, films were removed from the dishes and cleaned with ethanol before surface plasma treatment. Then the film was cut into small slides with dimension 1.5 cm × 2 cm for plasma treatment.

The details of the DC plasma unit used for surface treatment of the PVC films were described elsewhere [13,14]. The samples were supported on a glass rode and put in front of the cathode at the edge of the negative glow. The treatment time was varied from 15 to 60 min. Typical operating parameters are listed in Table 1.

Contact angle measurements

The influence of plasma treatment on hydrophilicity of the PVC films was examined by water and glycerol contact angles measurements using a travelling microscope. Measurements were carried out with distilled water and glycerol at room temperature. The volume of the liquids drop was about 5 µl using a micro syringe. Measurements were repeated five to eight times at different positions on the surface of the same sample to check the accuracy. The surface free energy for the substrates, using the water and glycerol contact angles, before and after plasma exposure were evaluated by applying Owens-Wendt method [15,16].

$$\gamma_l\left(1+\cos\theta\right)=2\left(\gamma_l^d\gamma_s^d\right)^{\frac{1}{2}}+2\left(\gamma_l^p\gamma_s^p\right)^{\frac{1}{2}} \quad (1)$$

Where γ_l γ_l^p and γ_l^d are the total surface energy, polar and dispersion components of the surface free energy of the liquid respectively. Similarly, γ_s, γ_s^p, γ_s^d are the values for the PVC films. θ is the contact angle between the sample and the liquid. The values of γ_l γ_l^p and γ_l^d, required for solid surface energy calculation were obtained from the literature [17].

RESULTS AND DISCUSSION

The influence of treatment conditions (exposure time, applied power and working pressure) on hydrophilicity of PVC film surface was examined.

Figure 1 shows the values of water and glycerol contact angles of plasma treated PVC film as a function of treatment time. The applied power and the working gas pressure were fixed at 3.5 W and 0.4 Torr, respectively. It is clear that the water contact-angle of untreated PVC film is 85° and decreases rapidly to 45° after a 30 min plasma treatment. The water contact-angle showing slow decrease with further increase in treatment time, showing a tendency to reach a saturation value of 350 after 60 min treatment. The large reduction in the values of the water contact-angle indicates that the hydrophilicity of the surface of PVC film is remarkably improved by the argon plasma treatment. This can be attributed to the activation of PVC film surface by the formation of new polar functional groups on the surface [18] (Figure 1).

Table 1: Typical operating parameters for plasma treatment

Parameter	Values Applied
Working pressure	0.1, 0.2 and 0.4 Torr
Electrode separation	7 cm
Applied power	2, 2.5 and 3.5 W
Exposure time	15 → 60 min
Working gas	Argon (Ar) gas

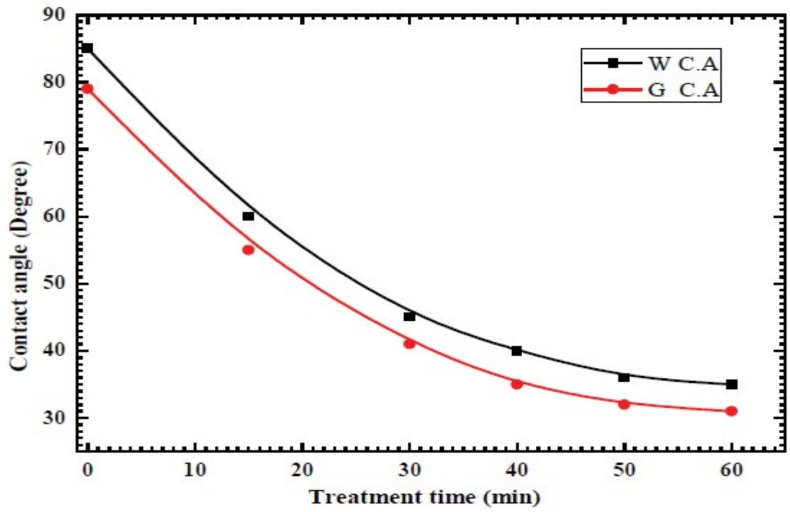

Figure 1: Variation of the water and glycerol contact angles of PVC with the treatment time at working pressure 0.4 Torr and applied power 3.5 W

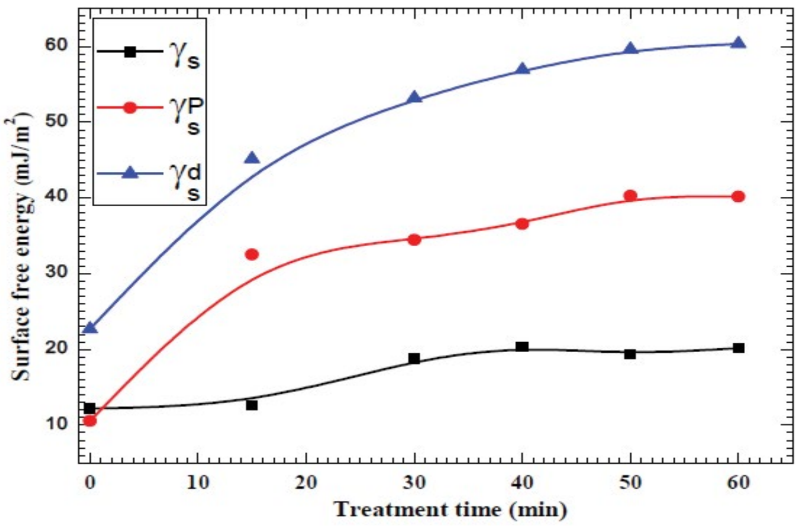

Figure 2: Variation of surface free energy of PVC as a function of the treatment time at working pressure 0.4 Torr and applied power 3.5 W

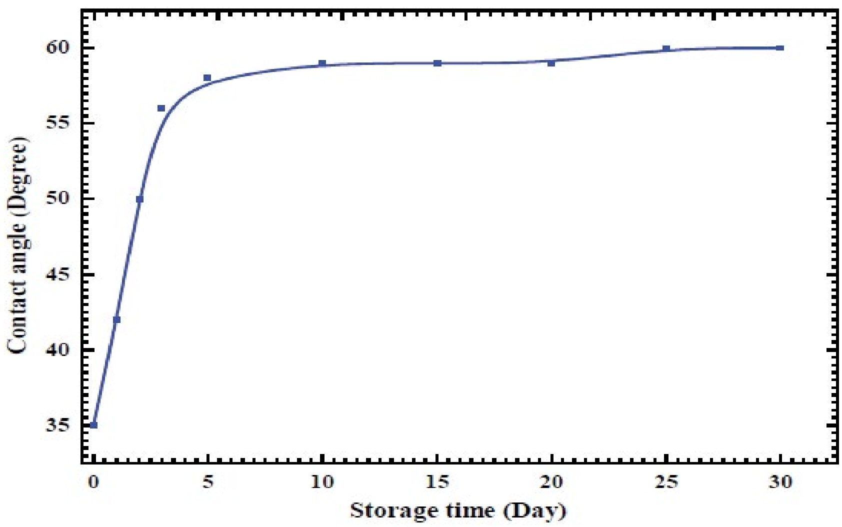

Figure 3: Variation of the water contact angle of plasma treated PVC as a function of the storage time

The influence of applied power on the hydrophilicity of PVC film was investigated, while the gas working pressure and treatment time were fixed at 0.4 Torr and 60 min, respectively. Table 2 shows the variation of water contact-angle of the surface of the plasma treated PVC as a function of applied power. It was found that water contact-angle decreases slowly with increasing applied plasma power. We can conclude that the optimum applied power in the present work is 3.5 W. These results are in agreement with literature [18] (Table 2).

The influence of the gas working pressure on the hydrophilicity of PVC film was also investigated, while the applied power and treatment time were fixed at 3.5 Torr and 60 min, respectively. Table 3 shows the change of water contact-angle of the surface of the plasma treated PVC as a function of the gas working pressure. It was found that water contact-angle has a decreasing behavior with the increase in the gas pressure. The decrease in contact-angle with increasing applied power and the gas working pressure may be attributed to the increase in concentration of reactive plasma species which responsible for surface activation and formation of new functional polar groups on surface with the increase in applied power and gas working pressure.

The values of total surface free energy, γ_s were estimated for the PVC films by adding polar and dispersive components γ_s^p ,γ_s^d . Figure 2 illustrates the values of total SFE, dispersive and the polar components of plasma treated PVC film as a function of treatment time. The applied power and the working gas pressure were fixed at 3.5 W and 0.4 Torr, respectively. It was found that the values of γ_s increase as treatment time increases. The polar component, changes almost in the same way as the surface free energy changes, while the dispersive component changes in a different way. According to our results, the values of γ_l , are mainly governed by the incorporation of the polar component of surface free energy as the changes of dispersive component are relatively unappreciable and almost constant after 30 min. This result is a common trend and agrees with previous works [19,20] (Figure 2).

Table 2 depicts the influence of applied power on the values of total SFE and the polar component of PVC film, while the gas working pressure and treatment time were fixed at 0.4 Torr and 60 min, respectively. It is clearly noted that the values of γ_s and γ_l increase when PVC film is treated at higher applied power.

Table 3 depicts the influence of the gas working pressure on the values of total SFE and the polar component of PVC film, while the applied power and treatment time were fixed at 3.5 Torr and 60 min, respectively. It is clearly noted that the values of γ_s and γ_l increase when PVC film is treated at higher pressure.

It is often noticed that the properties induced by the plasma treatment change with time and tend to revert back to the unimproved state. This phenomenon is known as ageing effect, which occurs due to the contamination of surface and polar groups orientation [21,22]. The improvement of hydrophilic properties of the polymer by plasma treatment is not the all desired but the stability of this improvement after plasma treatment is an important factor to suit different applications. To examine the stability of plasma-induced hydrophilicity improvement after plasma treatment, we investigated the aging effect of PVC films treated for 60 min. After plasma treatment, PVC samples were stored in ambient of air at room temperature (25-30°C).

Table 2: Values of water (W) and Glycerol (G) CA and total surface energy of plasma treated sample at working pressure 0.4 Torr

Exposure time (min)	Applied power (w)	Contact angle (degree)		Surface energy components (mJ/m^2)		
		W	G	Υ^d_s	Υ^p_s	Υ_s
60	2	43.7	39.3	19.4	34.81	54.22
	2.5	39	34	20.76	37.02	57.78
	3.5	35	31	20.17	40.18	60.35

Table 3: Values of water (W) and Glycerol (G) CA and total surface energy of plasma treated sample at applied power 3.5 W

Exposure time (min)	Working pressure (Torr)	Contact angle (degree)		Surface energy components (mJ/m^2)		
		W	G	Υ^d_s	Υ^p_s	Υ_s
60	0.1	46	41	19.83	32.79	52.62
	0.2	41	37	19.68	36.56	56.24
	0.4	35	31	20.17	40.18	60.35

Figure 3 shows the values of water contact angle of plasma treated PVC film as a function of aging time. It can be seen that, the water contact angle of the stored samples increases rabidly and reaches a plateau value after 5 days. The plateau value is still lower than 85° for pristine samples, this indicates that the PVC not loss all the improved hydrophilicity due to plasma treatment during the aging effect. This can be explained as: the plasma treatment not only form new polar functional groups on polymer surface but also increases the surface roughness which keeps the improvement in hydrophilicity during the ageing process. Therefore, PVC films are still suitable for further applications (Figure 3).

CONCLUSION

DC argon glow discharge plasma was used to improve the hydrophilic properties of PVC films. Plasma treatment was carried out at different treatment time, working pressure and applied power. The results showed clearly that the water contact angle decreases with increasing treatment time, working pressure and applied power but SFE and polar component take the reverse behavior. Also, the results of the aging effect showed that the water contact angle of the stored samples increases rabidly and reaches a plateau value after 5 days which is still lower than that for the pristine sample. Depending on our results, the optimum plasma treatment conditions as: treatment time 60 min, applied power 3.5 W and gas working pressure 0.4 Torr.

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