

Surface Characterization and Antibacterial Activity of Plasma Treated Polystyrene Thin Film

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Abstract

Cold plasma treatment has become a versatile technique for enhancing surface chemistries of polymers without bulk alteration. This treatment is significant in bringing microscopic and macroscopic surface changes without mortifying the polymer. With bulk properties remaining the same, surface modified polymers have many practical applications. Polystyrene is an extensively used polymer. It is used in packaging industry and has domestic and biomedical applications. This paper details the effects of cold plasma treatment on polystyrene thin film and antibacterial activity of the polystyrene thin film after plasma treatment. Cold plasma, which is produced in a glow discharge d.c plasma chamber, is used to modify the surface of the fabricated polystyrene thin film. Polystyrene thin films were treated in cold plasma for different exposure times with an applied voltage of 350V to the electrodes and a pressure of 0.8mb maintained in the chamber. The surface properties were characterized by FTIR, SEM and wettability studies. The antibacterial activity was studied by Agar Diffusion Test. Results show introduction of hydroxyl group, increase in hydrophilicity, very weak roughness change and antibacterial activity of polystyrene thin film surface after plasma treatment.

Key words: Cold plasma; fabrication; plasma chamber; hydrophilicity; antibacterial.

Introduction

Polymers have outstanding bulk properties but they don't often possess good surface chemistries due to their low surface energies. Surface modification of polymers without bulk alteration [1] is gaining lot of industrial importance. Various techniques

are available for altering surface chemistries, while keeping the bulk properties unchanged. Amidst a host of available techniques, cold plasma treatment of polymers is an established, economic and environmental friendly technique. Cold plasma production technique is economical as it consumes low power when compared with other techniques such as RF (or) microwave plasmas [2]. The important considerations which alter the surface morphology are plasma treatment time, pressure inside the chamber and voltage applied to the electrodes. By properly varying these parameters improved surface properties can be obtained. Polystyrene is broadly used polymer which has many domestic and medical applications. Among specific medical uses are sterilization trays, surgical instruments, and dental equipment. According to statistical data from the American Disease control and Prevention center, 1.8 million of 35 million patients in America experienced infection from bacterial infection of medical polymer tubes. Consequently, anti-infective properties are necessary for polymers in medical applications [3]. Polymers can be given antibacterial treatment such as plasma treatment [4]. This work details the change in surface morphology of polystyrene thin film surface after plasma treatment and antibacterial activity of plasma treated polystyrene thin films.

Experimental

Fabrication of polystyrene thin film

A 7% concentrated solution was prepared by dissolving polystyrene pellets obtained from Sigma Aldrich Company in benzene. The well cleaned glass substrates were dipped into the solution for 3 minutes and taken out and stored in a desiccator in which slow evaporation was performed under a controlled atmosphere. The thickness of the formed film was found to be $3.8\mu\text{m}$ from gravimetric method.

Plasma chamber

Figure.1 presents the experimental set-up used for the plasma treatment of polystyrene thin film samples. The plasma chamber consisted of a stainless steel vacuum chamber of length 50cm and diameter 25cm. The electrodes were placed at a distance of 5cm apart in a symmetrical plane to plane configuration. The pressure gauge heads, rotary pump, air admittance valve were connected to the chamber through thick walled PVC tubes. Once the chamber was put in the vacuum system, electrodes and substrate holder were cleaned by a discharge current of about $1\mu\text{A}$ applied for about 15 minutes.

Plasma treatment

Polystyrene thin film was placed inside the chamber at a distance of 2 cm from cathode. The chamber was firmly closed and the vacuum pump was switched on. When the required pressure of 0.8mb was obtained in the chamber, a voltage of 350V was applied to the electrodes. The samples were treated in the chamber one by one for 20, 40 and 60 minutes.

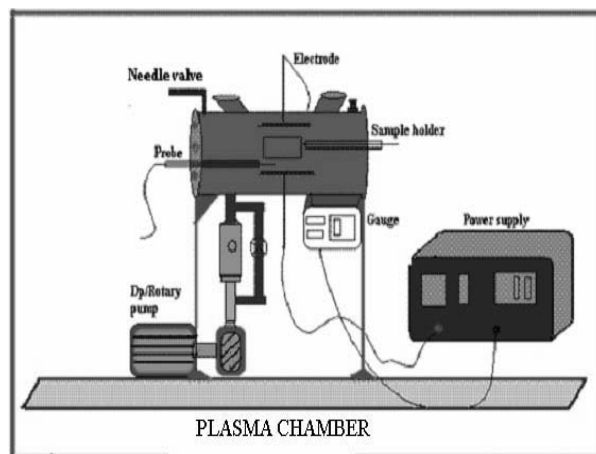


Figure 1: Schematic diagram of plasma chamber.

Characterization Studies

The untreated and plasma treated samples were analyzed using FTIR by Thermo Nicolet Avatar 370, spectrophotometer, wettability studies by Dataphysics Germany, Model:OCAH30 and SEM analysis by JEOL model JSM-6390LV scanning electron microscope. The antibacterial activity was performed using standard Agar Diffusion Test.

Results and discussion

FTIR studies

The FTIR spectrum of the untreated sample is shown in figure.2 (a). In the untreated sample the peaks at 2930.91 cm^{-1} , 3029.54 cm^{-1} corresponds to CH_2 symmetric stretching. $\text{C}=\text{C}$ aromatic vibrations can be interpreted by the peaks at 1451.5 cm^{-1} , 1491.55 cm^{-1} and 1630.50 cm^{-1} . The peaks at 691.91 cm^{-1} , 755.85 cm^{-1} and 899.82 cm^{-1} attribute to C-H out of plane bending.

The FTIR spectrums of 20, 40 & 60 minutes plasma treated samples are shown in figure. 2(b), figure 2(c) and figure 2(d) respectively. After plasma treatment, the peaks corresponding to C-H out of plane bending have completely disappeared. The $\text{C}=\text{C}$ aromatic vibrations have been directly affected [5] after plasma treatment. The peaks corresponding to aromatic rings in the $1400\text{-}1600\text{ cm}^{-1}$ wave number range have become almost vanished as shown in figure 2(b), figure 2(c) and figure 2(d). The introduction of hydroxyl functional group is clearly visualised with the observance of peaks in $3200\text{-}3600\text{ cm}^{-1}$ [6], wave number range which is absent in the untreated sample. The introduction of hydroxyl group is a direct indication of the increase in hydrophilic nature of the sample after plasma treatment, which is also confirmed by wettability studies. The energetic species in the plasma react with the surface of the polymer and the energy transferred to the polymer surface is dissipated within the

polymer which initiates plasma chemical reaction and form new types of compounds [4].

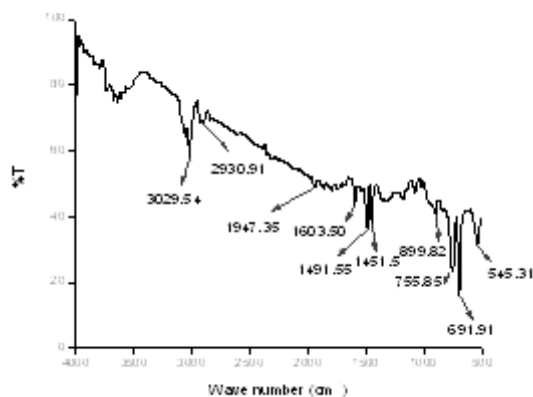


Figure 2(a): Untreated.

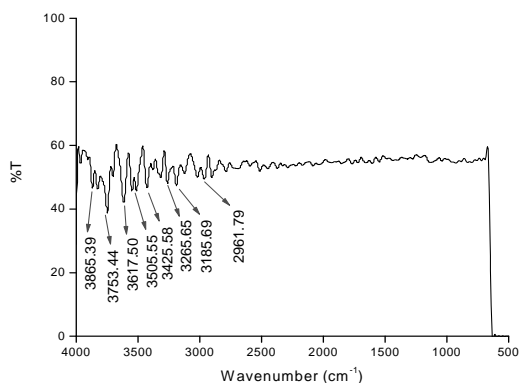


Figure 2(b): Plasma treated [20 minutes].

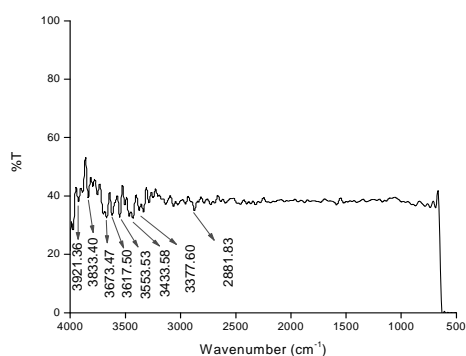


Figure 2(c): Plasma treated [40 minutes].

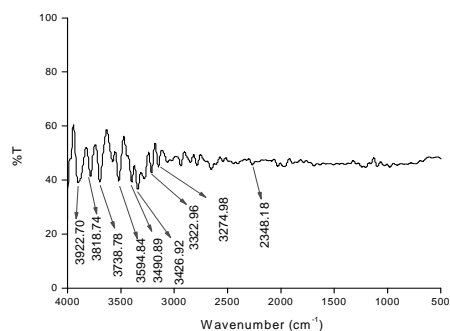


Figure 2(d): Plasma treated [60 minutes].

Figure 2: FTIR Spectrum of untreated and plasma treated samples.

Wettability Studies

Contact angle measurements were done to assess the wettability of the sample. The measurements were formed with a drop of de-ionized water on each sample after plasma treatment. The error in contact angle measurements was estimated to be $\pm 5^\circ$ to the actually measure contact angle. The contact angles of untreated as well as plasma treated samples at 20,40 and 60 minutes are shown in Table-1. The decrease in contact angle with the increase in plasma treatment time [5] is a direct indication of increase in wettability, which is nothing but an increase in hydrophylicity. The increase in wettability of the samples ensures adhesion improvement. The

hydrophobicity / hydrophilicity of polymers is important in the determination of various polymeric properties such as wettability, adhesion, colorability and anti-electrostatic properties[4].The improved wetting characteristics lead to a significant adhesion improvement with adhesives that cannot be used without surface treatment[8].

Table 1: Contact angles of untreated and plasma treated polystyrene thin film samples.

S.No	Sample	Contact Angle
1	Untreated	92
2	20 minutes plasma treated	58
3	40 minutes plasma treated	40
4	60 minutes plasma treated	32

SEM Analysis

The morphologies of untreated and plasma treated thin film for various exposure times are shown in figures 3(a), 3(b), 3(c) and 3(d).The SEM image of the untreated sample is shown in two magnification ranges of 100 μ m and 10 μ m, as the surface morphology is more clear in 100 μ m range. The images of the treated samples ,when compared with the untreated samples clearly indicates surface morphology changes during plasma treatment .In the case of plasma treated samples, weak roughness changes[9] appeared after plasma treatment. The active species present in the plasma etch the surface of the polymer and hence, the change in the morphology of surface is visualised. The increase in the roughness of the surface with the increase of plasma treatment time [10] can be clearly seen from SEM micro graphs shown in figures 3(b), 3(c) and 3(d).The research paper of Emerson et.al; [11] confirms the decrease in bacterial growth with increased surface roughness when nano-micrometer scales are considered.

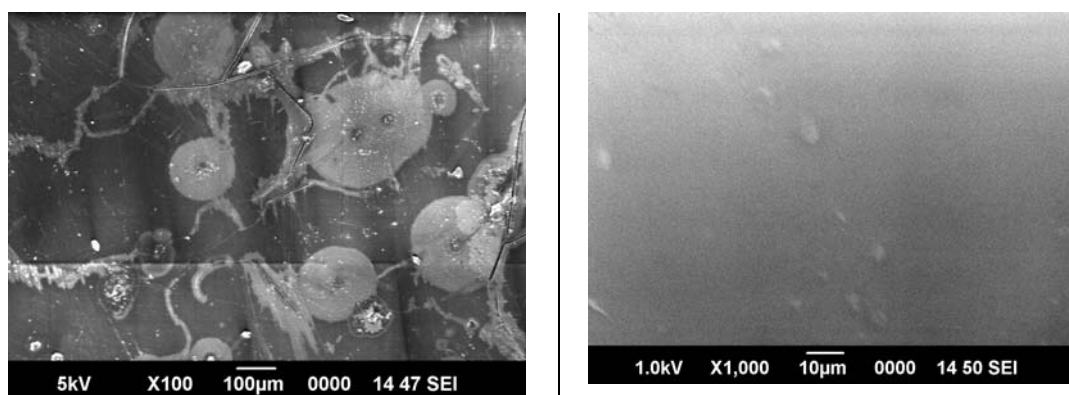


Figure 3(a): Untreated.

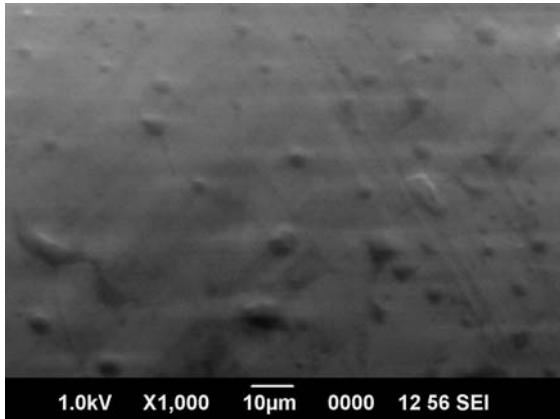


Figure 3(b): Plasma treated [20 minutes].

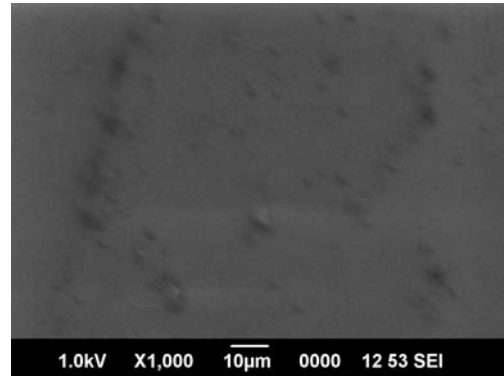


Figure 3(c): Plasma treated [40 minutes].

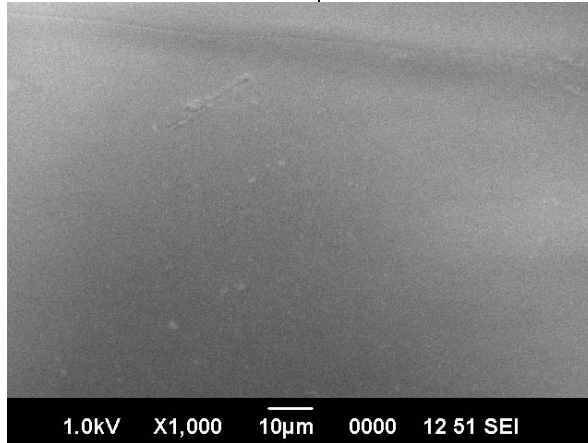


Figure 3(d): Plasma treated [60 minutes].

Figure 3: SEM micrographs of untreated and plasma treated samples.

Antibacterial Activity

The antibacterial performances against staphylococcus aureus (S.Aureus, gram positive) and Escherichia Coli (E.Coli, gram negative) were determined by qualitative Agar diffusion test. Most of the hospital infections are caused by the two organisms namely staphylococcus aureus and Escherichia Coli [6]. The evaluation of agar diffusion test was made on the basis of zone of inhibition of bacteria around the test sample. The zone of inhibition for untreated and plasma treated samples for various exposure times is shown in table-2. The zone of inhibition was absent in the untreated samples. The zone of inhibition gradually increases with the increase of plasma treatment time. It is obvious from these facts that the cold plasma treatment can be used as an anti-bacterial treatment. The ions, free radicals, neutrals etc. present in the plasma are all chemically active and lead to a variety of plasma chemical reactions and form new type of compounds. These new energetic species may act as anti-bacterial agents on the surface of the plasma -processed polymer [4].

Table 2: Agar Diffusion Assay (Anti-microbial Activity).

Sample	Zone of Inhibition(mm)	
	S.Aureus	E.Coli
Untreated	0	0
20 minutes plasma treated	2.2	2.0
40 minutes plasma treated	3.4	3.2
60 minutes plasma treated	4.9	4.3

Conclusions

The cold plasma treatment of polymers is an economical and novel method of surface modification. As the treatment is carried under soft conditions, the treated sample does not get spoiled. Increase in hydrophilicity of the sample is confirmed by both FTIR and wettability studies. Surface morphology changes, after plasma treatment, is clearly visualised from SEM analysis. The Agar diffusion test confirms the antibacterial activity of plasma treatment.

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