ATR-FTIR and UV-vis spectroscopy studies of microwave oven-generated oxygen plasma modification for PVA films

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Abstract

In this study, a microwave oven-based plasma generation process is disclosed that is both easy and low-cost. A Paschen-like curve is observed. Because of polyvinyl alcohol (PVA) polymer's excellent properties, it can be used in many fields, including food packaging and agriculture, after plasma treatment. A solution-casting approach was used to create pure polyvinyl alcohol (PVA) film. In the second regime, Oxygen plasma treatment was used to modify the PVA surface at a constant power of 1000W with different O_2 flow rates and pressures. XRD, ATR-FTIR, and UV-vis spectra were used to examine the surface properties of the films. An X-ray study revealed that the pure PVA film is semi-crystalline in nature. The transmission peaks of the treated plasma film are clearly intense at 15 sec, 26 mbar, and 6 L/min. At 26 mbar, a slight peak shift towards higher wavenumbers is observed, corresponding to the C-O stretching of acetyl groups. The highest transmittance, nearly 64 percent, is found in the UV region of the UV-vis spectra at the same optimised conditions as FTIR. As a result of these findings, PVA became a transparent material for greenhouses.

Keywords

Microwave oven-based Oxygen plasma generation, PVA, Paschen like curves, XRD, FTIR, UV-vis.

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1. Introduction

The electrical discharges generated by electromagnetic waves with frequencies approaching 300 MHz are called microwave discharges (MD), which should correspond to allowable microwave frequencies for industrial, medical, agriculture, and scientific applications [1,2]. The frequency of 2.45 GHz is currently used. The used microwave wavelengths range from millimetres up to several tens of centimeters. MD is a non-

electrode discharge with advantages over other types of electrical discharges. Firstly, plasma generation is simple, with both high (> 100W/cm^3) and low (1W/cm^3) levels of absorbed power; secondly, it is easy to control the plasma internal structure through changes in the electrodynamic characteristics of the microwave-to-plasma applicator, the broad region of operating pressures (from 10^{-5} Torr up to atmospheric pressure). Thirdly, the chance of plasma generation both in small and large chambers, including the free space and plasma generation in the electrode discharge systems without any pollution of gas-phase or plasma-treated samples by-products of the electrode erosion, Fourthly, the treatment of large gas volumes (including a cleaning process for the reactor walls) through scanning the plasma region (which is negligible as compared with chamber dimensions) over the chamber. Fifth, the ability is to achieve a joint action of the plasma and electromagnetic field on the treated substances (e.g., powders) in order to increase the energy efficiency of the plasma chemical process. Finally, it permits choosing the necessary design for any application from the developed family of highly effective microwave-to-plasma applicators [3-6]. With all these advantages, there are some constraints to using microwave drains, chief among them being that they are expensive, and the ingredients limit commercial success. Therefore, to produce a microwave vacuum with less expensive components, an alternative household microwave oven and glass flask [7] or Pyrex bowl [8] were used to achieve research purposes in laboratories. These systems have been used to modify the surfaces of some polymers. In addition to being less expensive, treatment times are a few seconds, unlike most other systems that go on for minutes. This regime of treatment time in seconds is very important for heat-sensitive materials [8]. Polymers are used in many applications, and new applications are being developed daily. Compared to other methods such as chemical modifications [9]. Plasma treatment is more convenient and cost-effective because it may be used to change the upper layer (a few nanometers) of a polymer surface without the need for a solvent or the production of chemical waste. Among the various synthetic polymers, polyvinyl alcohol (PVA) is one of the best choices due to its high thermal stability, non-toxicity, water-solubility, low cost, environmentally friendly, film-forming by solution casting, and biodegradability [10, 11]. The most distinctive advantage attributed to plasma treatment is that it allows reactive moieties to be incorporated onto the surface to improve the surface energy and reactivity for more functionalization and thus enhance the biocompatibility and surface properties without affecting the bulk properties. Plasma treatment has several other advantages as well. It is possible to achieve a wide range of functionalities by varying the discharge gas and operational parameters (power, pressure, time, and gas flow rate) [12]. The current work aims to develop a low-cost laboratory technique that may be used for a wide variety of surface treatments based on household microwave oven. Although plasma surface treatment was previously used to modify the surface of PVA, the use of this

technique is still limited in the second regime. The present work aimed to study the PVA polymer to demonstrate its usage in agricultural applications.

2. Experimental

2.1. Materials

Polyvinyl alcohol compound has an empirical formula [CH2CH(OH)] $_n$, it has a molecular weight of 1,15,000 g/mol, a melting point of 230C^o, and a purity of 98%. Purchased from Oxford LAB fine chem. (India).

2.2. Plasma production through a microwave oven

The cylindrical Pyrex chamber of 9 cm internal diameter, 15 cm length, and 1.2Litre volume is closed by two high heat resistant plastic plates of 14 cm diameter and 2.5cm thickness at its end. The vacuum system consists of an oil field rotary pump. The pressure achieved with this system is 10^{-3} bar. The throttling valve adjusted by hand is inserted between the chamber and the rotary pump for pressure control. The pressure in the chamber is determined by a compact capacitance gauge with a pressure range of (4-100) mbar. O_2 gas is admitted into the plasma chamber via a mass flow controller for a flow of10 L/min as a maximum. This combination of mass flow controller, throttling valve, and vacuum pump with a high pumping speed was sufficient to ensure both stable gas flow and pressure during all measuring periods. A schematic representation of the system is shown in Figure (1). In our system, the energy required for plasma generation is supplied through a constant power kitchen microwave of 1000 W, and the time the Pyrex chamber is exposed to microwave radiation determines the amount of energy supplied to the system [5,6,13].
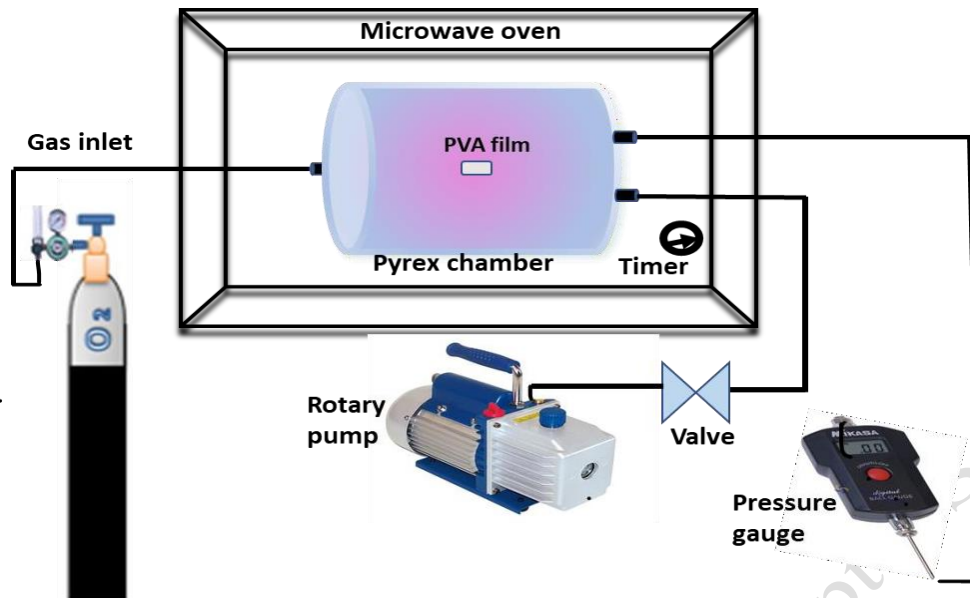
Figure 1Schematic diagram of microwave plasma system for treatment PVA

2.3. Preparation of polyvinyl alcohol (PVA) film

Polyvinyl alcohol is a creamy or whitish in color, tasteless, odorless, thermostable, granular, or powdered semi-crystalline or linear synthetic polymer [14]. As shown in Figure (2), the solution-casting process enables the refining of PVA films with a thickness of 44 mm.

In the present work, 5 g of PVA dissolved in 100 mL of distilled water was used to prepare pure PVA films. Using a magnetic stirrer with a hot plate, the samples were constantly stirred for 2 hours at 80 C^o to obtain the homogeneous solution of PVA of 5% concentration(w/v). The mixture then placed into petri dish to form a film. The solution of PVA was maintained for 5 days at room temperature in a dust-free environment for evaporation of solution to dry. Finally, films were carefully separated from the dishes. The uniform and plain surface of pure PVA films were selected and subjected to plasma treatment [15,16].

Following the preparation and drying of the PVA films, they were sliced into a rectangular strips of (2x2cm^2) area and subjected to a characterization
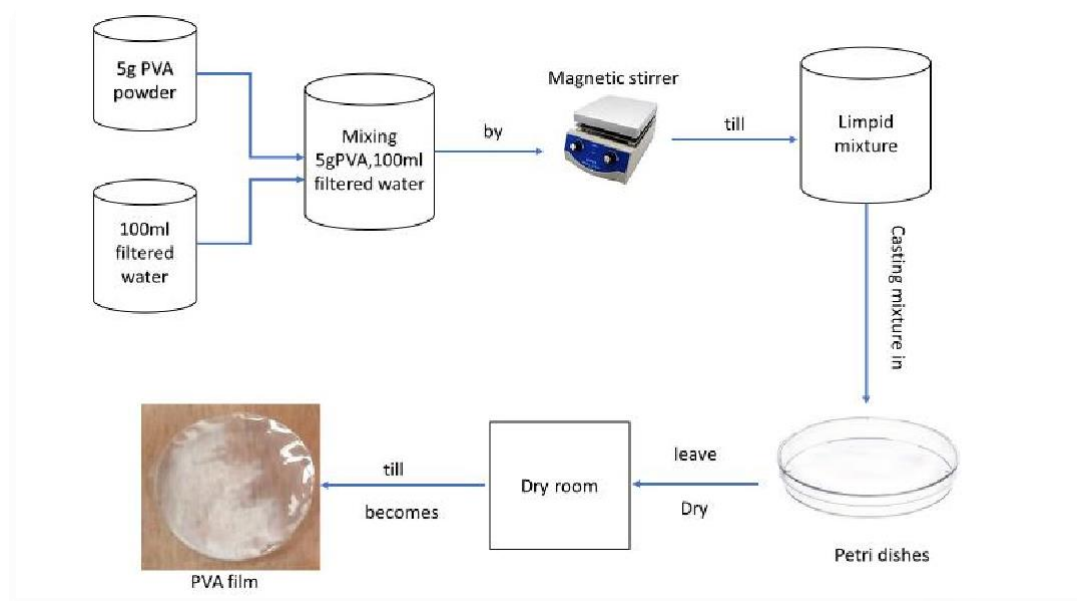
Figure 2 Schematic of solution-casting approach for preparation PVA film

analysis. The study of X-ray diffraction (XRD) patterns has proven to be a very valuable tool for determining the structure and crystallization of various materials over the years. In order to determine the structure of polymeric composites [17], an XRD structure analysis was performed.

2.4. Measurements and characterizations

Characterization of the polymeric PVA films produced was carried out. the X-ray diffraction (XRD) of pure PVA film was recorded at room temperature in a 2-theta range between $0°$ and $90°$ to characterize the prepared untreated sample using a Lab XRD-6000 (Shimadzu) X-RAY diffractometer. Attenuated Total Reflect Fourier transform infrared spectra (ATR-FTIR) of pure and Oxygen plasma-treated PVA films were recorded using the IS50 FT-IR model in the range of 500-4000 cm^{-1}. The Spectro UV-vis dual beam 8 Auto cell UVS 2700 spectrometer was used. In addition, characterization has been made in the gas phase.

3. Results

X-ray Diffraction (XRD)

The XRD pattern of the untreated PVA and oxygen plasma treated PVA films (6Lmin, 26mbar, 15sec) is shown in Figure 3. The untreated PVA film's characteristic peaks were observed at 19.7^o, corresponding to an orthorhombic lattice, indicating the partial crystalline nature. As reported in the literature [15].

In the case of plasma treated PVA film, the maximum peak is observed at 19.9^o for 6L/min, 15sec, and 26mbar. Furthermore, the intensity of the peaks around 11° and 50° was reduced in the oxygen plasma treated PVA film, which led the treated plasma to the increased crystallinity could be caused by both newly formed crystals on the plasma treatment surface and growth of existing crystals caused by additional thermal energy from plasma exposure [17], indicating an increase in amorphous nature However, there is no discernible difference in the structure of plasma treated PVA film when compared to pure PVA films [18,19].
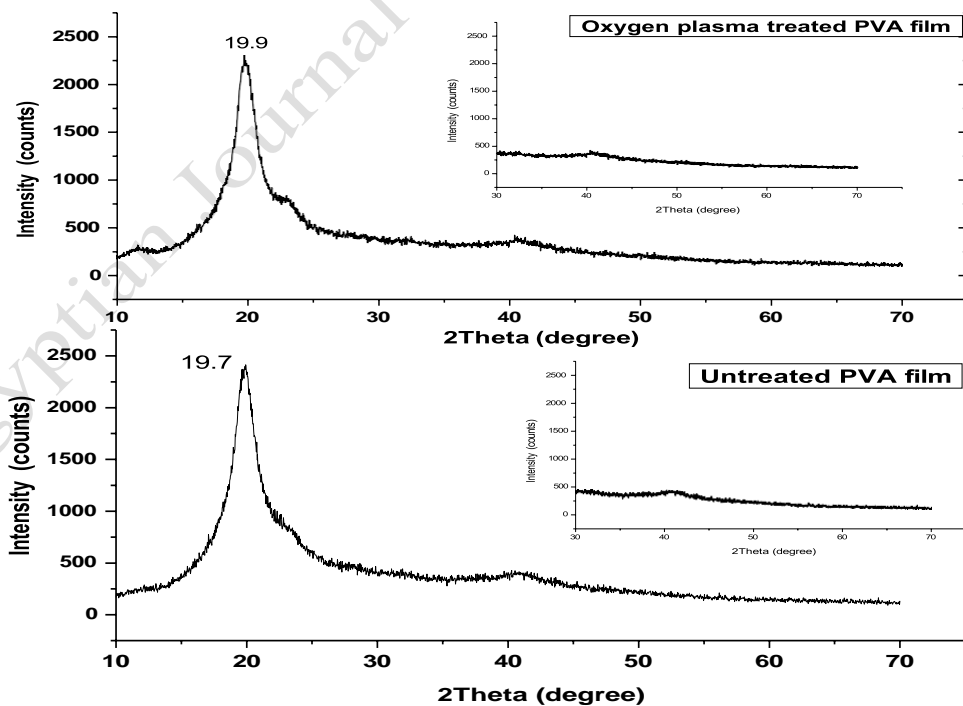

Figure3 X-ray diffraction pattern for untreated and treated PVA film

Characterization of the microwave generated plasma

A Paschen -like curve is generated by plotting the plasma initiation time versus the vacuum pressure inside the Pyrex chamber. The time difference between the first observation of plasma and the time of turning on the microwave oven, i.e., the plasma initiation time, is recorded for different vacuum pressures with different rate flows [7,8,11,12]. In the classical Paschen curve in a gas discharge tube, the potential (or energy required for plasma initiation) rises rapidly when further reduction is made in the pressure [20,21]. But in our system, the energy required for plasma generation is supplied through a constant power kitchen microwave, and the time the Pyrex chamber is exposed to microwave radiation determines the amount of energy supplied to the system [7]. So, the resulted curve in Figure 4, shows steady tendencies of low vacuum pressure at two oxygen gas flow rates of 2L/min and 6L/min
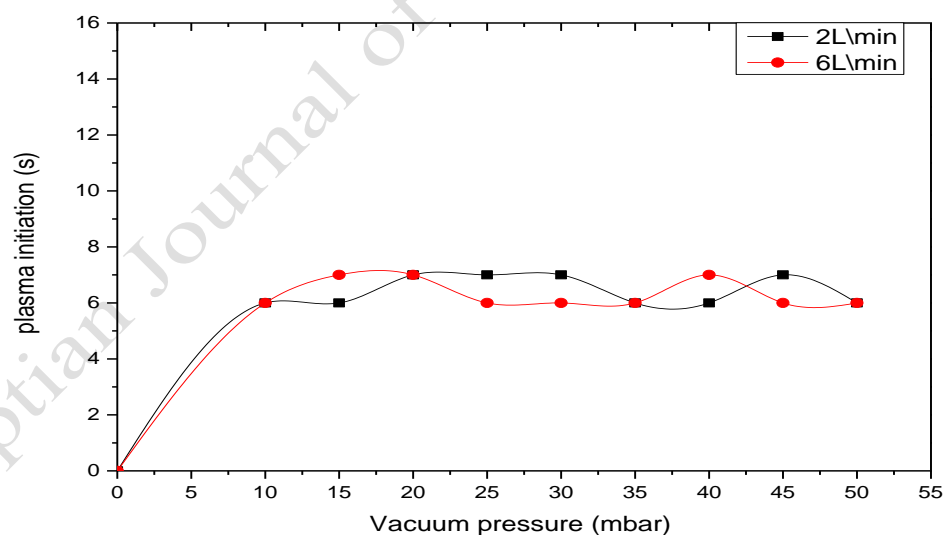

Figure 4: Plasma initiation time plotted as a function of vacuum pressure

ATR-FTIR

For obtaining useful information about the interactions between the functional groups, Fourier transform infrared spectroscopy (FTIR) is one of the most widely used techniques in the field of spectroscopy. Figure 5 shows

the results of an FTIR spectral analysis carried out to investigate the surface structural changes of the prepared pure PVA film in the wave number range of 500–4000 cm^{-1}. The findings of this investigation are presented in the following table1. The attenuated total reflect Fourier transform infrared spectroscopy (ATR-FTIR) technique is extremely sensitive to the formation
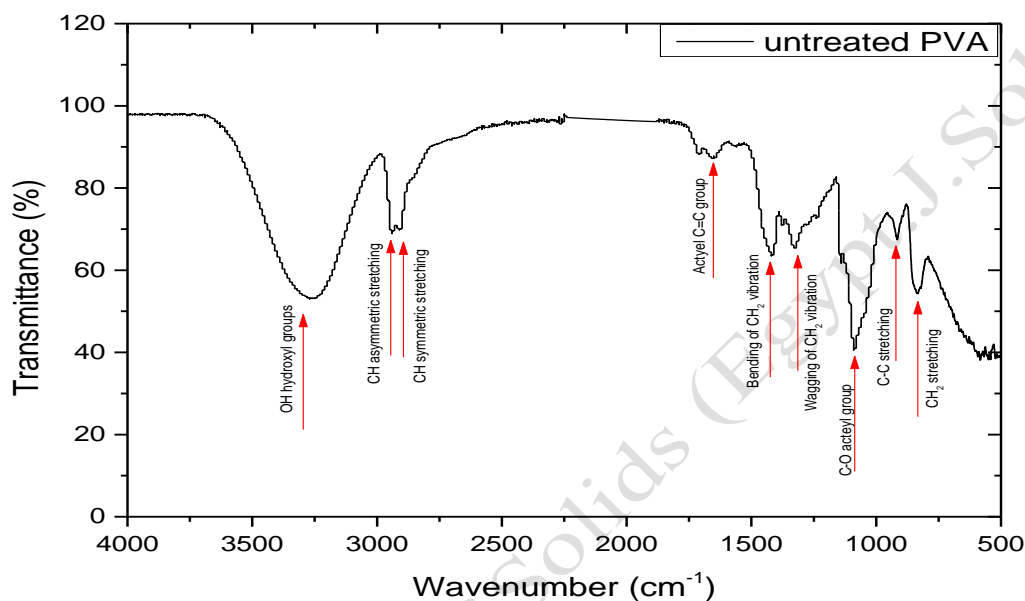

Figure 5: ATR- FTIR transmittance spectra for pure PVA (untreated) in the range from 4000 to500 cm^{-1}

Table 1:The Functional groups of ATR-FTIR bands of pure PVA

Functional groups	Wavenumber (cm^{-1})
Free OH stretching vibrations (hydroxyl groups)	3480-3250
CH asymmetric stretching	2980
CH symmetric stretching	2920
Acetyl C=C	1640
Bending of CH$_2$ vibration	1410
Wagging of CH$_2$ vibration	1320
C-O stretching of acetyl groups	1083
C-C stretching	945
CH$_2$ stretching	832

of hydrogen bonds. Moreover, it is extremely important because it has been used to determine the prominent characteristic peaks of pure PVA [18]. Transmission mode is used for all (FTIR) spectrum acquisition. The pure PVA undergoes a strong band at wavenumber range of 3480-3250 cm^{-1}, which is related to the Free OH stretching vibrations (hydroxyl group) within the PVA structure. Asymmetric and symmetric stretching vibrations of the C–H bond are attributed to the bands at 2980 and 2920 cm^{-1}. The Bending and wagging of CH_2 vibration bonds is attributed to the bands at 1410 cm^{-1} and 1320 cm^{-1}. Acetyl groups C–O stretching vibrations with wave number of 1083 cm^{-1}. Finally, it has been found that the wave number of 830 cm-1 which related to CH_2 stretching vibrations [19,21]. The ATR-FTIR spectrum of untreated and treated oxygen plasma of PVA film with treatment time variation as shown in figure(6a). At a flow rate of 2 L\min and a pressure of 16 mbar. This finding was optimized at three treatment times as following :5sec, 10sec, and 15sec, respectively. Our results show that the intensity of all functional groups at 15 sec appears more intense in the spectrum [24]. As shown in Figure, by increasing the treatment time till 15sec, led to increase in the Oxygen containing functional groups (free hydroxyl groups and acetyl groups) as shown in Figure (6b). This revealed the oxygen insertion into the polymer matrix. This finding is consistent with increased hydrophilicity and surface energy in treated PVA films [25].
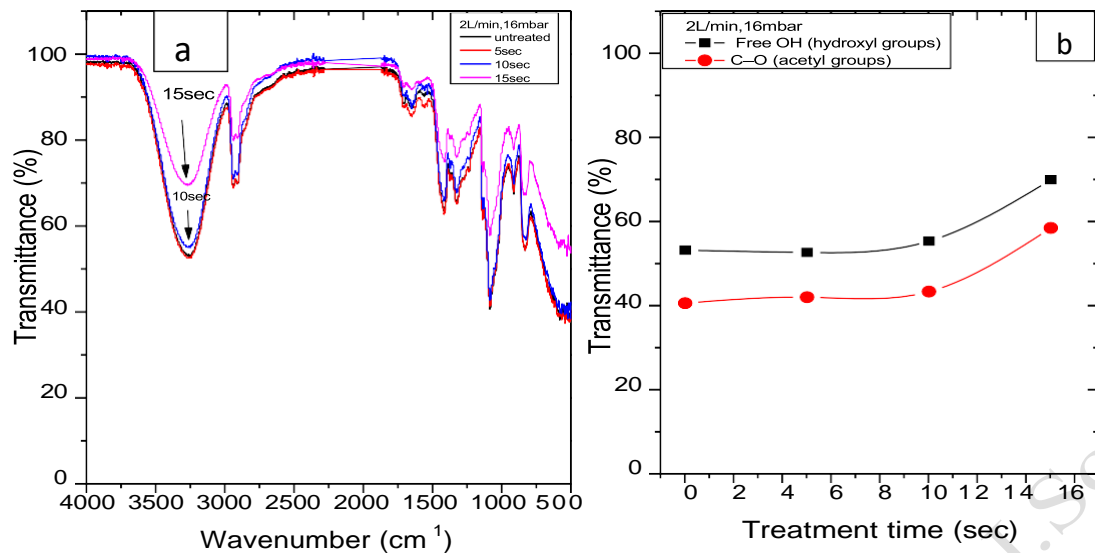
Figure 6: (a) ATR-FTIR spectra of untreated and treated oxygen plasma PVA film at treatment time 5 sec,10 sec and 15sec, (b) Transmittance spectra for free OH vibrations and acetyl groups
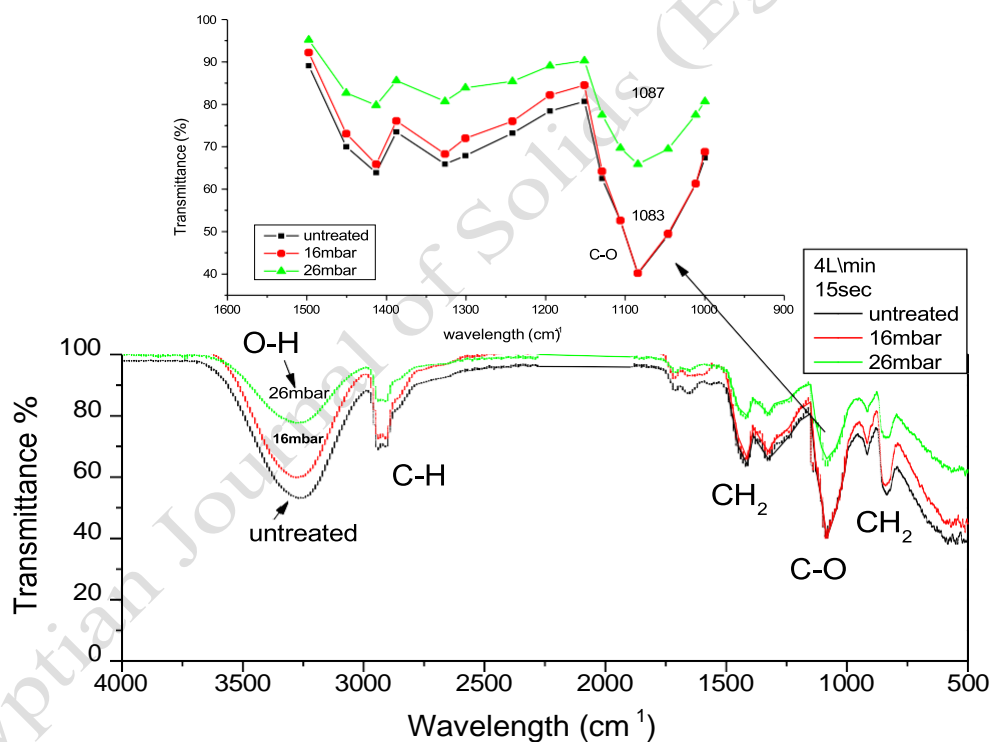

Figure 7: ATR-FTIR spectra of untreated and treated oxygen plasma PVA film at pressures 16mbar and 26mbar

Figure 7 illustrates the ATR-FTIR spectra of untreated and treated oxygen plasma PVA films at different pressures (16 mbar and 26 mbar). As seen from the figure, the intensity of all functional groups appears at 26mbar is more intense than at 16mbar in the spectrum. All the functional groups are the same of wavenumbers as the untreated PVA film as shown in table (1), except the

C–O stretching of acetyl groups has been shifted from 1083cm^{-1} at 16mbar to 1087cm^{-1} at 26mbar, this mean that the transmittance intensity is shifted to a higher wavenumber. This result indicates with increase in the pressure, the Oxygen is mainly incorporated in the film into the C–O bonding configuration [25]. Figure (8a) shows the ATR-FTIR spectrum of untreated and treated plasma of PVA film at pressure 26 mbar and time 15sec. this finding was optimized at three flow rates as follows: 2L\min,4L\min, and 6L\min. respectively. Our results display that the intensity of all functional groups at 6L\min appears more intense in the spectrum [25]. As shown in figure (8b), by increasing the flow rates of Oxygen till 6L\min, this leads to an increase in the Oxygen-containing functional groups (free hydroxyl groups and acetyl groups) revealed the Oxygen insertion into the polymer matrix. This finding correlates with the increase of hydrophilicity and surface energy for treated
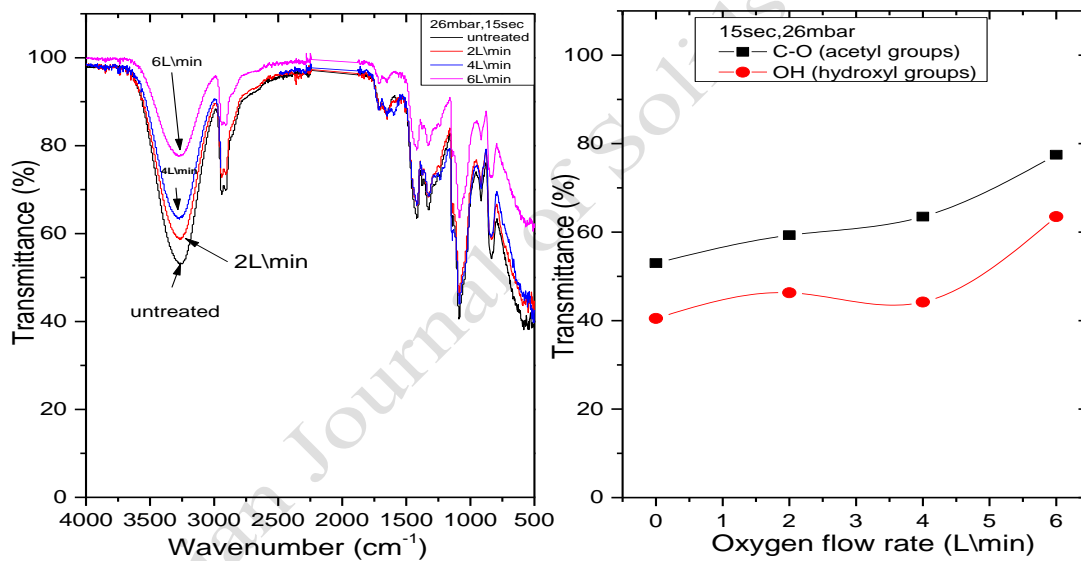

Figure 8: (a) ATR-FTIR spectra of untreated and treated oxygen plasma PVA film at flow rates 2L\min,4L\min, and 6L\min. (b) Transmittance spectra of free OH vibrations and acetyl groups

PVA films [26]. FTIR results can be used to determine the optimal values of plasma parameters for all the following measurements, which are listed in Table 2 below.

Table 2: Optimal values of plasma parameters

Plasma parameter	Optimal value
Treatment time (s)	15
Flow rate (L/min)	6
Pressure(mbar)	26

UV-vis measurements

Figure 9 shows the transmission spectra of glass, untreated, and oxygen-treated PVA films as measured by a UV-vis spectrometer). For comparing the film's performance under UV and visible light, wavelengths of 280 nm and 550 nm were chosen [20]. The experimental results showed that, the transmittance of the glass in the visible region at 550 nm is 91.5% compared with the pure PVA film at 72%only. The 15-second treated plasma for PVA films has a high transmittance of up to 85%which is near to transmittance, whereas the 10-second treated plasma PVA film transmittance up to 84% compared to pure PVA film. In the ultraviolet region, specially within the range (200-400 nm) the glass100% completely blocked the UV light, no absorption band is observed. At 280nm, transmittance of untreated PVA film is 47%. while the transmittance of the 10-second treated plasma and the 15-second treated plasma for PVA films is 53% and 64%, respectively. This means that the optimal values of plasma parameters give us higher transmission at the UV region than the pure PVA.

Our experiment confirms that the transmission increases in the wavelength range 280–400 nm in the UV region owing to weak absorption. This is caused by the plasma treatment. In addition, this transmittance increases as the plasma treatment time and pressure. The optical transmission maximum (about 72.5%, 85 % compared to the transmittance of glass (91%) has been discovered for untreated and treated PVA. Low levels of UV-B light (280 to 315 nm) induce photomorphogenic reactions that affect biochemical composition, photosynthetic competence, morphogenesis, and defense in plants [27]. Studies conducted in greenhouses are challenged because the plants are not exposed to UV-B. [28] In addition, Ultraviolet rays can impact the accumulation of plant biomass so that ultraviolet and visible rays help in photosynthesis. PVA polymer suitable for green house applications because its exceptional properties such as non-toxicity and have high tensile strength and abrasion resistance. Although PVA has limitations to use it in greenhouse with its low hydrophilicity but after treatment with Oxygen plasma the hydrophilicity is increased. This is showed in ATR-FTIR results, which show the intensity of two groups OH, C-O increased by treated Oxygen plasma. PVA film that has been treated with oxygen plasma is optically clear due to an increase in the hydrophilicity caused by oxygen content. Because all of this, the film can be used in greenhouses, to increase plant growth and for the cultivation of all plants throughout the year, particularly medicinal plants, which require specific conditions that are not available in all countries [29, 30].
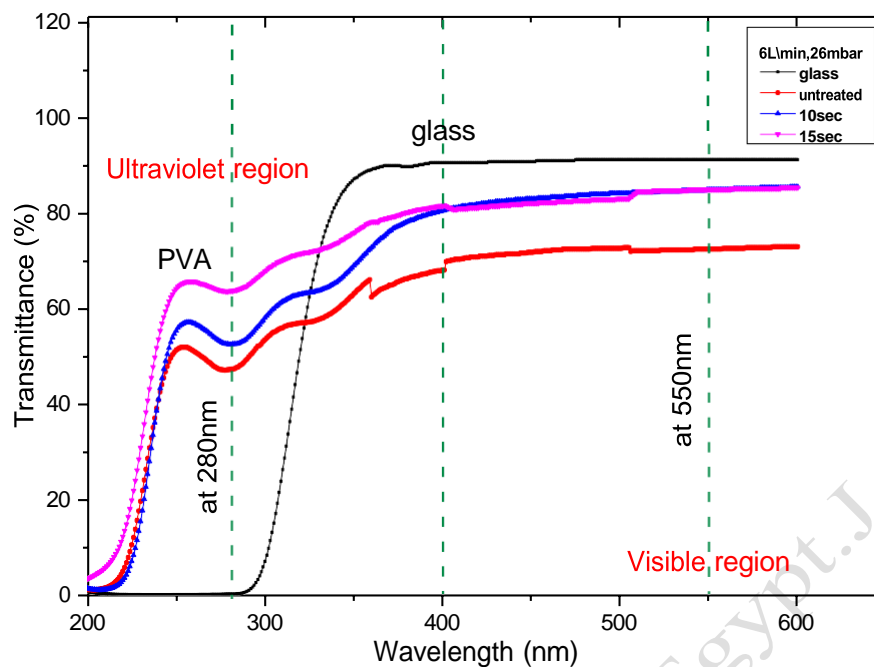
Figure 9: UV-vis Transmission spectra of glass, untreated and Oxygen plasma-treated PVA films at 6L\min and 26mbar

Conclusion:

In this work, A low-cost microwave oven-generated plasma has been successfully fabricated for surface treatments in the second regime. PVA polymer films have been prepared by the casting method using distilled water; at 80C∘, and constant stirring for 2hours. The XRD indicates the semi-crystalline nature of the prepared PVA film. A Paschen -like curve has been generated, the plasma initiation time versus the vacuum pressure inside the Pyrex chamber has been plotted. Steady tendencies of low vacuum pressure at two oxygen gas flow rates, 2L/min and 6L/min have been observed. ATR-FTIR results showed the intensity of all functional groups at 15 sec appears more intense in the spectrum. by increasing the treatment time from 5 sec till 15 sec. led to an increase in the oxygen-containing functional groups (free hydroxyl groups and acetyl groups), revealing the oxygen insertion into the polymer matrix. The C–O stretching of acetyl groups has been shifted from 1083 cm^{-1} at 16 mbar to 1087 cm^{-1} at 26 mbar; this means that the transmittance intensity

is shifted to a higher wavenumber. This result indicates that, Oxygen is mainly incorporated in the film in the C–O bonding configuration with an increase in pressure. Optimal values of plasma parameters are determined from the FTIR measurements. Higher transmission of PVA film treated at the optimal values of plasma parameters is obtained. Our finding concerning the Oxygen treated PVA film using microwave oven-generated plasma in the second regime could be used to increase the plant growth in the greenhouses for agriculture applications.

Declaration of Conflicting Interests

The author(s) declared no potential conflicts of interest concerning the research, authorship, and/or publication of this article.

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