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Original Research Article

Exploring surface diversification of polyvinyl alcohol/polyethylene glycol Composites by cold plasma: Ompact of Argon and oxygen plasmas on biomedical application

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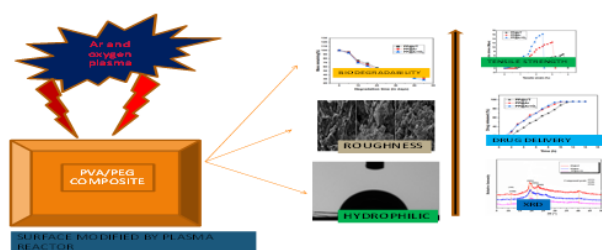
ABSTRACT

Tetraethyl orthosilicate was used as a crosslinker to create composites made of polyvinyl alcohol and polyethylene glycol (PVA/PEG (PP)). The composites were exposed to non-thermal plasma (NTP) treatment with an Argon and oxygen gas mixture. The NTP treatment resulted in an improvement in surface hydrophilicity. Physiographical investigations indicated surface nanotexturing, but bulk properties were unaffected. After twenty days of exposure to air, there was no detectable ageing effect, showing that the NTP-modified composites were extremely robust. The composites swelled more in intestinal pH than at gastric pH. The NTP-modified composites shown significant Biofilm eradication activity against *E. coli*. Plasma treated composites shown Greater antibacterial activity against *E.coli* and enterobacilous bacteria. Mechanical properties enhances with application of different carrier gases in the non-thermal plasma process. Release characteristics of the composites validated the controlled delivery of anticancer drug sulforaphane to the intestine. Biodegradability character increases for the plasma treated composites over the subsequent days. It was also discovered that the hydrogels were biodegradable. PVA/PEG composites treated with O₂ and Ar plasma are therefore effective for a variety of biomedical applications.

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1. Introduction



The application and use of thermoplastic polymers has elevated dramatically throughout the last three decades. Applications include grocery merchandise, food container

caps and closures, among other things, drinking glasses, household appliances, kid's toys, and building supplies. Emulsifiers, adhesion, packaging, cosmetics, and cosmetic composites are just a few of the many uses for water-soluble polymers like PEG and PVA. Among other things, PVA composite materials have several applications in the medical and business industries, and they have also been intensively explored by researchers.^{1, 2-13} Products are generated as a result of surface modification of composites, which leads to Mechanical, thermal, optical, and biological uses are among the many. This qualifies them as alternatives for other engineering materials, such as. Over the last few years, biodegradable polymers have discovered to be particularly effective for medication transport, antibacterial potential, tissue engineering application, the

food packaging, pharmaceutical, engineering, and textile industries, as well as a novel use for these polymers that involves blending them with other polymers and components.^{6,14} These composites may be modified using a variety of traditional physical and chemical techniques to make them useful in various contexts.¹⁵ Mixing and the creation of nanocomposites with enhanced characteristics have been achieved by physically blending several polymers.¹⁶ Research has examined the possibility of obtaining materials Abdel Tawab & Associates studies on how the PEG content affects the PVA/PEG blend's compatibility up to 60%. PVA/PEG mixes with a decent film are reported by other authors.¹⁷ mixes with a PEG concentration more than 40% are reported to not produce a cast film because of phase separation. But the primary drawback of hydrophilic polymers, such PVA and PEG, was discovered. They have poor mechanical qualities and little potential for biological reaction.¹⁸ When added to the polymer matrix, the nanoparticles at extremely low loading content demonstrated enhanced characteristics for nanocomposite systems.^{8,19} nanoscale layers, the PVA matrix's mechanical properties.²⁰ To the best of our knowledge and a review of the literature, no prior research has been done on the PVA/PEG nanocomposite based on grapheme; hence, In this study, the goal is to generate cast films with desirable physical properties by first examining the effect of PEG loadings on PVA/PEG blends.¹ El Sayed and Morsi²¹ used a hematite (α -Fe₂O₃) nanofiller to create PVA/PEG nanocomposites, which showed improved optical and dielectric properties. They discovered that increasing the filler content resulted in significant increases in both the refractive index and ac conductivity.²² Adding α -Fe₂O₃ nanoparticles to PVA improved its thermal stability.²² Sengwa et al. used this material to study the effect of nanoclay addition on a PVA/polyethylene oxide (PEO) mixture. Montmorillonite (MMT) clay was employed as a nanofiller in the development and testing of PVA/PEG nanocomposites.¹⁰ MMT clay's hydrophilic properties make it easy to disperse in water-soluble polymers such as PVA and PEG.¹⁰ Including MMT up to four weight percent enhances the mechanical characteristics of the PVA matrix.¹² According to our knowledge and a review of the literature, no previous research has been published on the PVA/PEG nanocomposite based on grapheme. This study examines the impact of PEG loadings on PVA/PEG blends to produce cast films with desirable physical qualities for future research. Additionally, PVA/PEG nanocomposites were created with graphene as a nanosheets to assess its impact on the PVA/PEG blend's mechanical characteristics, a nanosheets, to assess its impact on the PVA/PEG blend's mechanical characteristics. The interactions between the cell interface are crucial to the overall functionality of a biomaterial when it is designed.^{23,24} It is well recognized that surface characteristics, including as wettability,

energy, and topography, are important factors in enhancing the mechanical, tribological, cytocompatibility, and multifunctionality of devices.^{25,26} In summary, surface properties play a major role in determining a material's biocompatibility. Surface material diversification is therefore usually justified. Of all the methods, plasma-induced characterization is unquestionably the most well-known.^{27–35} This method is well-known since it doesn't require the use of chemical solvents, enables uniform surface characterization, and results in nano-and/or micro-topographies.^{28,32,33} Since non-thermal plasma (NTP) treatment often occurs at room temperature and generates no hazardous chemicals, its use has expanded dramatically.^{33–37} Numerous writers have documented the improvement in polymer bioefficacy subsequent to NTP adjustment.^{38–40}

In this work, the nontoxic crosslinker tetraethyl orthosilicate (TEOS) was used to generate composites of polyvinyl alcohol and polyethylene glycol (PVA/PEG) (PP). Using pure Ar and a combination of Ar and O₂, PP composite sheets were surface modified in an atmospheric pressure DBD plasma reactor. Contact angle measurement (CA), X-ray diffraction study (XRD), optical emission spectroscopy (OES), Fourier transformed infrared spectroscopy (FTIR), atomic force microscopy (AFM), field emission scanning electron microscopy (FESEM), tensile strength, and thermo gravimetric analysis (TGA) were among the analytical methods used to examine the composites. Furthermore, tests were conducted on the water vapour permeability and swelling property.

2. Materials and Methods

Sigma-Aldrich Company, USA supplied polyethylene glycol (PEG) (molecular content= 4000 g/mol) and polyvinyl alcohol (PVA) (Hydrolysis degree = 99%, molecular content= 27,000 g/mol, Polymerization degree,1750) are used for synthesis process.

2.1. Preparation of composite

PVA/PEG (1:1) Composites are prepared as follows: for preparation of each composite 2 g of PVA was dissolved in 50 ml of double distilled water under 800 C and stirring for 2 hr for the complete dissolution of sample with the help of magnetic stirrer. 2 g of PEG was dissolved in 50 ml of distilled water for 2hr with constant stirring and after that mixed with PVA solution with the help of crosslinker. Polymer mixtures were agitated at 400 rpm and 80°C for 2 hours to ensure thorough dissolving and mixing. Then, the entire mixture was degassed in Vacuum oven for 10 minutes. Then it has been casted into glass petri dishes and placed in an oven at 360C for 2 days In hot air oven. The produced composite was taken from petri dishes and stored in a desiccator containing calcium chloride to prevent

moisture absorption.¹ The obtained samples are used for further study in subsequent research work.

2.2. Cold atmospheric plasma treatment of PVA/PEG(PP) composite

Plasma surface diversification of PVA/PEG (PP) composites was carried out in a Dielectric Barrier Discharge (DBD) plasma reactor at atmospheric pressure. The Non representational diagram of the reactor is represented in Fig. 1.

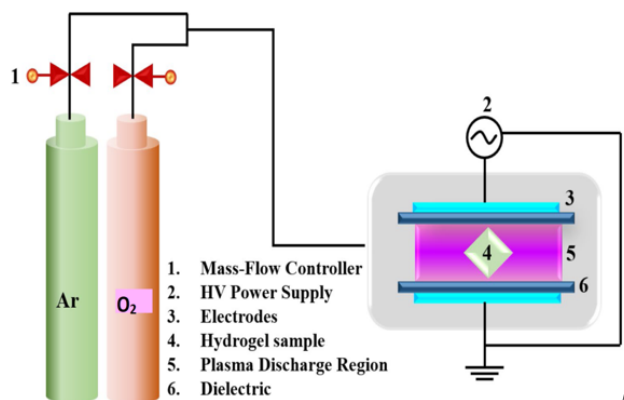


Figure 1: Non representational diagram of DBD reactor

The plasma reactor comprises of a chamber (20 cm x 20 cm) with two parallel alumina electrodes (10 cm x 10 cm) and a 2mm thick copper plate covering both electrodes. The upper electrode was linked to a high voltage pulse power source ($V_{max}=20kV$, output current = 100 mA, Frequency range = 10 kHz-100 kHz, duty cycle = 70% max obtained from Hydro Vac Technologies, Bangalore, India), while the bottom electrode was connected to earth. The space between the two electrodes were constant at 2 mm throughout the experiment.³⁵ The composite was inserted in between the electrodes. The gas flow was controlled by MFC (Aalborg MFC, Pravartaka Infotechnates, and Bengaluru-04). Generation of plasma For this work two gases were used: Ar (99.99%) and O₂ (99.99%). The flow rate was The plasma flow rate was kept constant at 1Lpm throughout the therapy. Table 1 below displays the parameters of the treatment. Depending on the type of plasma gas utilized, the samples that were CAP-treated were labeled as PP@Ar or PP@Ar+O₂, whereas the untreated PP film was labeled as PP@UT.

2.3. Characterization of hydrogels

2.3.1. Contact angle (CA) and surface free energy (SFE) measurements

With the aid of the sessile drop method, the contact angle (CA) and surface energy (SFE) of the aforementioned

composites were determined using the Rame-HartT ensiometer, USA. Two liquids, distilled water and ethylene glycol, are employed as polar and non-polar probe liquids, respectively, to measure static angles. We applied a drop of test liquid to the composite surface for base line correction, and after adjusting, we were able to measure the surface energy and contact angle values and take an instant digital picture. For every sample, three measurements were made, and the results are given as mean $\pm$ SD. The OWRK (Owens, Wendt, Rabel, and Kaelble) method was also used to compute the surface free energy (SFE).

2.3.2. Fourier transformed infrared spectroscopy (FTIR)

The samples were comminuted with dry KBr, constricted into small pellets with the help of hydrolic pressure and scanned in the wave length range of 4000-400 cm^{-1} and the spectra were collected in a Thermo Fischer iS5 FTIR spectrophotometer.

2.3.3. X-ray diffraction (XRD)

The samples' XRD patterns were examined using a RIGAKU ULTIMA-IVX-Ray diffractometer with Ni-filtered Cu Ka radiation (1.54056Å), scanning at a speed of 3°/min per minute from 5 to 40 degrees

2.3.4. Atomic force microscopy (AFM)

Surface roughness of the composites was analysed in a in a Veeco

di Innova atomic force microscope (AFM). Images were taken at a fixed scan rate of 0.5 Hz by tapping mode method. The roughness of composites has been studied in terms of rms (root mean squared) values.

2.3.5. Field emission scanning electron microscopy (FESEM)

To measure the porosity of the plasma induced surface composite pre and post plasma NTP treatment, were observed directly under JEOL JSM 6480LV SEM. The samples were frozen at -20°C for 5hr and then lyophilized at -55°C for 10 hr (Biobase Freeze Dryer).

2.3.6. Tensile strength

Tensile strength is defined as the amount of load or stress that a material can handle until it stretches and breaks. Tensile strength is normally measured in megapascals (Mpa) or newtons per square millimeter (N/mm²). The composites were tested in UTM machine (Instron, Model: 3382). For our study the load cell was 1 KN.

2.3.7. Thermo gravimetric (TGA analysis)

TGA, or Thermogravimetric analysis, is a powerful method for figuring out how heat stable a material is, especially a polymer. This method detects changes in a hydrogel's weight as its temperature rises. A ShimadzuDTG-60H

simultaneous DTA-TGA thermal analyzer is used for Thermogravimetric analysis. In a platinum pan, the samples weighing between 4 and 7 mg were heated to 900°C at a rate of 10°C/min while nitrogen was purged at a rate of 30 mL/min.

2.3.8. Optical emission spectroscopy (OES).

Photon emission in this area can be detected using an optical emission spectrometer. The acquired spectra reveal information about the plasma's composition and electron excitation, making it easier to calculate electron temperature and density. The UV-visible emission spectra from the plasma reactor were obtained using an Ocean Optics USB MAYA 2000 spectrometer with a lens coupled to a detector via a fiber optic cable. The lens was mounted to the quartz glass plate on the plasma reactor's view side. The integration time was set at 500–1000 ns.

2.4. Swelling response of hydrogels

One of the main characteristics of composites is swelling in an aqueous media. Therefore, the behavior of the composites was examined by submerging them in PBS at 37 °C (pH= 7.4). The hydrogels were removed and weighed at specific intervals until a consistent weight was reached. The following formula was used to determine the degree of swelling percentage:

$$\text{Swelling (\%)} = \frac{W_s - W_d}{W_d} \times 100$$

Where W_s and W_d are the weights of the equilibrium swollen

and dried composites respectively.

2.5. In vitro drug release kinetics

To get rid of any last traces of moisture, the PP composites were vacuum-dried for 24 hours. The ability of a composite to expand, the drug's solubility in the release media, and the drug's interaction with the polymers all play a major role in determining drug release from a composite.¹⁷ Several physiological changes, such as distilled water, simulated gastric fluid (SGF) (pH2.2), and simulated gastro intestinal fluid (SIF) (pH7.4), were used to study the drug release of Composite. By soaking the composites in 10 milliliters (1 grams per milliliter) of sulforaphane/ethanol solution (drug solution) for 48 hours in the dark, the sulforaphane medication was infused into them. For in vitro drug release, the sulforaphane-loaded composites were continuously agitated while submerged in 50 milliliters of PBS (pH= 7.4) at 37 °C with constant stirring. Next, five milliliters of the solution were taken at specific time and after that absorbance is measured using UV-Vis spectrophotometer. Measurements of absorbance were used to estimate the amount of sulforaphane released. The following formula was utilized to determine the composites' drug loading efficiency.

$$\text{Released drug (\%)} = \frac{\text{Quantity of drug released}}{\text{Quantity of drug loaded}} \times 100$$

2.6. Kinetics of drug release

The drug release calculation data were fitted to four basic kinetic equations 4-7^{29–32}. The drug release data were fit to four basic kinetic models given by Equations 4-7^{29–32} and the best equation was examined against the highest value of correlation coefficient, R^2 :

Zero Order: $M_t/M_\infty =$	$K_0 t$	(4)
Higuchi: $M_t/M_\infty =$	$K_H t^{1/2}$	(5)
Ritger _ Peppas: $M_t/M_\infty =$	$K_{RP} t^n$	(6)
Peppas _ Sahlin : $M_t/M_\infty =$	$K_1 t^m + K_2 t^{2m}$	(7)

Where, M_t/M_∞ represents the fractional drug release at time t . K_0 , K_H and K_{RP} represents as the kinetic rate constants for the zero order, Higuchi and Ritger-Peppas equations respectively. n represents as exponential diffusion in drug mechanism. For a thin film/composite, when $n=0.5$, the drug release is calculated by Fickian kinetic equation.; $n=1$ indicates Case II transport calculated by zero-order kinetics. When n lies between 0.5 and 1, anomalous transport in drug release mechanism is observed. For Peppas-Sahlin model, the first part of Eq. 7 represents the contribution of Fickian diffusion and the second term refers to the macromolecular relaxation contribution on the overall release process. K_1 is the diffusion and K_2 is the relaxation rate constant. The coefficient m is the Fickian diffusional exponent and its value is 0.5 for thin films. Using the estimated parameters K_1 and K_2 from Eq. 7, the ratio of relaxation (R) and Fickian (F) contributions was calculated using Eq. 8 given as: $R/F = (K_2/K_1) t^m$ (8).

2.7. Biodegradability study

By measuring the weight loss of the composites (3 cm x 3cm) that buried in soil, the composite's biodegradability was analysed. Water sprinkles continuously at a certain interval of time to keep drying out from the soil. The samples are taken out after 20 days ,washed it completely and then dried to weight the amount of weight loss by the composite.¹⁹ Then SEM analysis was done to get clear degradation image.

2.8. Antimicrobial propensity

Composites PP@UT and PP@ T response towards antimicrobial activity was evaluated against gram positive bacteria like E.coli and Gram negative bacteria like S.aureus by the traditional Disc diffusion method . The polymeric films were cutted into small disks of 6 mm diameter, sterilized and placed on agar plates. The experimental plates were incubated for 24 h at 37 °C and the zone of inhibition was measured. Experiments have been performed in triplicate and mean data represented.

2.9. Antibiofilm property

Acridine orange dye binding to the biofilm-forming bacterium *E. coli* was used to measure the impact of composites on biofilm formation. An overnight-grown culture of *E. coli* was used to create a 0.4 McFarland suspension, which was then injected. Add 4 mm diameter and 1.5 mm thick composites to the LB broth on a 24-well plate. Glass slides were autoclaved, partially immersed in media, then incubated for 48 hours at 37°C in a static environment. Following incubation, glass slides were dyed for 20 minutes with a 0.01% acridine. Acridine orange dye solution and then cleaned with PBS. After using 200 μ L of PBS to eliminate extra dye, the slides were completely dried. A confocal laser scanning microscope was used to monitor the developing biofilms. A control set was maintained without any supplementation the composites.

3. Results and Discussion

3.1. Composite synthesis and NTP modification

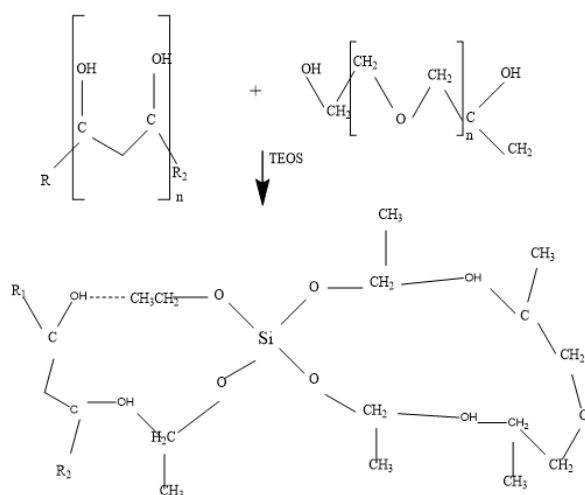


Figure 2: Schematic representation of formation of PVA/PEG composite

3.2. Surface topographical analysis (AFM)

The topography of the composites after NTP alteration was examined using AFM, and the images are shown in Figure 3. 3D AFM scans revealed a significant topographical shift in the composites after plasma treatment. Images shows that PP@UT appeared regular rough surface with smaller bumps over the surface. Whereas the PP@Ar and PP@Ar+O₂ composites were found to be more irregular surface area, higher bumps high roughness, irregular, and coarse. The degree of roughness were assessed using root mean squared (rms) values. Lower rms values suggest a smoother surface. The predicted rms values for PP@UT, PP@Ar, and PP@

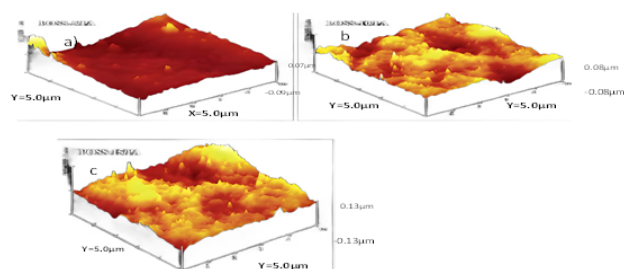


Figure 3: AFM images of a) PP@UT b) PP@Ar c) PP@Ar+O₂

Ar+O₂ composites were 2.45 ± 0.88 nm, 8.28 ± 1.55 nm, and 10.04 ± 1.73 nm, respectively. The mixing of Ar and O₂ plasma caused more surface roughness on the composite than Ar alone did. The combined impacts of reactive Ar and O₂ plasmas impinging on the composite surface could be accounted for, resulting in increased etching. The AFM results confirmed that NTP therapy caused topological changes in the composites at the nanoscale level while the bulk properties of sample remains unchanged.

3.3. Fourier electronic scanning microscopy (FESEM)

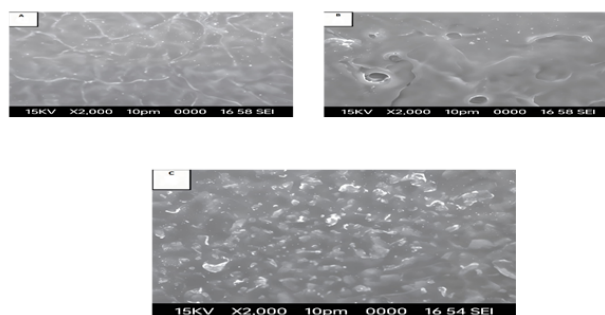


Figure 4: FESEM images of a) PP@UT b) PP@Ar c) PP@Ar+O₂

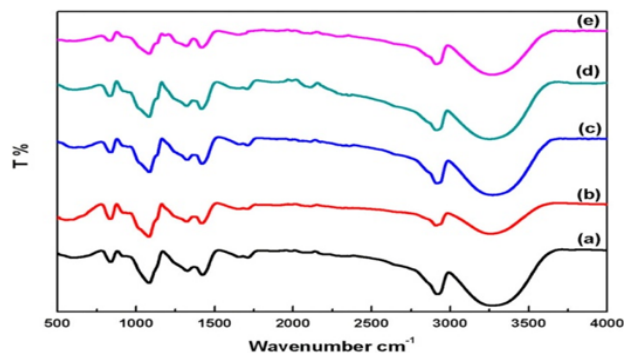
The surface morphology of the composites after NTP alteration was examined using a SEM, as shown in Figure 4. PP@UT had a smooth, homogeneous, and flaw-free surface, while NTP-treated composites had uneven and rough surfaces with dents and crystallites caused by etching. Plasma treated composites shows greater porous character than untreated one because plasma etching process leads to creates rupturing of surface due collective effect of carrier gases like Ar and O₂ gases. above such plasma treated surfaces have been already reported for PVA/Cellulose work.³³

3.4. FTIR analyses

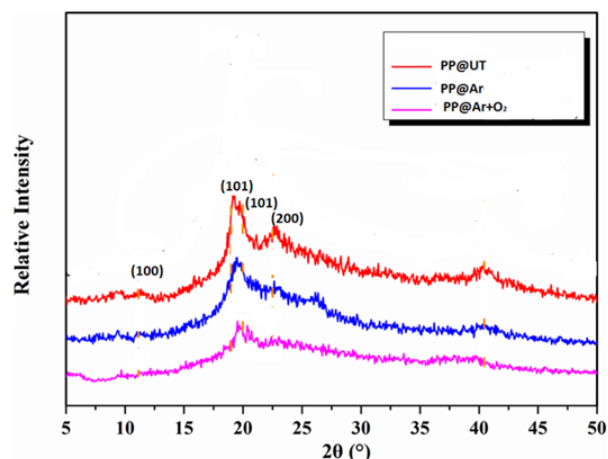
The interaction of polymers in a composite is implied by FTIR explanations in terms of modifications or shifts in distinctive absorption bands. Figure 5. The composite

Table 1: Contact angle and surface energy for PP composite

Samples Parameters	PP @UT	PP@Ar+O ₂	PP @Ar
	2		
Water(Θ_w)	49.20 $\pm$ 1.17	16.55 $\pm$ 0.93	25.38 $\pm$ 0.88
EthyleneGlycol (Θ_{EG})	25.28 $\pm$ 0.51	15.33 $\pm$ 0.74	19.71 $\pm$ 0.37
	Surface Free Energy (mJ/m ²)		
D	12.51 $\pm$ 0.98	2.05 $\pm$ 0.14	4.06 $\pm$ 0.48
Dispersive(γ)			
P Polar(γ)	37.40 $\pm$ 2.05	81.84 $\pm$ 0.96	67.72 $\pm$ 0.96
Total	49.90 $\pm$ 1.08	83.89 $\pm$ 0.82	71.31 $\pm$ 0.82
Total(γ)			

**Figure 5:** FTIR images of PVA/PEG composites

PVA/PEG FTIR spectrum before (PP@UT) and after (PP@Ar and PP@Ar + O₂) plasma treatment are shown. From FTIR data, we were able to know the structural changes and the principal bonding interactions between these two polymers. In comparison to the other two composites, the PVA/PEG(PP)composites that were treated in an Ar and oxygen plasma environment exhibit a somewhat wider band which corresponds to the stretching of the O-H (hydroxyl) group. This might be because of the involvement of O-H in the the hybrid complex.² Furthermore, a wide band was seen in the spectra of every Composite at roughly 1068 cm⁻¹. This finding indicated that the crosslinker TEOS had produced a siloxane bond (Si-O).³³ The PP@UT's FTIR spectrum characteristics bore a striking resemblance to those of the composites changed by plasma. In contrast to PP@UT and PP@Ar, the intensity of hydroxyl absorption of PP@Ar+O₂ was discovered to be somewhat considerable. This observation supported our CA results by indicating that the composites obtained after NTP treatment were hydrophilic.

**Figure 6:** XRD analysis of a) PP@UT b) PP@Ar c) PP@Ar+O₂

3.5. XRD analyses

X-ray diffraction is a valuable tool for studying lattice arrangements and determining a material's crystallinity. Figure 6 shows the Composites diffraction patterns. The crystallinity property decreases as we go from PP@UT to PP@Ar+O₂. The diffraction pattern for the composite without plasma treatment appeared at $2\theta=19.5^\circ$ corresponding to (101) plane which is due to the semi-crystalline nature of PVA. After undergoing non-thermal plasma treatment, there is a decrease in the intensity of these peaks, indicating decreasing crystallinity character. It might be due to the interpolymeric interaction of PVA and PEG, through hydrogen bonding that disturb the parent polymer composite and reduce the crystallinity of the composites.³⁴ The crystallinity of PP@Ar and PP@Ar+O₂ remained unaffected, plasma did not impair much the organization of the polymer chains in the composite as plasma only changes the surface properties it does not affect the bulk properties of composites.

3.6. Smart swelling responsivity

When evaluating a polymer composite for its potential in drug delivery, swelling is an important factor to consider. At 37 °C the composite's swelling reactions at pH 1.2 (gastric pH) and pH 7.4 (intestinal pH) were assessed; the results are shown in Figure 7. The composite exhibited swelling properties that were sensitive to pH, reaching their maximum swelling at pH 7.4 and decreasing at pH 1.2. Because the hydroxyl and ethane groups stay in neutral ion form at lower pH values, the complex becomes less capable of absorbing water and becomes hydrophobic. Ionization of the aforementioned groups results in anion-anion electrostatic repulsion at neutral pH. This made sure that the complex could hold more water molecules, which increased the swellability as a result³⁵. The combination of

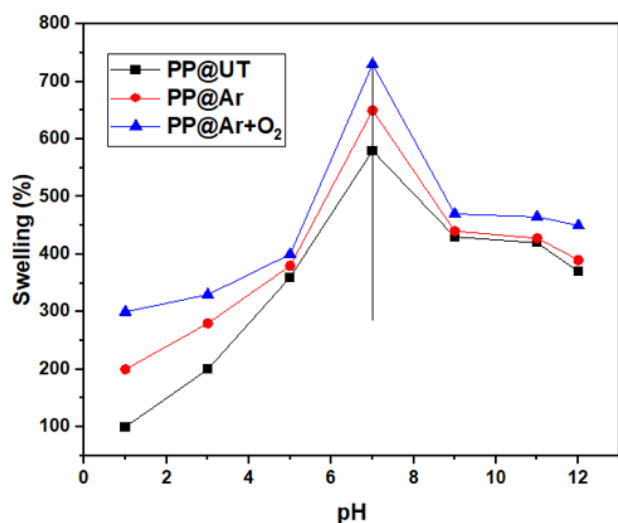


Figure 7: Smart swelling response of PVA/PEG composites at 37°C

PP@Ar+O₂ exhibited the greatest swelling character due to higher surface wettability among the other two.

3.7. *In vitro* sulfarophane release studies and kinetics

The encapsulation efficiency of sulfarophane in composites was found to be 57.8%, 59.5% and 62.3% for PP@UT, PP@Ar and PP@Ar+O₂ like this. This concludes that the EE of drug generally rely on the swelling capacity of composite. With increase in swellability drug encapsulation efficiency increases.

3.7.1. Sulfarophane release studies

The Sulfarophane drug release graph from the above composites at room temperature (37 °C) have been shown in Figure 8. A and B. From, Plasma treated composites in presence of oxygen and Argon carrier gases shown faster release rate compared to pure composite. This difference in release rate can be analysed through swelling behavior of the composite. It is anticipated that polymeric composites with greater swelling capacities may discharge more quickly than others. Drug release occurs sooner since the PP@Ar+O₂ matrix is the most hydrophilic of the others. But in all three scenarios, the burst release effect is removed, meaning that these hydrogels could be used as long-term delivery vehicles for sulfarophane in cancer treatment. Sulfarophane release from the composite was investigated in SGF and SIF to better mimic the conditions of the gastrointestinal system. Following a two-hour immersion in SGF, the hydrogels were moved to SIF, where the drug release was observed. The Sulfarophane release profile in the SGF and SIF settings is shown in. In the first two hours in SGF, almost 12% of the sulfarophane was released. But the rate at which sulfarophane is released profile in SGF

and SIF environments. Approximately 12% of Sulfarophane was released throughout the first 2 hours at SGF. However, the rate of Sulfarophane release rose considerably when the composites were transferred to SIF. This release profile of Sulfarophane meets the standards of the US Pharmacopeia for oral medication delivery to the lower section of the gastrointestinal system, targeting the colon.

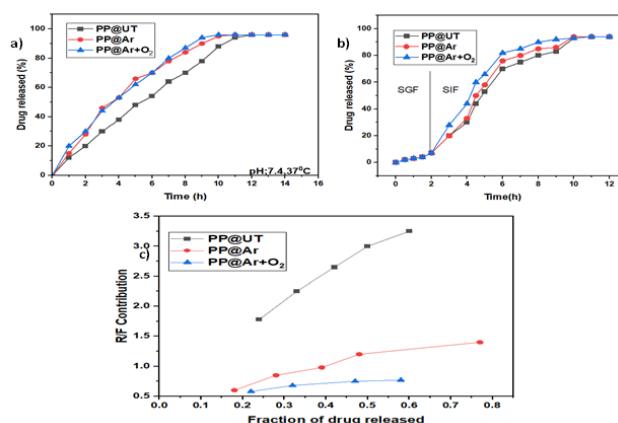


Figure 8: Drug release from hydrogels at pH 7.4, 37 °C, SGF, and SIF in (A), and a plot of R/F vs the percentage of drug released from hydrogels in (B) and (C).

3.8. Antimicrobial activity

It was investigated how well the composites treated with and without plasma inhibited the growth of both gram-positive and gram-negative bacteria. Below displays the zone of inhibition for gram-positive *Bacillus* and gram-negative *Enterobacter* bacteria. The range of 7.4–14.01 mm is where the inhibitory zones for *Bacillus* bacteria are obtained. Additionally, inhibitory zones for *Enterobacteriaceae* are found to be between 7.5 and 14.67 mm. PP@Ar+O₂ composites outperform PP@UT and PP@Ar composites in terms of performance. This is because, despite the increased wettability following plasma treatment, the presence of reactive electrons and hydroxyl groups oxidizes a group and increases anti-microbial activity. Wettability is therefore a crucial component for improving the connection with biological processes. The results showed that the composites are effective materials for wound healing.

Table 2: PP composites' antimicrobial study against *Enterobacteria* and *Bacillus*

Samples	<i>Bacillus</i> Bacteria; Zone of inhibition (mm)	<i>Enterobacteria</i> ; Zone of inhibition (mm)
PP@UT	7.4±0.6	7.5±0.6
PP@Ar	10.75±0.4	10.63±0.5
PP@Ar+O ₂	14.01±0.5	14.67±0.5

3.9. Mechanical strength properties

The mechanical characteristics including tensile strength, Young's modulus, and elongation at break (%) of PP composites after undergoing plasma treatment were illustrated in Figure 9.

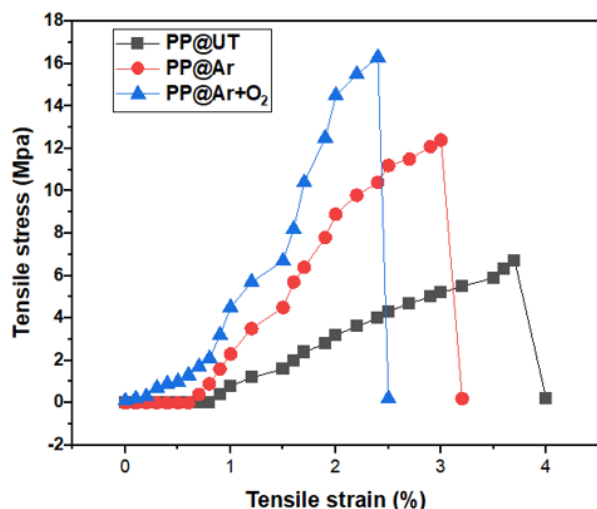


Figure 9: Tensile stress and tensile strain of PVA-PEG composites after NTP treatment

The thickness of the prepared composite was found to be in the range of 0.10 to 0.15mm and the width was 14 mm. Elasticity and strength are the two important factors for any composite material. A material's tensile strength is the amount of strain it can sustain before failing or breaking when it is stretched or pulled. The term "elongation at break" refers to the films' extensibility or flexibility. The stiffness or rigidity of the film is determined by Young's modulus. The synthesized samples were tested after being conditioned in a laboratory environment for 24hrs under identical conditions at break (%) with respect to different composites are shown in supplementary figure below. Tensile Strength is an important measure for determining the mechanical strength of composites before and after plasma treatment. The tensile strength went up from 58.513 ± 0.78 MPa for PP@UT to 79.80 ± 1.42 MPa and 92.8 ± 0.81 MPa for PP@Ar and PP@Ar+O₂, respectively. The tensile strength and Young's modulus of the composites are observed to rise while the Elongation at break(%) decreases, indicating an increase in stiffness of PP@Ar and PP@Ar+O₂ composite. Very strong H-bonding and other chemical interactions that take place in the composites after treatment may be used to explain the increase in tensile strength and Young's modulus of the materials as well as the decrease in Elongation at Break (%). The composites exhibited an increased cross-linked density due to the Ar and O₂ plasma treatment, resulting in improved load capacity within the composites. It was observed that

the elongation at break (%) decreases from 4.5% to 4.03% in case of PP@Ar composite and 2.7% for PP@Ar+O₂ composite. So Compared to PP@UT Composite, the plasma treatment gave the polymer chains inside the composite matrix stiffness and rigidity.

3.10. Biodegradability

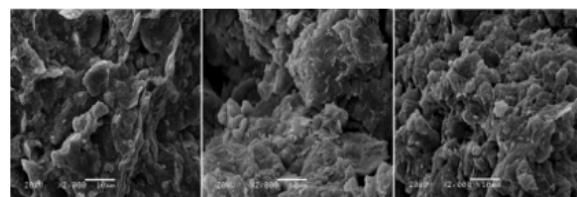
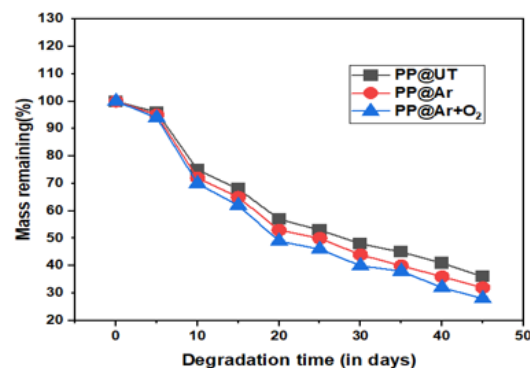


Figure 10: a) Degradation profiles of the hydrogels upon burying in soil. SEM images of the biodegraded hydrogels; (b) PP@UT, (c) PP@Ar and (d) PP@Ar+O₂.

Figure 10. a displays the breakdown profiles of the hydrogels treated with plasma, demonstrating their remarkable biodegradability. The presence of soil microorganisms like fungi and bacteria is what causes these hydrogels to degrade. The porous matrix structures of the NTP-modified hydrogels allow more water to permeate into the matrix, accelerating breakdown compared to the untreated one. This may be the cause of the composite's greater degradability. After 45 days of burial, the SEM images of the biodegraded PP@UT, PP@Ar, and PP@Ar/O₂ composites are shown in Figure 10 (b–d). As can be seen, the composites have distinct morphologies with fissures that amply demonstrate the deterioration and erosion of the samples. Due to its hydrophilic character, the PP@Ar/O₂ was shown to be more biodegradable when compared to the other two. The breakdown of these composites is brought on by the presence of soil microorganisms including bacteria and fungi. The greater degradability of the NTP-modified hydrogels may have been facilitated by their porous matrix designs, which allowed more water to permeate into the matrix and accelerated deterioration in c. It is evident that the composites have unique morphologies and cracks that

clearly show how the samples have eroded and deteriorated. The reason the PP@Ar/O₂ turned out to be so much more biodegradable than the other two is likely due to greater plasma itching treatment compared to other two.

4. Conclusion

In this study, we used TEOS, a nontoxic green crosslinker, to create biocomposites made of PVA and PEG. FTIR spectrum investigations verified the effective cross linking by TEOS. We have modified the surface of the Composite by NTP treatment using Ar and a combination of Ar and O₂ gases in order to further elaborate on it for possible biomedical uses. Following plasma alteration, it was found that surface wettability and energy were significantly increased. From SEM studies, surface etching caused by plasma treatment was also visible. According to the AFM investigations, hydrogels underwent topographical alterations at the nanoscale level as a result of NTP treatment, while their bulk physical structures remained unaffected. Even after 20 days of air exposure, the NTP-modified Composites showed negligible signs of aging, the composites exhibit smart swelling with maximal swelling at a pH of neutral and had a macro porous structure. Prominent characteristics of biofilm eradication against *Escherichia coli* were detected in the composites treated with NTP. The PP@Ar and PP@Ar+O₂ composites' FTIR study shows a rise in cross-link density, which results in better mechanical qualities such a higher tensile strength and Young's modulus. At pH 7.4, the composite exhibited good swellability. The release of the medication sulforaphane in the simulated intestinal fluid (SIF) and simulated gastric fluid (SGF) environments points to the possibility of using these systems to administer sulforaphane specifically to the colon. Antimicrobial investigation shows that the PP@Ar+O₂ composite experienced excellent inhibition. Furthermore demonstrating good biodegradability are these treated composites. Other possible uses for the atmospheric DBD plasma surface functionalized PP composites include both in the tissue engineering and biomedical industries. Additionally, the theoretical computations of the products can give a light on surface chemistry interactions.

5. Source of Funding

None.

6. Conflict of Interest

None.

References

1. Jose J, Harthi MA, Aimaadeed MAA, Dakua JB, De S. Effect of graphene loading on thermo mechanical properties of poly(vinyl alcohol)/starch blend. *J App Polymer Sci*. 2015;16:132–5.
2. Jose J, Shehzad F, Al-Harathi M. Preparation method and physical, mechanical, thermal characterization of poly(vinyl alcohol)/poly(acrylic acid) blends. *Polymer Bull*. 2014;71(11):2787–802.
3. Bin-Dahman OA, Jose J, Al-Harathi M. Compatibility of poly(acrylic acid)/starch blends. *Starch - Stärke. Biosynthesis Nut Biomed*. 2015;67:1061–9.
4. Jose J, Al-Harathi M. Citric acid cross linking of poly(- vinyl alcohol)/starch/graphene nanocomposites for superior properties. *Iranian Pol J*. 2017;26(8):579–87.
5. Bin-Dahman O, Rahaman M, Khastgir D, Al-Harathi M. Electrical and dielectric properties of poly(vinyl alcohol)/starch/graphene nanocomposites. *Canad J Chem Eng*. 2018;96(4):903–11.
6. Sreekumar PA, De AHMA. Reinforcement of starch/polyvinyl alcohol blend using nano-titanium dioxide. *J Compo Mat*. 2012;46(25):3181–7.
7. Appu SP, De SK, Khan MJ, Al-Harathi MA. Natural weather ageing of starch/polyvinyl alcohol blend: effect of glycerol content. *J Polymer Eng*. 2013;33(3):257–63.
8. Sreekumar PA, Al-Harathi MA, Gondal MA, De SK. Heterogeneity of laser-irradiated films of polyvinyl alcohol/ starch blends: effect of glycerol content. *Surface Interfac Anal*. 2013;45(6):104–51.
9. Jose J, De S. Compatibilizing role of carbon nanotubes in poly(vinyl alcohol)/starch blend. *Starch - Stärke. Stärke*. 2015;67(1-2):147–53.
10. Sengwa RJ, Choudhary S, Sankhla S. Dielectric properties of montmorillonite clay filled poly(vinyl alcohol)/poly(- ethylene oxide) blend nanocomposites. *Comp Sci Technol*. 2010;70(11):1621–7.
11. Tawab A, Magida K, Ibrahim MM, Sengwa S, Choudhary S. Effect of ionizing radiation on the morphological, thermal and mechanical properties of polyvinyl alcohol/polyethylene glycol blends. *J Pol Environ*. 2011;19(2):440–6.
12. Hussein MZ. Plasticized poly(lactic acid) with low molecular weight poly(ethylene glycol) mechanical, thermal, and morphology properties. *J Appl Pol Sci*. 2013;130(6):26–9.
13. Guo Z, Zhang D, Wei S. Effects of iron oxide nanoparticles on polyvinyl alcohol interfacial layer and bulk nanocomposites thin film. *J Nanoparticle Res*. 2010;12(7):2415–26.
14. Borges MG, Benetoli LO, Lic_Inio MA, Zoldan VC, Silva S, Pasa J, et al. polymer films with surfaces unmodified and international journal of polymeric materials and polymeric biomaterials 13 modified by non-thermal plasma as new substrates for cell adhesion. *Mater Sci Eng Mater Biol Appl*. 2013;33(3):1315–24.
15. Chen M, Zamora PO, Som P, Pena LA, Osaki S. Cell Attachment and Biocompatibility of Polytetrafluoroethylene (PTFE) Treated with Glow-Discharge Plasma of Mixed Ammonia and Oxygen. *J Biomater Sci Polym*. 2003;14(9):917–35.
16. Chu PK, Chen JY, Wang LP, Huang N. Plasma-Surface Modification of. *Biomater Mater Sci Engg*. 2002;36(5-6):143–206.
17. Perez PL. Effect of Chitosan Membrane Surface Modification via Plasma Induced Polymerization on the Adhesion of Osteoblast-like Cells. *J Mater Chem*. 2007;17(38):4064–71.
18. Desmet T, Morent R, Geyter D, Leys N, Schacht C, Dubruel E. Nonthermal Plasma Technology as a Versatile Strategy for Polymeric Biomaterials Surface Modification: A Review. *Biomacromolecules*. 2009;10(1):2351–78.
19. Hoffman A. Surface Modification of Polymers: Physical, Chemical, Mechanical and Biological Methods. *Macromol Symp*. 1996;101:443–54.
20. Fridman G, Friedman G, Gutsol A, Shekhter AB, Vasilets VN, Fridman A. Applied Plasma Medicine. *Plasma Pro Polym*. 2008;5(6):503–33.
21. Hetemi D, Pinson J. Surface Functionalization of Polymers. *Chem Soc Rev*. 2017;46:5701–13.
22. Han Y, Manolach SO, Denes F, Rowell R. Cold Plasma Treatment on Starch Foam Reinforced with Wood Fiber for Its Surface Hydrophobicity. *Carbohydr Polym*. 2011;86(2):1031–7.
23. Chan CM, Ko TM, Hiraoka H. Polymer Surface Modification by Plasmas and Photons. *Surf Sci Rep*. 1996;24(1-2):1–54.
24. Wang Y, Lu L, Zheng Y, Chen XJ. Hydrophilicity PHBV Films Plasma Trea. 2006;76:589–95.

25. Das P, Ojah N, Kandimalla R, Mohan K, Gogoi D, Dolui SK, et al. Surface Modification of Electrospun PVA/Chitosan Nanofibers by Dielectric Barrier Discharge Plasma at Atmospheric Pressure and Studies of Their Mechanical Properties and Biocompatibility. *Int J Biol Macromol*. 2018;114(5):1026–32.
26. Pandiyaraj N, Deshmukh K, Arunkumar RR, Ramkumar A, Ruzybayev MC, Halim MH, et al. Evaluation of Mechanism of Non-Thermal Plasma Effect on the Surface of Polypropylene Films for Enhancement of Adhesive and Hemo Compatible Properties. *Appl Surf Sci*. 2015;347:336–46.
27. Dolci LS, Liguori A, Panzavolta S, Miserocchi A, Passerini N, Gherardi M, et al. Non- Equilibrium Atmospheric Pressure Plasma as Innovative Method to Crosslink and Enhance Mucoadhesion of Econazole-Loaded Gelatin Films for Buccal Drug Delivery. *Colloids Surfaces B: Biointerfaces*. 2018;163(1):73–82.
28. Padil VVT, Nguyen NHA. Fabrication and Antibacterial Properties of a Plasma Modified Electrospun Membrane Consisting of Gum Kondagogu, Dodecenyl Succinic Anhydride and Poly (Vinyl Alcohol). *Surf Coat Technol*. 2015;271(1):32–8.
29. Dalei G, Das S, Das SP. Non-Thermal Plasma Assisted Surface Nano-Textured Carboxymethyl Guar Gum/Chitosan Hydrogels for Biomedical Applications. *RSC Adv*. 2019;9(3):1705–16.
30. Owens D, Wendt R. Estimation of the Surface Free Energy of Polymers. *J Appl Polym Sci*. 1969;13(8):1741–7.
31. Serra L, Domenech J, Peppas NA. Drug Transport Mechanisms and Release Kinetics from Molecularly Designed Poly(Acrylic Acid-g-Ethylene Glycol) Hydrogels. *Biomaterials*. 2006;27(31):5440–51.
32. Higuchi T. Mechanism of Sustained-Action Medication. Theretical Analysis of Rate of Release of Solid Drugs Dispersed in Solid Matrices. *J Pharm Sci*. 1963;52(12):1145–9.
33. Peppas NA, Sahlin JJ. Simple Equation for the Description of Solute Release. III. Coupling of Diffusion and Relaxation. *Int J Pharm*. 1989;57(2):169–72.
34. Yuan X. Enhanced interfacial interaction for effective reinforcement of poly(vinyl alcohol) nanocomposites at low loading of graphene. *Polymer Bull*. 2011;67(9):1785–97.
35. Mansur HS, Costa DS, Mansur E, Barbosa-Stancioli JR. Cytocompatibility Evaluation in Cell-Culture Systems of Chemically Crosslinked Chitosan/PVA Hydrogels. *Mater Sci Eng*. 2009;29(5):1574–83.
36. Denes F, Young RA. Surface Modification of Polysaccharides Under Cold Plasma Conditions. *Indus Crops Prod*. 1998;115:1087–135.
37. Morent R, Geyter D, Desmet N, Dubruel T, Leys P. Plasma Surface Modification of Biodegradable Polymers: A Review. *Plasma Pro Polym*. 2011;8(3):171–90.
38. Ali ZI, Eisa W. Characterization of Electron Beam Irradiated Poly Vinyl Alcohol/Poly Ethylene Glycol Blends. *Journal of Scientific Research*. 2014;6(1):29–42.
39. Li Y, Wu W, Lin F, Xiang A. The interaction between poly(vinyl alcohol) and low-molar-mass poly(ethylene oxide). *J Appl Pol Sci*. 2012;126(1):162–8.
40. Sreekumar PA, Al-Harhi. Effect of glycerol on thermal and mechanical properties of polyvinyl alcohol/ starch blends. *J Appl Polymer Sci*. 2012;123(1):135–42.

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