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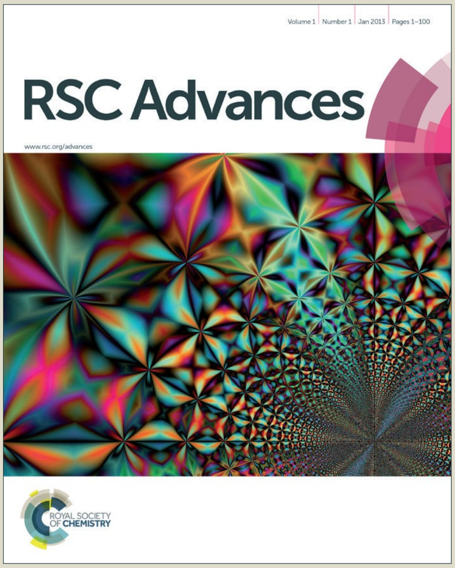

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Effect of TEOS plasma polymerization on Corn Starch/Poly(ε-caprolactone) film: characterization, properties and biodegradation

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Considering the impact of non-degrading polymers and plastics on environment

ABSTRACT:

Polymeric packaging materials are preferred because of lightweight and cost-effective as compared to conventional packaging. Plasma enhanced chemical vapor deposition (PECVD) of organo-silicon compounds is one of the ways to deposit silicon oxide (SiOx) coating on polymers to improve barrier properties. In this paper, Tetraethyl orthosilicate (TEOS) precursor was used to deposit SiOx coating on Corn Starch/Poly(ε-caprolactone) (CSPCL) films by PECVD. The effect of deposition time on various properties was studied. ATR-FTIR XPS and XRD revealed that coating has highly cross-linked SiOx glass like structure. AFM and SEM suggested smooth and conformal morphology. Adhesive properties were studied from peel strength and co-related with work of adhesion. Barrier properties were studied from water vapor and oxygen transmission rate showed significant improvement. Effect of plasma polymerized TOES (ppTEOS) coating on biodegradation of CSPCL films was evaluated by indoor soil burial method (to simulate natural degradation) and with single micro-organism, *Bacillus subtilis* MTCC 121(BS 121) (to understand interaction between micro-organism & modified surface). Biodegradation by indoor soil burial method was assessed by measuring change in tensile properties and growth of soil micro flora on surface by optical light microscopy. Biodegradation by BS 121 was assessed by measuring increase in its number along with the changes it brought about in the sample surface by optical light microscopy and SEM. It was observed that reduction in adhesion of soil flora and reduced growth of BS121 on ppTEOS coated CSPCL films. Thus ppTEOS coated CSPCL films seem to be an attractive option for environmentally benign packaging applications.

KEYWORDS: Corn Starch/Poly(ε-caprolactone) (CSPCL); TEOS-plasma deposition; XPS; surface free energy; barrier properties; biodegradation.

INTRODUCTION

Packaging materials find applications in various sectors like food, pharmaceuticals, consumer products, etc. A barrier property is one of the important properties that a packaging material should have. Polymeric packaging materials are of great use in the current globalization era because of lightweight, cost-effective, excellent barrier properties, etc. But use of homo-polymer as packaging material has few drawbacks like defects in homo-polymer may compromise the barrier performance or high thickness may not be cost-effective and lightweight. To overcome these drawbacks and improve barrier performance thin film coating on polymer was initiated. Commercial use of thin film coatings as gas barrier coatings on polymeric substrates begins in early 1970s for food packaging.[1] The optically transparent coatings were developed, and preferred over metallized thin coatings, since 1980s due to commercial demand of packaging industry wherein product visibility, microwaveability, sterilized packaging are required.[2] Glass-like coatings are preferred because of high barrier, transparency, thermal resistance, chemical stability/inertness, etc. Use of plasma enhanced chemical vapor deposition (PECVD) is preferred route to deposit glass-like coatings on temperature sensitive polymers as well as for retention of bulk properties.[3] The plasma polymerization of organosilicon precursors is preferred over silane due to toxicity and hazardous nature of latter.[4, 5] Tetraethylorthosilicate (TEOS) based PECVD method produces silicon oxide films with high deposition rate, good conformality and step coverage at low temperature.[6] Further depending on the plasma parameters and admixture gases used the resulted silicon oxide coating can vary from polymer like (organic) or pure SiO_2 (inorganic) or hybrid with desired specification like hydrophilic or hydrophobic, gas and moisture barrier coatings with good uniformity and good adherence to the substrate, chemically inert, transparent and dense.[7-11] M. Abbasi-Firouzjah et. al describes deposition mechanism, structure and chemical composition of ppTEOS films as a result of O_2 and Ar carrier gas as well as input power.[12] Barrier performance of silicon oxide coating on conventional packaging materials like PET, LDPE, HDPE, PP, etc. was well documented experimentally as well as theoretically.[13-17]

After utilization, long-term existence of conventional packaging materials in ecosystem creates environmental concerns due to their non-degradability and synthetic origin. Use of biodegradable polymers as packaging has been initiated.[18] However, for its application as packaging material, it is necessary to improve its barrier properties. Applying silicon oxide coatings on biodegradable polymer using PECVD technique provides a novel way to utilize biodegradable polymers as packaging materials having good barrier properties and retaining its biodegradability. Deposition of silicon oxide film on biodegradable polymers like chitosan, starch, polylactic acid (PLA) for various applications have been studied.[19-22] However, deposition of silicon oxide film using PECVD on starch-polycaprolactone system has not been explored much. Instead of synthesizing new polymers, researchers are working on blends of existing polymers to obtain desired properties for specific applications from economical point of view. Starch-based biodegradable polymers are very useful in this context. Starch is a natural biopolymer and in synthetic biodegradable polymer, Poly(ε-caprolactone) (PCL) has inherent biodegradability, good mechanical properties, compatibility with other polymers, hydrophobic nature, and easy availability. Starch and PCL blends, possessing comparable properties, were synthesized and studied by various researchers to provide an environmental friendly substitute for currently used synthetic and non-degrading polymers.

In present paper, ppTEOS film was deposited on cornstarch/poly(ε-caprolactone) (CSPCL) films for different durations of time. The effect of ppTEOS film deposition on CSPCL films was evaluated with respect to chemical composition, surface morphology, wettability, adhesion properties and barrier properties. Similarly, the effect of ppTEOS film/coating on biodegradation behavior of CSPCL films was studied by indoor soil burial method as well as using a single bacterial *Bacillus subtilis* MTCC 121 (BS 121).

EXPERIMENTAL DETAILS AND METHODS

Materials and Chemicals

CSPCL polymer films (supplied by EarthSoul India) having thickness 30 μm were used in the present investigation. Prior to plasma processing, films were sonicated in distilled water for 3 minutes followed by air drying at room temperature and stored in desiccator until use. Tetraethyl orthosilicate (TEOS) was procured from Merck India Ltd. and used as received. AR grade chemicals such as Glycerol (G), Formamide (F), Ethylene Glycol (E), Di-iodomethane (D) were purchased from SD Fine-Chem Limited (India).

Plasma Processing Chamber and Polymerization Method

Plasma reactor made of a glass tube having thickness 4 mm, height 120 mm and internal diameter 300 mm was used for this purpose. The diameter and distance between two aluminum electrodes was 200 mm and 25 mm respectively. Samples were kept between the electrodes on the quartz stand. Electrodes were capacitively coupled to Radio Frequency power supply (ν = 13.56 MHz), as shown in Figure 1. After purging 3 times with the precursor, working pressure was adjusted at 0.15 mbar. A stable glow discharge of TEOS vapors was created at 20 Watt. The deposition was carried out for 5, 10, 15 and 20 minutes on CSPCL films. The deposition was also simultaneously carried out on a polished Si-wafer (Make: Wafer World Inc.) and KBr IR disc window (Pike Technologies) for further characterization.

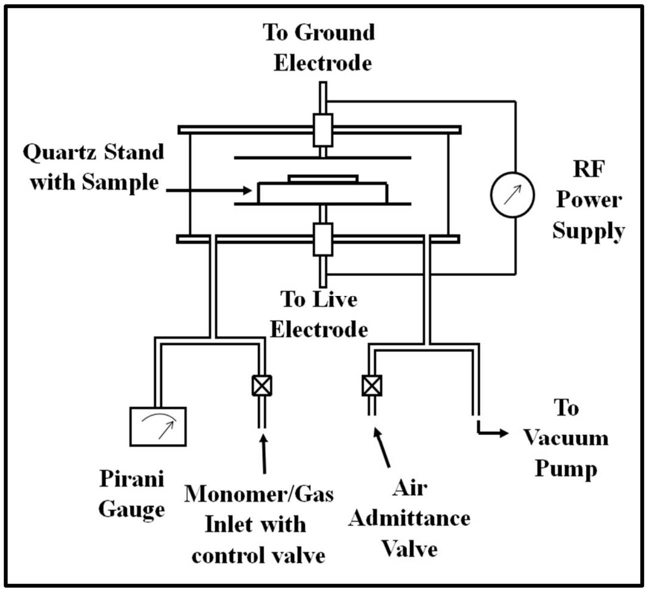


Fig. 1 Schematics of Plasma Reactor

Characterization Methods

The deposition of plasma polymerized TEOS (ppTEOS) film was estimated by measuring weight gain (%). Weight of CSPCL films before and after TEOS plasma polymerization was measured on METLER AE240 weighing balance. The weight gain (%) is calculated by given equation (1)

$$\text{weight gain (\%)} = \frac{(w_f - w_i)}{w_i} \times 100 \qquad \dots (1)$$

where W_i and W_f denotes the weight of sample before and after TEOS plasma polymerization respectively.

In order to determine the thickness and refractive index of the ppTEOS film using spectroscopic ellipsometry (SE 800, Sentech Instruments, GmBH), Si wafer was kept in the plasma reactor near the sample and the deposition was carried out on Si wafer. The samples were measured in the range of wavelengths from 350 nm - 850 nm with 2 nm resolution. The angle of measurement was 70°-70°. A Cauchy model was used for fitting of measured data. Refractive index (RI) was measured at 633 nm. The rate of deposition of ppTEOS coating/layer is expressed in nm/min unit and is calculated from equation (2). The packing density of ppTEOS coating/layer is calculated from equation (3)[23]

$$\text{Rate of deposition of ppTEOS coating} = \frac{\text{thickness of ppTEOS coating}}{\text{deposition time}} \quad \ldots (2)$$

$$\text{Packing density (\%)} = \frac{n_C - n_V}{n_S - n_V} \text{ X } 100 \quad \ldots (3)$$

where n_C, n_V (= 1), n_S (= 1.52) = RI of coating, void & silica glass respectively.

The chemical composition of ppTEOS film deposited on KBr window and Si wafer was analyzed using Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) on Perkin Elmer, model spectrum 100 series and Omicron Surface Science instruments with EAC2000-125 energy analyzer respectively. FTIR spectra were recorded in the range of 4000 cm^{-1} - 400 cm^{-1} with 64 scans having resolution of 4 cm^{-1}. XPS instrument having X-ray source Al Kα at 1486.6 eV was used. The C1s, O1s and Si2p envelopes were analyzed and peak-fitted using a combination of Gaussian and Lorentzian peak shapes using the XPSPEAK41 software.

X-ray diffraction (XRD) measurements were performed using PANalytical (Philips), model XpertPro operating at 40 KV and 30 mA using CuKα radiation of 1.542 A°. The XRD patterns were recorded in the 2θ range of 5° to 50°. In order to obtain XRD pattern of ppTEOS deposited on CSPCL film, deposition was carried out for quite long time to get thickness of 1.5 microns. For powder XRD (pXRD), the material deposited on electrodes and walls of the reactor was scratched and collected.

The wettability of ppTEOS film coating on CSPCL films was calculated from Sessile Drop contact angle (CA) measurements with respect to five different probe liquids (of known surface tension parameters) such as distilled water (W), glycerol (G), Formamide (F), ethylene glycol (E) and di-iodomethane (D). CA was calculated from equation (4)

$$\theta = 2 \tan^{-1}\left[\frac{h}{r}\right] \quad \ldots (4)$$

where θ = CA of given liquid on sample surface, h = height of the drop of liquid and r = half the base length of drop. For each sample, with each liquid 10 readings were recorded and the average was taken for further calculations. The surface free energy (SFE) was estimated from CA data using Fowkes method extended by Owen and Wendt as explained elsewhere.[24-29] To study effect of ageing, samples were stored in dry conditions in desiccator and CA was measured at every 7 days.

To study the surface morphology of ppTEOS coating, the deposition was carried out on polished Si wafer & CSPCL films and characterized using AFM (Benyuan Co. Ltd CSPM 4000) & SEM (JEOL JSM 6380LA) respectively. AFM was used in tapping mode with horizontal and vertical resolution of 0.26 nm and 0.10 nm respectively. Samples for SEM were coated with gold using SPT sputter coater (JFC-1600 auto fine coater).

The adhesion properties of ppTEOS films were studied from peel strength and compared with work of adhesion. A 180° T-peel test was carried out using Lloyd Instrument (model LR10Kplus) at a rate of 10 mm/min at room temperature. Peel strengths were reported as force of peel per unit width of adhesive joint. Sample preparation was done using modified ASTM 1876 as given elsewhere.[30] The work of adhesion, Wadh, was calculated from Water CA (WCA) data using equation (5) as explained elsewhere.[30]

$$W_{adh} = \gamma_l(1 + \cos\theta) \qquad \ldots (5)$$

Barrier properties were studied for water vapor and oxygen gas. Water Vapor Transmission Rate (WVTR) was measured using desiccant method as per ASTM E96-95. Oxygen Transmission Rate (OTR) was measured on Labthink, BTY-B1 using ASTM D1434-82 pressure method. The test performed with pressure difference of 0.1 MPa at 25 °C.

Biodegradation studies

The initiation of biodegradation occurs at the site of microbial localization followed by their proliferation and colonization, hence it is important to study the effect of ppTEOS coating on the surface of CSPCL films and consequently on its degradation. When ppTEOS coated CSPCL films were exposed for degradation, the ppTEOS coating on CSPCL films was first exposed to the microbial flora from soil and B. subtilis MTCC 121 (BS 121) than the CSPCL film. The biodegradation of silicon based materials by soil micro-organisms has been reported.[31-33] Also the interaction between cells and silicon oxide layers has been documented.[34-36] Recently, Zhang et. al.[37] have reported the use of post plasma grafting of polyacrylic acid to control degradation of biodegradable polymers. But there are very few reports regarding the biodegradation of silicon oxide coated biodegradable polymers.[19]

To observe the effect of ppTEOS thin film coating on the biodegradation, degradation was carried out via indoor soil burial method and bacterial degradation using BS 121 were performed as given in previous work.[38]

RESULTS AND DISCUSSION

%Weight gain, thickness, deposition rate, refractive index and packing density of ppTEOS coating

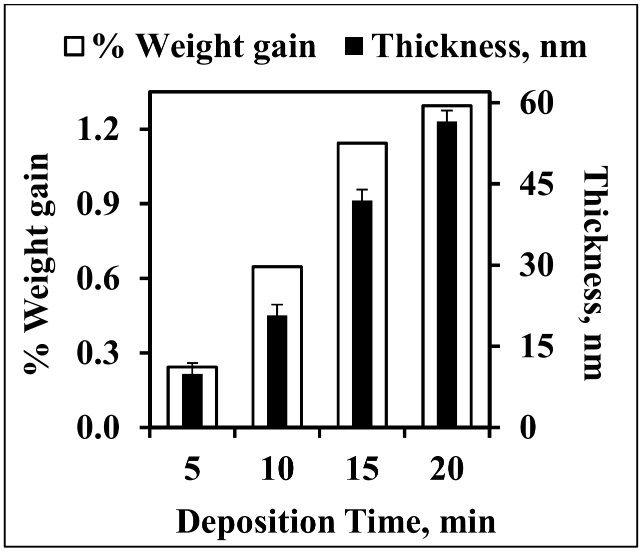


Fig. 2 % Weight gain and thickness of ppTEOS coating deposited on CSPCL film substrate

Figure 2 shows variation of % weight gain and thickness of ppTEOS with deposition time. As the deposition time is increased the % weight gain and thickness, both, increases. It is well known that, during plasma polymerization, competitive ablation and polymerization (CAP) takes place simultaneously.[39] The observed weight gain implies deposition is predominant over ablation when monomer precursor vapors were passed through the plasma reactor.

The deposition rate calculated from the equation (2) is given in Table 1. Initial slow deposition rate is indicating the fact that some time is required to initiate plasma polymerization process. Once the process is established, the rate of deposition becomes stable thereby giving linear increase in the thickness of the deposition with time. The refractive index (RI) of ppTEOS films / coatings is in the range of 1.42 to 1.45, which is quite close to the RI of thermally grown SiO_2 (RI_{ox} = 1.46).[40] The packing density (%) is found to be increasing with deposition time suggesting highly dense nature of ppTEOS coating.

Table 1 Deposition rate, Refractive index and Packing density of ppTEOS coating

Deposition Time, min	Deposition rate, nm/min	Refractive index	Packing Density, %
5	1.98	1.420	80.77
10	2.07	1.423	81.35
15	2.80	1.431	82.88
20	2.83	1.451	86.73

Chemical composition of ppTEOS coating

FTIR spectroscopy

Figure 3 shows normalized FTIR spectra of TEOS monomer and ppTEOS film deposited on KBr window. The peak assignments of TEOS monomer[41, 42] and ppTEOS film[7, 43-48] is given in Table 2. The significant differences observed between TEOS monomer and ppTEOS film were as follows: loss of doublet structure around 1100 cm^{-1}, loss of peaks in the range 1300 cm^{-1}-1487 cm^{-1}. The doublet peaks at 1081 cm^{-1} and 1105 cm^{-1} found in TEOS monomer were due to ethoxy groups (Si-O-C-C).

In ppTEOS coatings, peak at 1081 cm^{-1} was retained and peak at 1105 cm^{-1} appears as shoulder. These peaks were assigned for Si-O-Si and Si-O-C stretching. A peak around 800 cm^{-1} was assigned to (Si–(CH$_3$)$_2$) and Si–O stretching mode of dimer silicate chains. A weak peak at 1391 cm^{-1} was assigned Si-C and at 887 cm^{-1} was assigned Si-C or Si-H group.[49] A weak and broad peak at 3600 cm^{-1} -3200 cm^{-1} assigned to OH group from Si-OH. In present study, high CHx and low OH content at lower power and low temperature was observed which was in accordance with Yamaoka et al.[48] The changes in FTIR peaks clearly indicate plasma polymerization of TEOS.

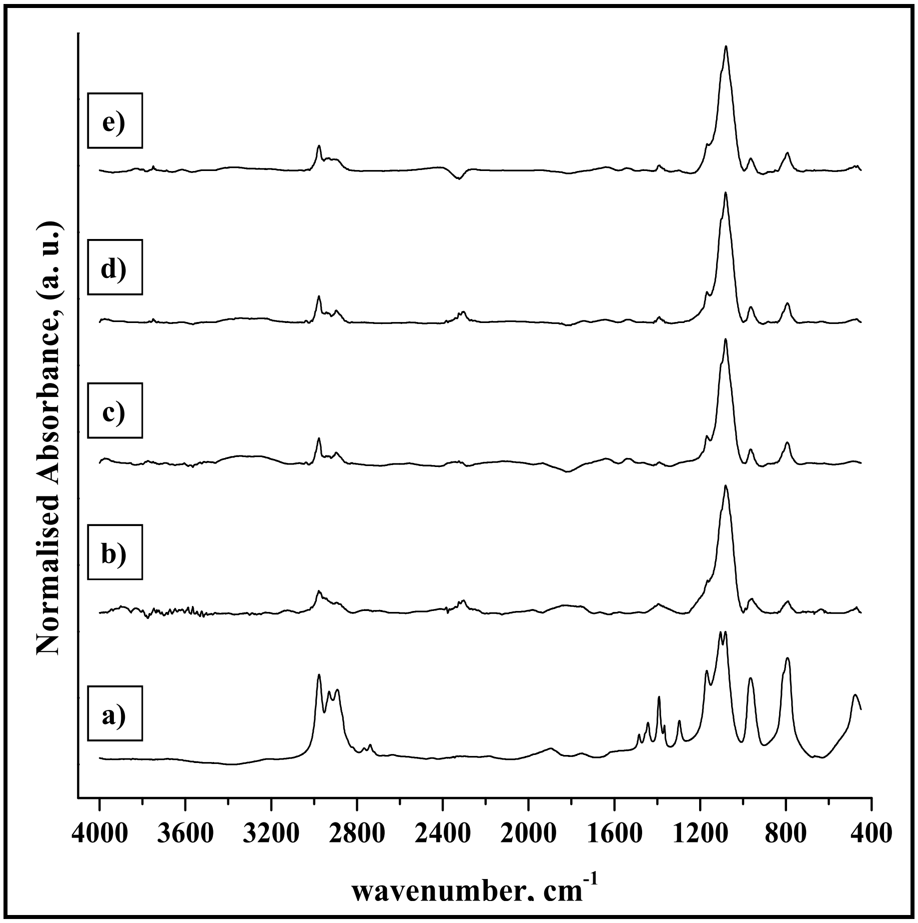


Fig. 3 Normalized FTIR spectra of a) TEOS monomer and ppTEOS coating deposited on KBr window for b) 5 min, c) 10 min, d) 15 min, and e) 20 min

Table 2 Peak assignments of TEOS monomer and ppTEOS coating

TEOS monomer[41, 42]		ppTEOS coating[7, 43-48]	
Peak position, cm^{-1}	**Peak assignment**	**Peak position, cm^{-1}**	**Peak assignment**
		3600-3200	OH group from Si-OH and water
2980	CH_3 asym stretching and CH_2 asym stretching	2980	CH_3 asym stretching and CH_2 asym stretching
2930	CH_2 sym stretching	2930	CH_2 sym stretching
2890	CH_3 sym stretching	2890	CH_3 sym stretching
1487	CH_2 bending		
1457, 1447	CH_3 asym deformation		
1396, 1380	CH_2 wagging	~1391	Si-C
1300	CH_2 twisting		
1170	CH_3 rocking in Si-O-C_2H_5	1170	CH_3 rocking in Si-O-C_2H_5 or Si-O-Si
1105, 1081	doublet Si-O-C asym stretching	1105	Si-O-C
		1080	Si-O-Si
965	CH_3 rocking	965	Si-O-C_2H_5 or Si-OH
		887	Si-C or Si-H
814	CH_2 rocking	814	(Si–$(CH_3)_2$) and Si–O stretching mode of dimer silicate chains
790	SiO_4 asym stretching	792	Si-O-Si or Si-O-$(CH_3)_{x=1, 2}$

XPS

To identify and quantify the chemical composition of ppTEOS film/coating, XPS was performed. The elemental composition was determined from survey scan. The survey spectra detected the presence carbon, oxygen and silicon. The % atomic concentration of C, O and Si for different deposition time is shown in Figure 4. It was found that % atomic concentration of C, O and Si not varying much with respect to deposition time.

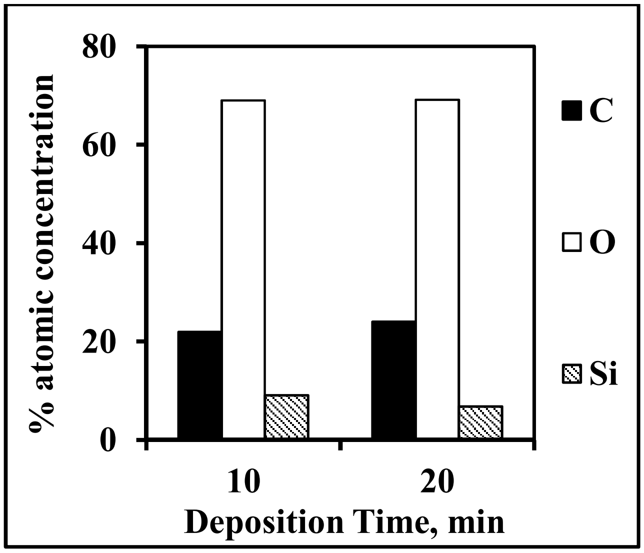


Fig. 4 % Atomic concentration of ppTEOS coating deposited for 10 min and 20 min on Si wafer

Figure 5 shows de-convoluted C1s, O1s and Si2p peaks of 10 min and 20 min ppTEOS films deposited on Si wafer. Peak assignments[50-53] and relative concentration (%) of de-convoluted C1s spectra are given in Table 3. The C1s peak was de-convoluted in 4 peaks namely C1 (284.38 eV), C2 (285.03 eV), C3 (286.44 eV) and C4 (287.89 eV). They were assigned as C-Si, C-C/C-H, C-O and O-C-O respectively. It was observed that relative concentration of C1 and C3 has increased and relative concentration of C2 and C4 has decreased with increasing deposition time. The O1s peak was de-convoluted in 2 peaks namely O1 (531.30 eV) and O2 (532.06 eV). They were assigned as non-bridging (NBO i.e. Si-O-C/C-O-C) and bridging oxygen (BO i.e. Si-O-Si) respectively. It was observed that relative concentration (%) of BO has increased and that of NBO decreases with increasing deposition time. Increase in BO concentration in turn increases cross-linked structure. The Si2p peak was de-convoluted in 4 peaks namely Si1 (100.82 eV), Si2 (101.78 eV), Si3 (102.65 eV) and Si4 (103.50 eV). They were assigned as C_3-Si-O, C_2-Si-O_2, C-Si-O_3 and Si(O_4) respectively. With increasing deposition time, it can be seen the increased conversion from Si4 to Si3, Si2 and Si1. It can be concluded that the ppTEOS coating has glass-like structure along with some inherent carbonaceous impurity.

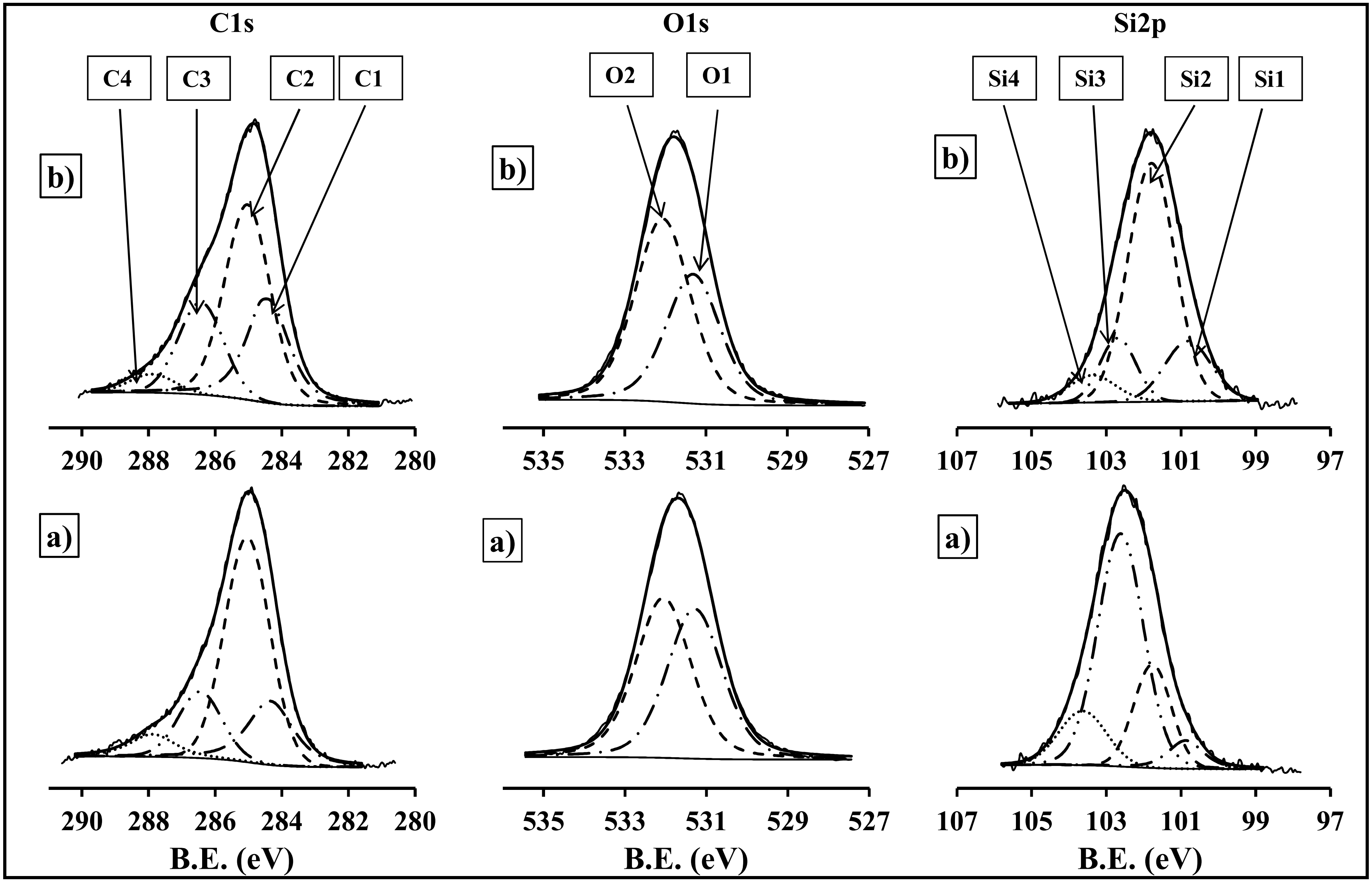


Fig. 5 De-convoluted C1s, O1s and Si2p peaks of a) 10 min and b) 20 min TEOS-plasma deposited on Si wafer

Table 3 Peak assignments and % relative concentration of de-convoluted C1s, O1s and Si2p peaks of TEOS-plasma deposited on Si wafer

	C1s				**O1s**		**Si2p**			
BE (eV)	**284.38**	**285.03**	**286.44**	**287.89**	**531.30**	**532.06**	**100.82**	**101.78**	**102.65**	**103.50**
Peaks	**C1**	**C2**	**C3**	**C4**	**O1**	**O2**	**Si1**	**Si2**	**Si3**	**Si4**
Peak Assignment	**C-Si**	**C-C/ C-H**	**C-O**	**O-C-O**	**Si-O-C/ C-O-C (NBO)**	**Si-O-Si (BO)**	**C_3SiO**	**C_2SiO_2**	**$CSiO_3$**	**SiO_4**
					% Relative Concentration					
10 min TEOS-plasma	20.21	56.08	16.62	7.09	48.04	51.96	6.51	20.82	58.92	13.75
20 min TEOS-plasma	27.38	47.33	21.11	4.17	41.40	58.60	16.16	63.11	12.99	7.74

X-ray Diffraction (XRD):

In order to confirm glass-like structure of ppTEOS coating, XRD analysis was carried out. Figure 6 shows XRD patterns of untreated CSPCL film, ppTEOS coated CSPCL film and ppTEOS powder. XRD patterns do not show any distinguishable peaks to indicate crystallization. These coatings are more or less amorphous in nature. The ppTEOS coating and powder shows broad and hollow spectrum, clearly indicating non-crystalline nature. The crystallanity of ppTEOS deposited CSPCL film is only 18.13% as calculated from Manjunath formula.[54, 55]

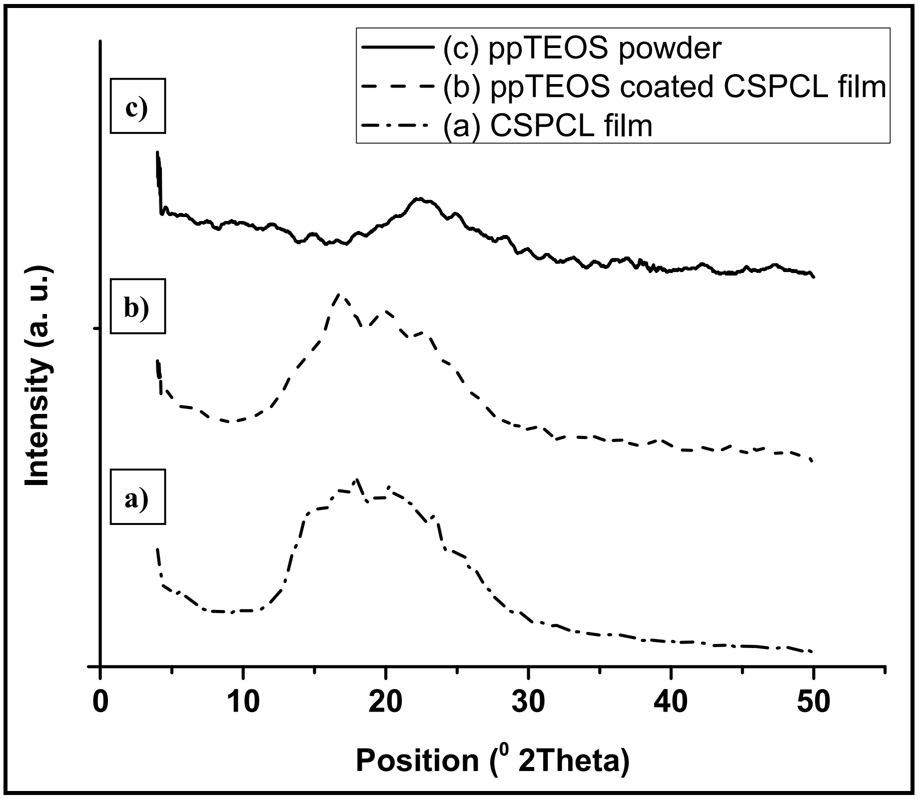


Fig. 6 XRD patterns of a) CSPCL film, b) ppTEOS coated CSPCL film and c) ppTEOS powder

Contact Angle (CA) and Surface Free Energy (SFE):

The CSPCL film is relatively hydrophilic in nature. The contact angle with water is 71.96°. Contact angle increases with the deposition of ppTEOS layer indicating relatively hydrophobic nature of the depositing layer (Figure 7). It was observed that with increase in deposition time, CA is increased suggesting that the deposition is becoming conformal and more uniform thus creating nano-structured films. Nano-structure is helpful in further enhancing the hydrophobic effect. Table 4 lists the total SFE and its components of ppTEOS coating deposited on CSPCL films calculated using equation (5). The decrease in total SFE is due to the both decrease in polar and dispersion components.

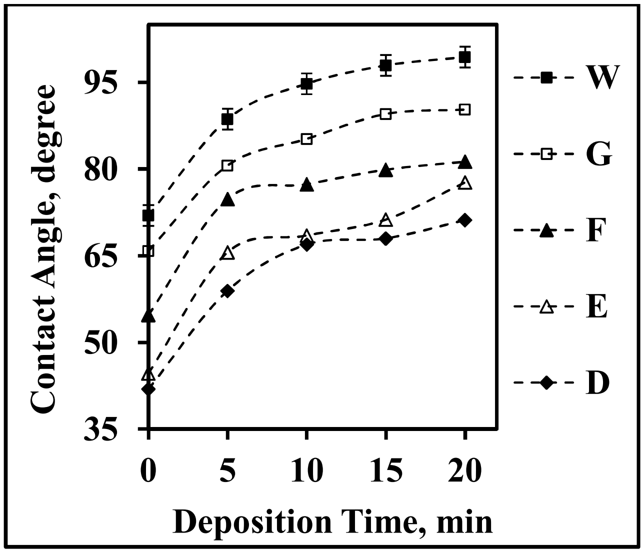


Fig. 7 Contact Angle of CSPCL film and ppTEOS coating on CSPCL film

Table 4 Total SFE and its components of ppTEOS coating deposited on CSPCL films

Deposition Time, min	Polar comp., (γ_s^p) mJ/m^2	Dispersion comp., (γ_s^d) mJ/m^2	Total SFE, (γ_s) mJ/m^2
0	8.50	28.97	37.46
5	3.45	23.16	26.61
10	2.41	21.55	23.96
15	1.66	21.19	22.84
20	1.62	19.42	21.03

Ageing effect

It is often observed that the properties imparted by the plasma treatment changes with storage time. This phenomenon is commonly called as ageing. It has been reported in the literature that functional groups created on the polymeric and textile materials are reduced with ageing.[30, 56, 57] The ageing effect depends on the type of polymer and the type of gaseous plasma treatment.[58] Therefore, it was thought interesting to study the ageing behavior of ppTEOS films. The ageing study was performed with respect to water contact angle (WCA) for 7, 14, 21 and 28 days stored in dry condition. As seen from Figure 8, the WCA does not change significantly with ageing time. Generally, diffusion of low molecular weight oligomers and hydrophilic groups into the bulk causes ageing effect.[59] In general ageing process of plasma polymerized layer is very complex in nature.[60] The absence of ageing may imply that low molecular weight oligomers and hydrophilic groups are not present in ppTEOS coating. IR, XPS and CA study indicate absence of polar functional groups and hydrophobic nature of the ppTEOS films.

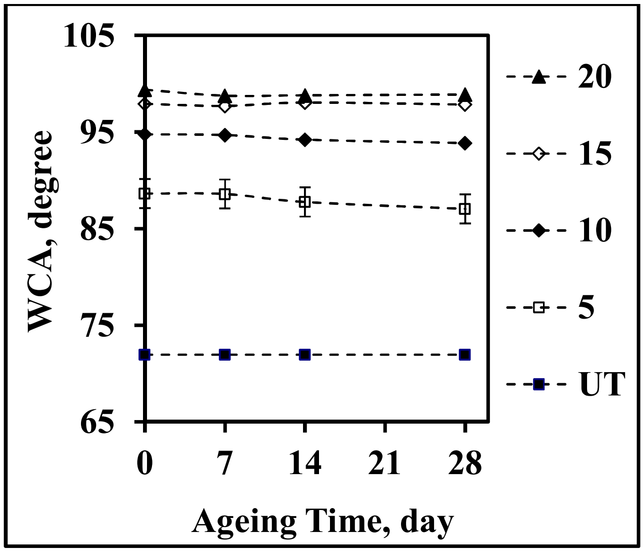


Fig. 8 Water Contact Angle (WCA) of CSPCL film and ppTEOS coating on CSPCL film during ageing

Surface Morphology

The surface morphology of the ppTEOS coating on CSPCL films was analyzed using SEM (Figure 9) and on Si wafer using AFM (Figure 10). Figure 9 (b) and (c) revealed that ppTEOS coating deposited on CSPCL films mask the CSPCL films and reduces the surface roughness. Figure 10 revealed that ppTEOS coating on Si wafer was homogeneous and smooth. Figure 11 indicates that the surface roughness decreases with increasing deposition time, reaching to saturation at 15 min deposition. SEM and AFM study indicate that the plasma polymerized film is uniform and conformal.

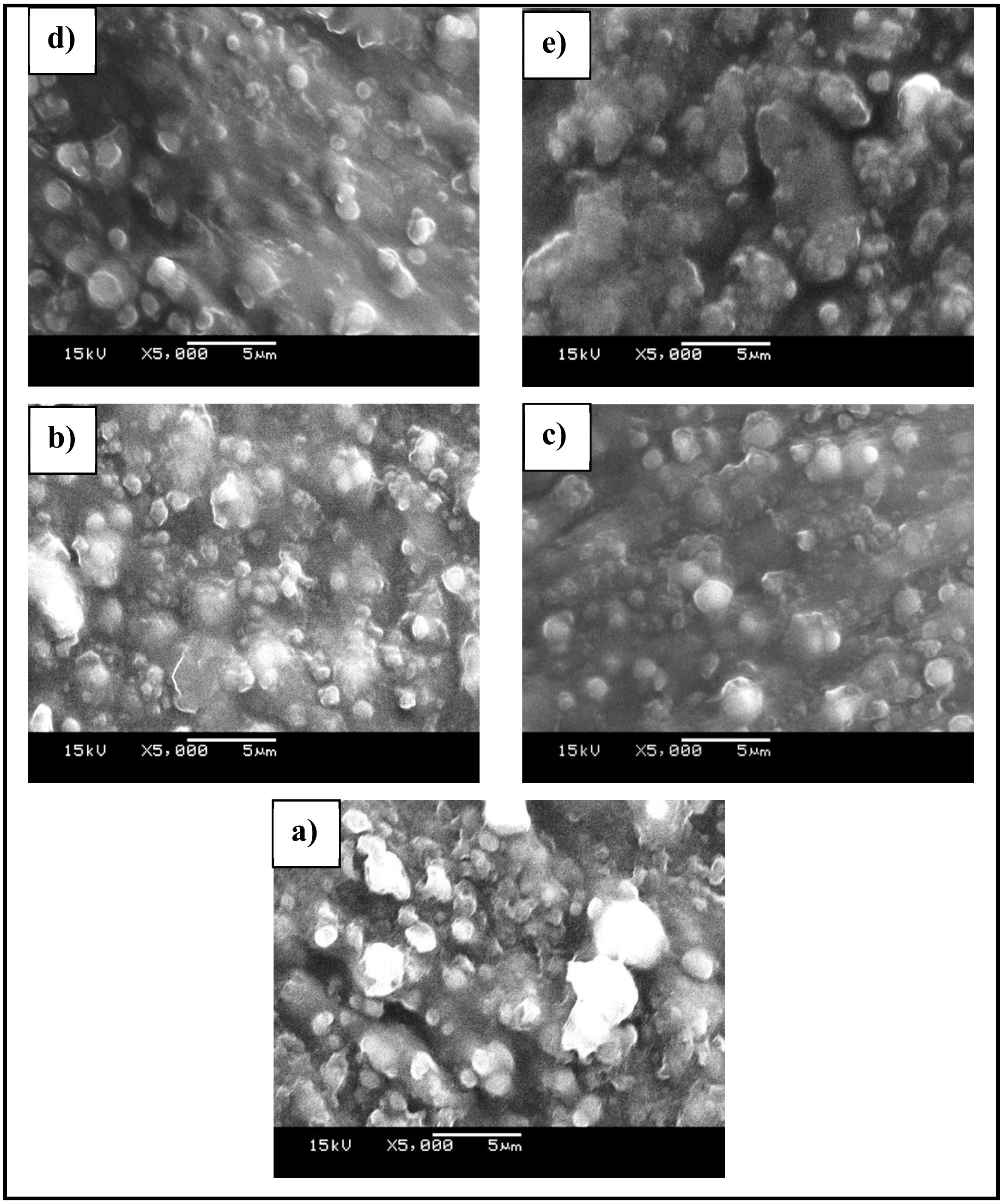


Fig. 9 SEM Morphology (5000x) (a) Untreated CSPCL film and ppTEOS coating deposited for (b) 5 min, (c) 10 min, (d) 15 min and (e) 20 min

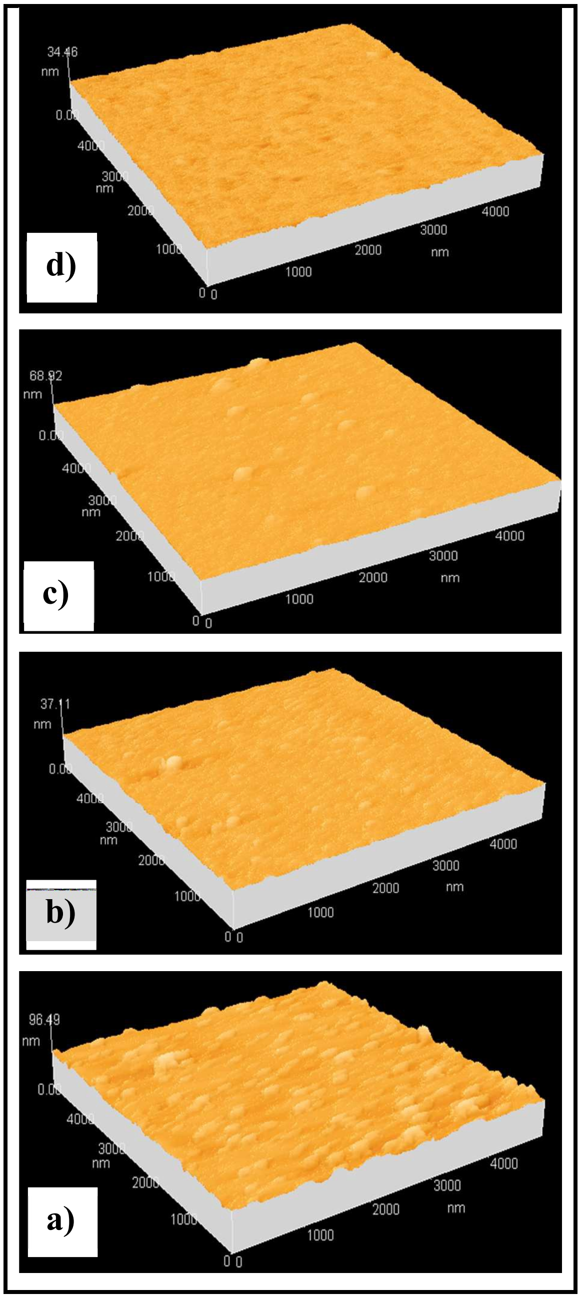


Fig. 10 AFM Morphology of ppTEOS coating on Si wafer (a) 5 min, (b) 10 min, (c) 15 min and (b) 20 min

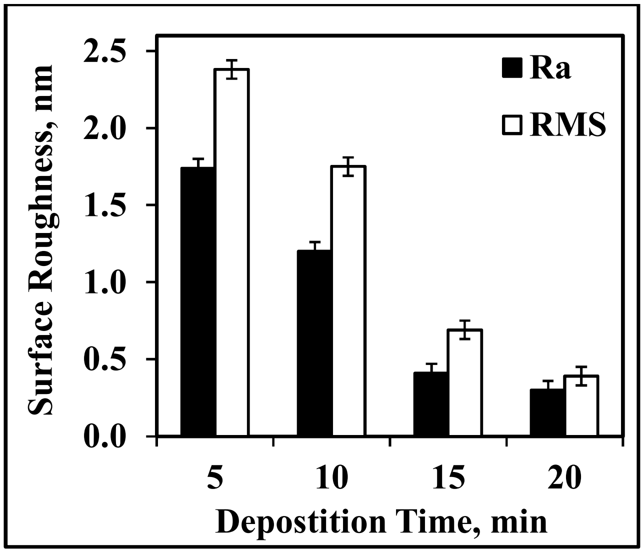


Fig. 11 Surface Roughness of ppTEOS coating deposited on Si wafer

Adhesion property-Peel strength and work of adhesion

Adhesion of plasma polymers to the substrate is one of the most important properties for practical application. It depends on factors like deposition rate, film thickness, and nature of the substrate surface. The adhesion between the substrate and the deposited film should be stronger than that of the adhesion between the deposited film and the adhesive layer. Failure in adhesive indicates that the adhesion between the substrate and the deposited layer is stronger. Therefore, peel strength measurement was employed to analyze the adhesion between ppTEOS coating and adhesive. Figure 12 shows peel strength as a function of deposition time. It can be seen that peel strength decreases with increasing deposition time but for higher deposition time (10 min and onwards) the peel strength saturates. The work of adhesion, calculated from equation (5), found to be decreasing suggesting that ppTEOS surface was non-wettable. Also the surface roughness of ppTEOS coating was found to be decreasing. This limits the spreading of adhesive on surface of ppTEOS coating. It was found that adhesive from adhesive tape was not transferred on ppTEOS coated CSPCL films. Hence the observed decrease in peel strength can be attributed to hydrophobic nature of ppTEOS coating and smoother morphology as evident from WCA data and AFM. It also indicates stronger adhesion between the substrate CSPCL film and the ppTEOS film.

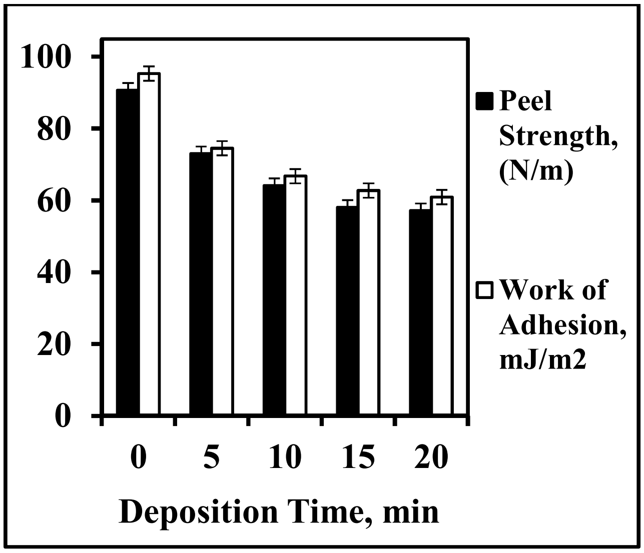


Fig. 12 Peel strength and Work of adhesion of CSPCL film and ppTEOS coated CSPCL films

Barrier Properties-WVTR and OTR

Resistance (barrier) to the permeation of gas and water vapor is a very important aspect from packaging viewpoint. The barrier properties of ppTEOS deposited CSPCL films were studied by measuring OTR and WVTR. Figure 13 shows decrease in WVTR and OTR with increasing deposition time. With increasing deposition time, barrier properties were found to be improving. It was observed that a very thin layer (10 nm due to 5 min deposition) of ppTEOS deposited on CSPCL improves oxygen barrier properties of the films by 80.12% and water vapor barrier by 43.8%. This improvement in barrier properties was attributed to highly cross-linked, conformal, pinhole free/dense, hydrophobic coating of the ppTEOS on CSPCL films.

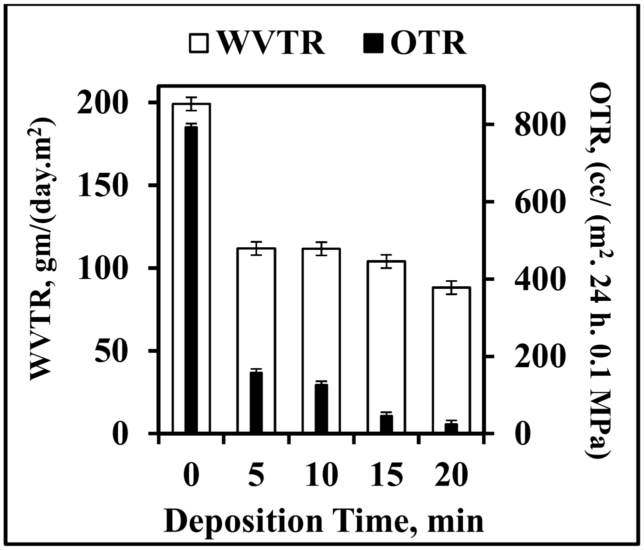
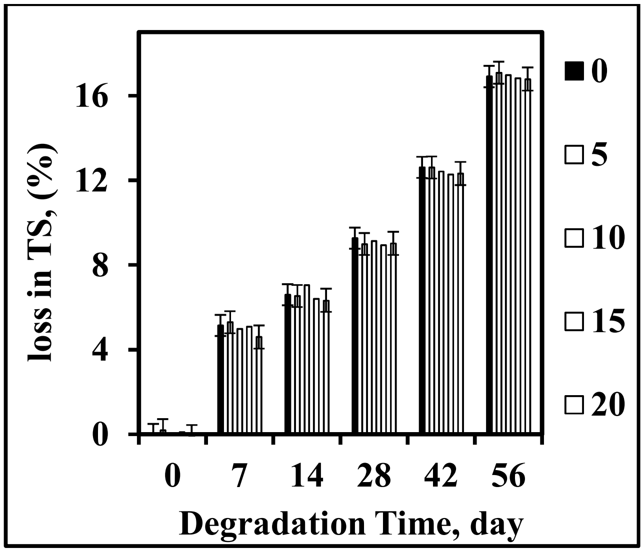


Fig. 13 WVTR and OTR of CSPCL film and ppTEOS coated CSPCL films

Biodegradation study

Degradation studies with indoor soil burial method

Studies conducted in conditions mimicking natural environment using indoor soil burial method of the samples provides a real picture of the degradation of polymers in nature because of the similarity to onsite conditions of use and disposal. The microorganisms present in the soil use the polymer material as a source of carbon for their growth thereby degrading the polymer. Degradation of polymer was indicated by the alterations in its mechanical properties which included loss in tensile strength (TS) and % Elongation at break (Eb). The loss in TS (%) and loss in Eb (%) of samples un-soiled (0 day) and soiled (7, 14, 28, 42 and 56 days) was calculated with respect to pristine (untreated and un-soiled) CSPCL film and listed in Figure 14.



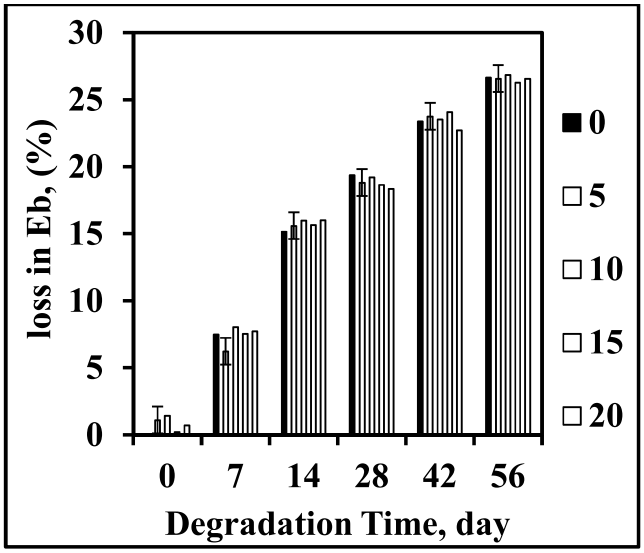


Fig. 14 Loss in TS (%) and loss in Eb (%) of untreated and TEOS-plasma deposited CSPCL films in indoor soil burial method

It was observed that unsoiled TEOS-plasma deposited CSPCL films do not show significant change in tensile properties but overall reduction in tensile properties of untreated CSPCL polymer films was observed over soiling time. The loss in tensile properties of ppTEOS deposited CSPCL films was in close range with that of untreated CSPCL films. Thus the presence of ppTEOS coating on CSPCL films was not adversely affecting biodegradability of the material. Secondly, mechanical properties represent bulk properties of the material which may not be sensitive to the growth or colonization of micro-organisms. Therefore, it was thought interesting to study biodegradability using optical method as well.

Figure 15 shows OLM images (40X) of pristine and TEOS-plasma deposited CSPCL films soiled for 56 days. It can be seen that TEOS-plasma deposited films (Figure 15 c and d) show reduced growth of soil flora than that of untreated CSPCL films (Figure 15 b). This could be possible due to presence of hydrophobic and smooth nano structured ppTEOS coating.

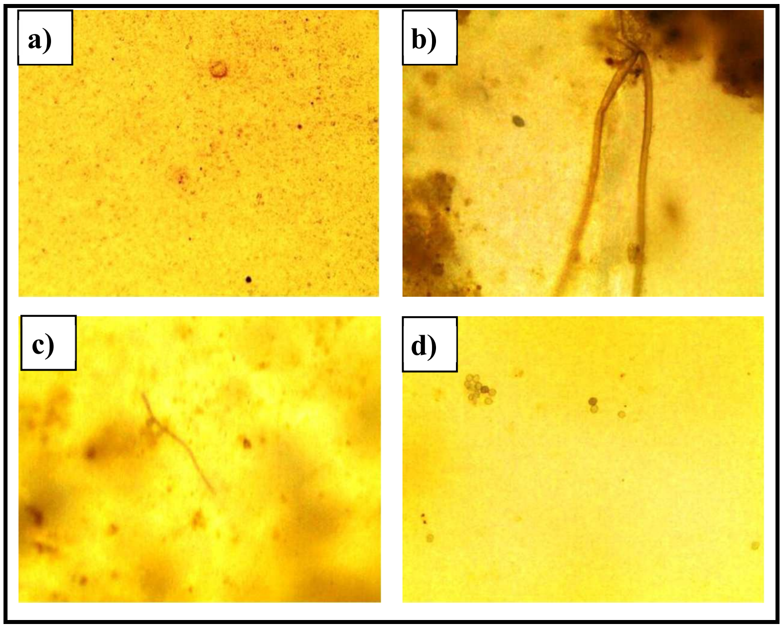


Fig. 15 OLM images (40X) of CSPCL films a) pristine (untreated & not soiled) and soiled for 56 days b) untreated and TEOS plasma deposited for c) 10 min and d) 20 min

Degradation studies with BS 121

Control (untreated) CSPCL film and ppTEOS deposited CSPCL films exposed to BS121 through 56 days showed the lag, log, stationary and death phases of microorganisms used as indicated from Turbidimetric studies (Figure 16). It can be seen that difference in turbidity of untreated CSPCL and ppTEOS deposited CSPCL goes on increasing from 14 days onwards. The continuous increase in turbidity till 42 days in the case of untreated CSPCL film indicates that the carbon source is available to the micro-organisms for growth. Whereas ppTEOS film contains SiOx layer i.e. less carbaneous content and hence decrease in turbidity was observed in this case. The decrease in turbidity of ppTEOS deposited films compared to untreated CSPCL films indicates reduced growth of BS 121 suggesting decrease in biodegradation. OLM images (Figure 17) reveal changes in visual appearance of surfaces exposed to BS 121 for day 7, day 14 and day 56 as compared to pristine CSPCL film. These changes in visual appearance were attributed to alterations in sample surfaces due to colonization and adhesion of BS 121 on sample surface. A decreasing trend in colonization and adhesion of BS 121 was observed throughout the study was in agreement with turbidimetric studies. The SEM images (Figure 18) shows the morphological changes on samples exposed to BS 121 for 56 days. It can be seen that the ppTEOS coated surfaces do not show significant morphological changes compared to untreated CSPCL films. The presence of hydrophobic, smooth ppTEOS coating possibly limited the adhesion and growth of BS 121 which is in accordance with turbidity results.

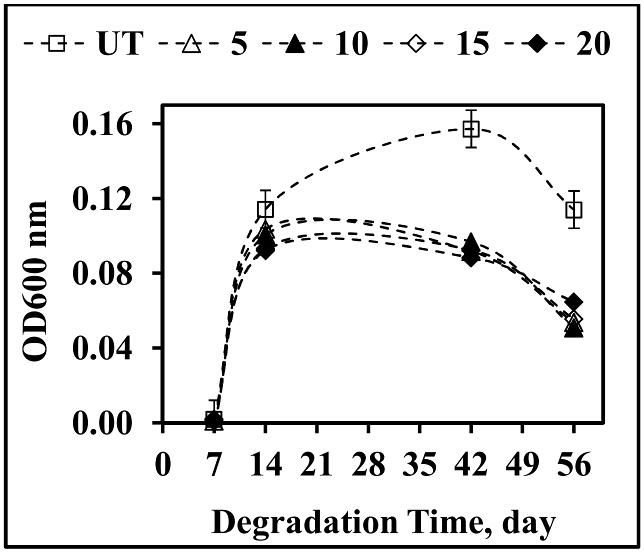


Fig. 16 OD600 nm for untreated and TEOS-plasma deposited CSPCL and exposed to BS 121 through 56 days

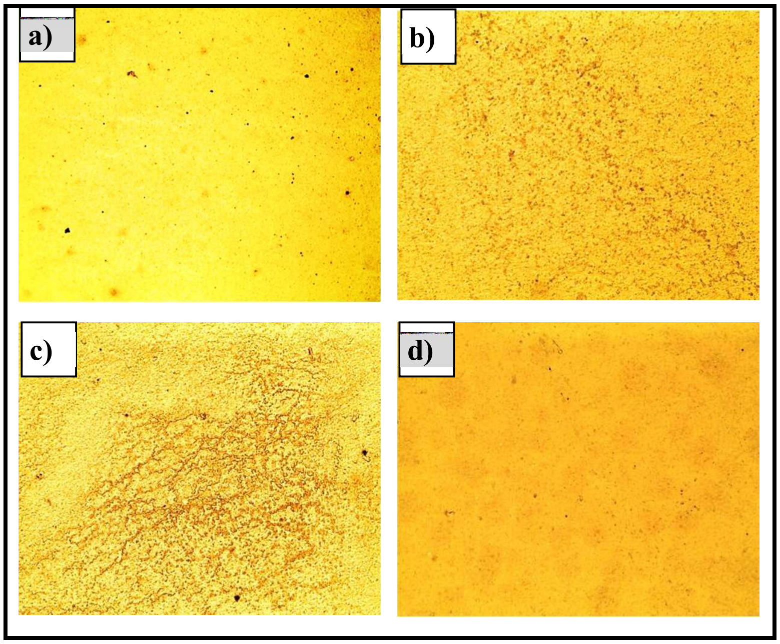


Fig. 17 OLM images (10X) of a) pristine (untreated & not soiled) CSPCL films and 10 min TEOS plasma deposited CSPCL films exposed to BS121 for b) 7 days, c) 14 days d) 56 days

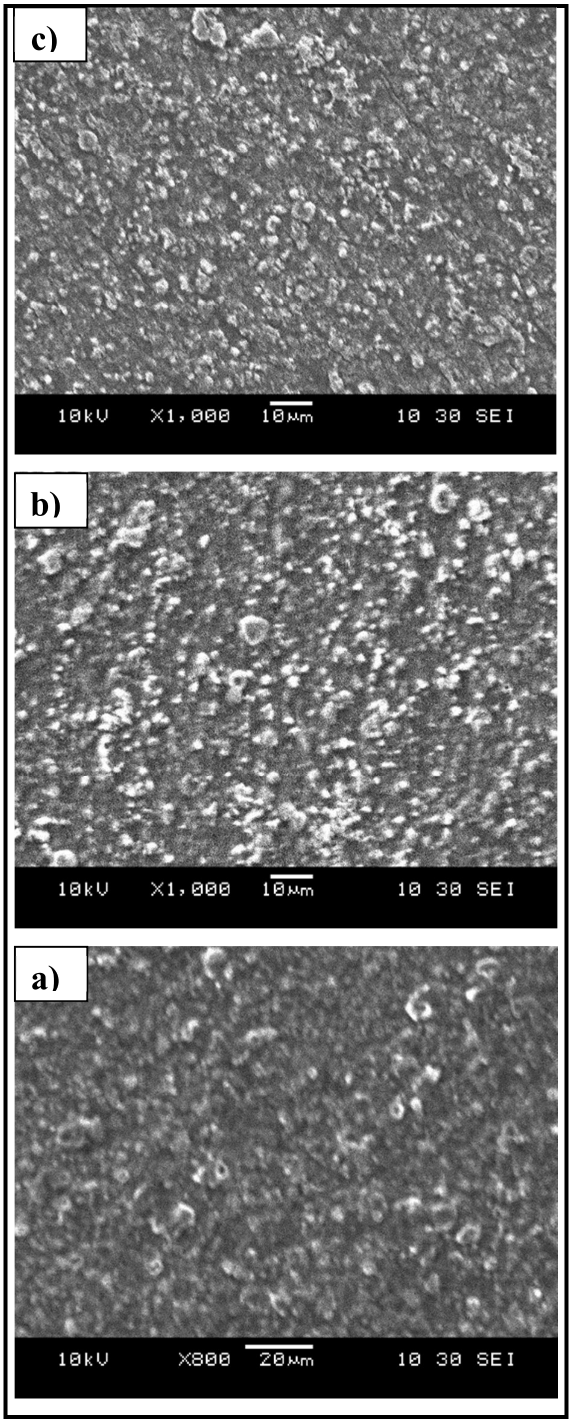


Fig. 18 SEM images of CSPCL samples exposed to BS 121 for 56 days a) untreated and TEOS plasma deposited for b) 10 min and c) 20 min

Conclusion:

Out of many properties of silicon oxide coating, gas barrier properties are of great importance regarding packaging applications. Silicon oxide coated biodegradable polymer is one of the environmentally friendly solutions for increased packaging utilization. Plasma enhanced chemical vapor deposition of TEOS formed nano (<100 nm), hydrophobic, highly cross-linked, pin-hole free/dense ppTEOS coating. FTIR, XPS and XRD studies revealed that ppTEOS coating has glass like structure along with inherent carbonaceous impurities. Morphological study showed that ppTEOS coating was smooth and conformal. A thin layer of ppTEOS coating (10 nm at 5 min deposition time) reduces OTR and WVTR by 80.12% and 43.8% respectively. Biodegradation studies in indoor soil environment showed no significant loss in tensile properties whereas OLM images showed reduced soil flora on ppTEOS coated CSPCL films with respect to TEOS deposition time. In case of bacterial degradation, with increasing TEOS deposition time, slightly reduced growth of BS121 on ppTEOS coated CSPCL was observed. Thus ppTEOS coated CSPCL films seem to be an attractive option for environmentally friendly packaging applications.

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Improvement in barrier properties of biopolymer CSPCL films without affecting biodegradability using plasma polymerization technique