



## Comparison of Fabrication Process of Poly(methyl methacrylate) (PMMA) Membranes and their Amine Functionalization Studies for Application in Biosensing

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Received: 11 June 2024;

Accepted: 6 July 2024;

Published online: 30 August 2024;

AJC-21730

The comparison of the fabrication process of poly(methyl methacrylate) (PMMA) membranes and their functionalization on the basis of various characterization studies to produce a robust, stable and adherent amine functionalized surface for application in biosensing was attempted in present work. PMMA membrane fabricated using solution casting and compression moulding were characterized morphologically using electron microscopy (SEM) and functionalized with O<sub>2</sub>, N<sub>2</sub> and He plasma at the same discharge conditions followed by deposition of (3-aminopropyl)triethoxysilane (3-APTES), an alkoxysilane, on the membranes in three different concentrations (5%, 10% and 15%). Using contact angle measurements, changes within the surface hydrophilicity were determined for pristine PMMA, plasma treated and plasma followed by 3-APTES treated PMMA membranes while amine functionalization was confirmed by Fourier transform infrared spectroscopy (FTIR). Further, the density of reactive amine groups on the membrane was estimated using fluorescent reagent in confocal microscope, which revealed that although all the plasma and 3-APTES treatments resulted in functionalization of PMMA membranes, however treatment with He plasma and 10% APTES displayed 10 to 15 times more reactive amine groups on PMMA membranes in comparison to the other plasma and 3-APTES treatments. Moreover, among the two fabricated membranes, it was found that solution casted PMMA membrane yielded twice more reactive amine groups than the compression moulded membrane. The results suggested the stability and ability of He plasma and 10% APTES treated PMMA membrane to immobilize DNA and other biomolecules efficiently and thereby can act as biosensing platform.

**Keywords:** Membrane, Poly(methyl methacrylate), Plasma treatment, Alkoxysilane, DNA, Confocal microscopy.

### INTRODUCTION

With the development of planar technologies and the concept of miniaturization in the manufacture of integrated circuits in the 1950s, the technology of microelectromechanical systems (MEMS) emerged [1]. Soon, the transition of MEMS took place to the field of analytical chemistry with the design and manufacture of the miniaturized gas chromatography equipment for molecular analysis by Terry *et al.* [2]. During the 1990s, the concept of total chemical analysis system (TAS) emerged to automate processes in analytical chemistry. Manz *et al.* [3] were the first to propose the miniaturized total chemical analysis system wherein the complete laboratory processes of sample pretreatment, separation and analysis was designed into an integrated system of microscale dimensions, also called as

micro-total analytical system ( $\mu$ -TAS) or Lab-on-a chip (LOC). Various such devices with sample in and answer out capability have found widespread biosensing applications in the realms of molecular diagnostics, clinical and forensic analysis where functional recognition of biomolecules and their immobilization takes place [4-6]. The principle behind the working of these devices is the forces of interaction between the biomolecules and the substrate material, which could be either physical (electrostatic, van der Waals interactions, hydrophobic interactions) or chemical interactions (covalent bonding or cross linking) [7].

A wide array of materials including silicon, glass and other materials sourced from the electronic industry have been utilized for fabricating LOC devices [8]. Polymers and plastics have emerged as attractive alternatives, due to their enhanced

biocompatibility, low thermal and electrical conductivities and cost effectiveness, making them particularly well suited for fabrication in biological and chemical domains [9,10]. Amongst these polymers, poly(methyl methacrylate) (PMMA), an acrylic based thermoplastic, has been extensively employed owing to its mechanical stability, chemical resistance, toughness and low cost [9,10]. With these advantages, PMMA has been the focus of many researchers for its wide applications ranging from synthesis of organic thin film transistors or permanent memory devices in the electronic industry to making of the PMMA based prosthetic material for use in biomedical industry along with its application in biosensors because of its ability to immobilize biomolecules [11]. However, these briefly mentioned applications require substrate functionalization to overcome drawbacks such as poor adhesion and hydrophobicity [11].

A variety of surface functionalization techniques such as chemical, mechanical, thermal and physical treatments have been employed in polymers making them suitable for immobilization of biomolecules [12]. All these techniques are performed in two steps *i.e.* surface pre-treatment also called as surface cleaning or etching and post-treatment also called as deposition process [13]. Plasma is one such fast, straight forward physical method of surface pre-treatment done to modify the top few nanometres of a polymer surface without the use of solvents and generation of chemical waste [14]. In 2016, Wang *et al.* [15] described the influence of gas composition of plasma by comparing the surface modification effect of He and Ar plasma jets on the PMMA membrane. Recently, Jaffer *et al.* [10] described synthesis and characterization of PMMA films treated by O<sub>2</sub>, Ar and N<sub>2</sub> glow discharge plasma to study changes within the morphology and surface hydrophilicity of the treated samples [10]. Plasma modifies the surface chemistry by generating surface hydroxyl groups through oxygenation [16]. These oxide surfaces can be amine functionalized using various organosilanes such as 3-APTES ((3-aminopropyl)triethoxysilane), APTMS ((3-aminopropyl)trimethoxysilane), AEAPTES ((N-(2-aminoethyl)-3-aminopropyltrimethoxy-silane)), *etc.* [13]. Among all organosilanes, 3-APTES is the most frequently used candidate molecule used for coating oxide surfaces either by solution phase deposition or vapour phase deposition technique. In 2021, Zarinwall *et al.* [17] reported an extensive study on the binding of 3-APTES on hydrous boehmite nanoparticles in correlation to different parameters like concentration, time and pH. In 2022, Sypabekova *et al.* [13] outlined various APTES deposition methods on polymeric solid phases for biosensing applications. Despite the wide-spread application of APTES, there has been limited work on its quantitative characterization after modification of the surface. Moreover, there has been no direct comparison between different functionalization methods with respect to influence of plasma gas composition and APTES concentrations.

Herein, we compared differently fabricated PMMA membranes exposed to three plasma gases (O<sub>2</sub>, N<sub>2</sub> and He) at the same discharge conditions followed by the surface deposition using APTES in three different concentrations (5%, 10% and 15%) to activate the surface. The role of respective plasma

species treatment and APTES treatment of varying concentrations on polymer surfaces was evaluated using contact angle and FT-IR analysis. Also, the reactivity of the functionalized surfaces were we have determined using confocal microscopy to obtain a robust, stable, adherent amine functionalized film for immobilizing different biomolecules to be used as biosensors.

## EXPERIMENTAL

The chemicals used in this study included poly(methyl methacrylate) (PMMA) (m.p. > 150 °C, *m.w.* 996k by GPC and size 120-160 mesh), dimethyl formamide (DMF) (> 99.9%, molecular biology grade, *m.w.* 73.09), toluene (99.8% anhydrous, *m.w.* 92.14), phosphate buffered saline-tablet (PBS) (total tablet weight-1814.5-2005.5 mg/tab), FITC (fluorescein 5(6) isothiocyanate) (> 99%, HPLC, *m.w.* 389.38) and (3-aminopropyl)triethoxysilane (3-APTES) (99%, *m.w.* 221.37) supplied by Sigma-Aldrich Chemicals Pvt. Ltd.

**Fabrication of PMMA membranes:** Two types of fabrication methods were carried out to fabricate PMMA membranes *viz.* (i) solution casting method, where a casting solution of 5% PMMA was dissolved in a solvent DMF followed by heating at 80 °C for 4 h. The prepared solution was dried overnight at 56 °C before use; (ii) compression moulding method, where PMMA films of thickness 0.25 mm were produced using a hydraulic compression moulding press (Santec Hydro Comp Holding Press, India). PMMA contents of 0.729 g were taken onto the stainless-steel mould placed on the Teflon sheet between the two heated platens of the press. The platens were subsequently heated above the melting point of PMMA (160 °C). Once the platens reached the required temperature, a pressure of 70 bars at 200 °C for 10 min was applied. The platens were then cooled to 90 °C and the compression moulded films were retrieved.

**Analysis of surface morphology:** The surface morphology of solution casted and compression moulded PMMA membranes were studied using a scanning electron microscope (Zeiss Gemini SEM 500, Germany), operated between 10 and 30 kV.

**Surface pre-treatment of PMMA membranes:** Surface pre-treatment in vacuum plasma using three different gases O<sub>2</sub>, N<sub>2</sub> and He was carried out in a Henniker Plasma (HPT-300, U.K.) treatment system which consists of a multilevel electrode shelf with a frequency of 40 kHz consisting of shower head for uniform gas feed into the vacuum chamber. Prior to plasma, PMMA membranes were sonicated in ultrapure water for 10 min and then dried at 40 °C in oven for 30 min. The working parameters of plasma treatment are described in Table-1.

TABLE-1  
WORKING PARAMETERS OF PLASMA TREATMENT

Parameters	Values applied
Working pressure	3.8 mbar
Power supply	60 %
Flow rate of gas	20 mL/min
Exposure time	5 min
Working gas	O <sub>2</sub> , N <sub>2</sub> , He

**Solution-phase 3-APTES deposition on PMMA membranes:** Plasma treated PMMA membranes were immersed

in 5%, 10% and 15% (v/v) 3-APTES (prepared in toluene) separately and kept at 55 °C for 1 h in a vacuum oven. The membranes were then washed with 70% ethanol for 15 min followed by extensive rinsing with distilled water and then dried in a vacuum incubator at 37 °C overnight to stabilize the coating layer.

**Water contact angle measurement:** The hydrophilicity of (i) untreated and plasma treated PMMA surfaces (ii) plasma followed by 3-APTES treated surfaces was evaluated by measuring their water contact angle (WCA) using a kruss DSA100 (Germany) contact angle analyzer. Contact angle describes the shape of a liquid drop resting on a solid surface. Droplet of distilled water was put on the surface and the angle formed at the interface of the droplet and the membrane was measured using an optical microscope.

**FTIR analysis:** The chemical composition of untreated solution casted and compression moulded membrane along with the changed chemical composition of the plasma and APTES treated PMMA membranes was identified using a Nicolet iS50 Fourier transform infrared (ATR-FTIR) spectrometer (Thermo scientific, United States). The FTIR spectra were collected within the wavenumber range of 3700–650  $\text{cm}^{-1}$ .

**Estimation of density of reactive amine groups on the surfaces of treated PMMA:** Amine functionalized samples were incubated in a 2 mL FITC solution (prepared in 100 mM phosphate buffer, pH = 9) for 20 min followed by washing in PBS for the removal of unbound FITC molecules. A Nikon A1R confocal microscope (Eclipse Ti2, Melville, New York) coupled to an upright microscope was used to scan samples using Z-stack at 525 nm, the emission wavelength of FITC. The observation parameters that were kept constant for each sample are given in Table-2.

Estimation of density of reactive amine groups was done by analyzing the confocal images using Nikons acquisition and analysis software-NIS elements. The average mean intensity produced by the fluorescein groups, calculated using ROI (region of interest) statistics corresponds to the density of reactive amine group present throughout the membrane.

TABLE-2  
OBSERVATION PARAMETERS OF CONFOCAL MICROSCOPY

Parameters	Values applied
Magnification	20x
Scan size	1024 × 1024 pixels
Scan speed	0.25 s
Z- stack step size	2 $\mu\text{m}$
Range	28 $\mu\text{m}$

## RESULTS AND DISCUSSION

The current study illustrates the fabrication of PMMA membranes by two different methods *i.e.*, solution casting and compression moulding and exposing their surfaces to similar modification techniques using plasma and 3-APTES to obtain a stable, well adherent, amine-functionalized surface. The process was analyzed using a four-step methodology.

**Morphological studies:** The surface morphology of untreated PMMA membranes was studied by scanning electron microscopy (Fig. 1a-b). PMMA of 5% concentration was chosen for fabricating solution casted PMMA membranes, because of its desirable mechanical strength and porosity, as reported previously [18]. Whereas, the PMMA membranes fabricated using compression moulding resulted in more stable and mechanically strong membranes due to close packing of the PMMA chains because of the compressive force applied during moulding. SEM image (Fig. 1a) of the PMMA film shows surface with the small cavities, which are generated due to the entrapped solvent while SEM image (Fig. 1b) showed plane view micrographs which revealed a more homogenous, smooth and uniform surface with no defects because of the solvent free process.

**Contact angle measurements:** The effect of different species of the plasma and different concentrations of 3-APTES deposited on the PMMA surface was studied by contact angle measurements (Fig. 2a-d). Prior to determine the impact of additional surface modification using 3-APTES, the impact of plasma treatment on the surface hydrophilicity of PMMA was also determined. Pristine PMMA being relatively inert and hydrophobic

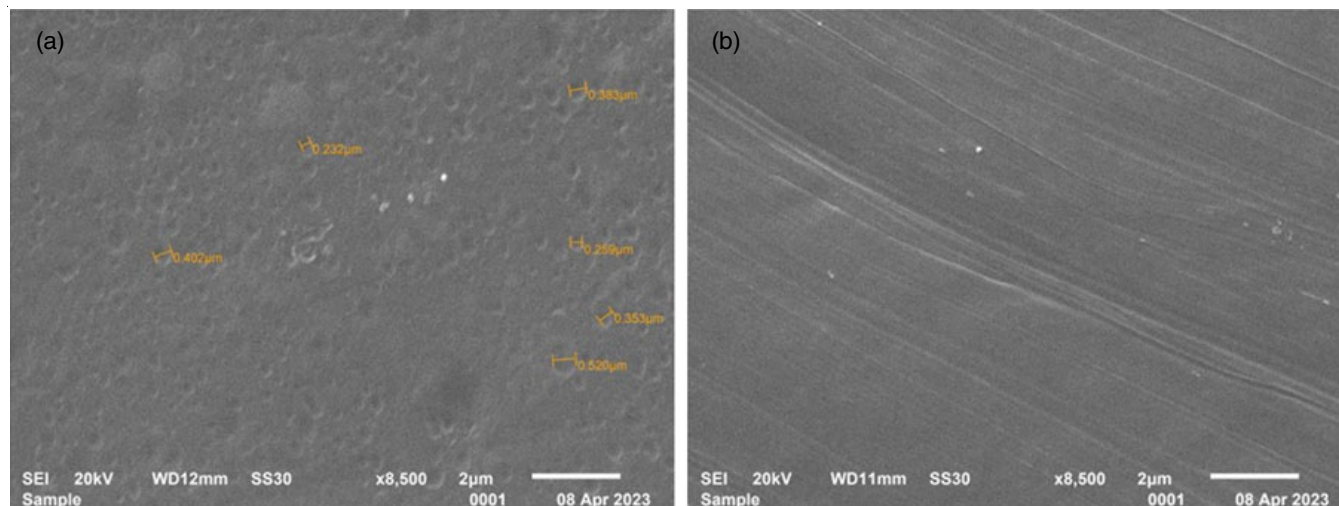


Fig. 1. SEM image of (a) 5% PMMA solution casted membrane and (b) PMMA compression moulding membrane



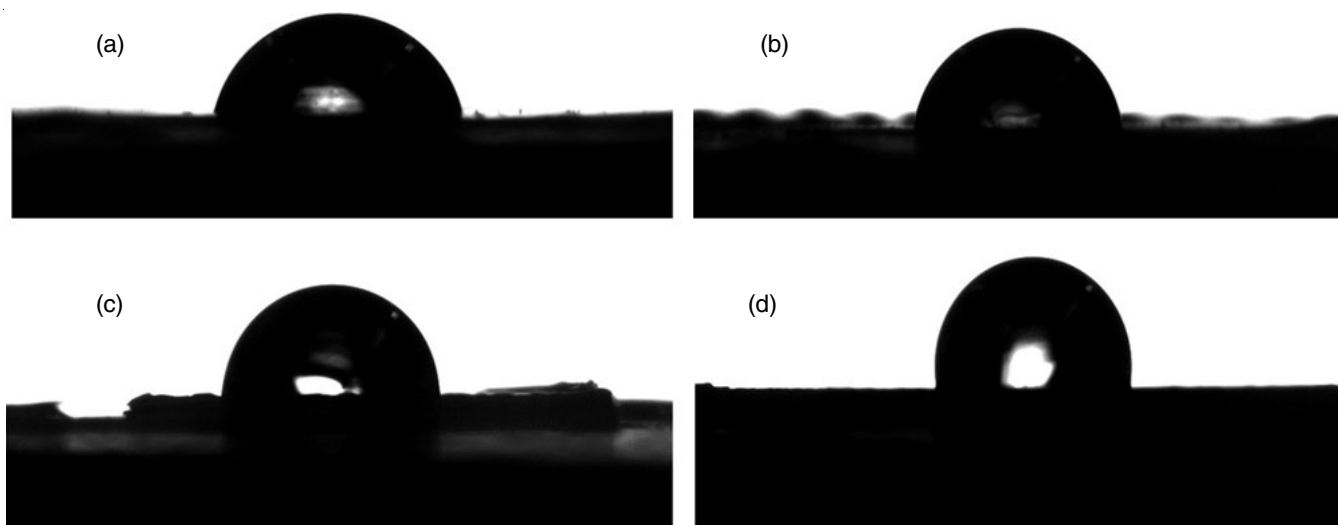


Fig. 2. Contact angle images of PMMA membranes (a) untreated PMMA (b) plasma treated PMMA (c) He plasma + 10 % APTES treated solution casted PMMA (d) He plasma + 10% APTES treated compression moulded PMMA

material was functionalized using plasma of different gasses ( $O_2$ ,  $N_2$  and He) to improve the surface wettability. During the plasma treatment, native OH groups were added to make hydroxylated surfaces, leading to an increased number of attachment sites. In their own unique ways, each plasma gas affects the hydrophilic surface properties of PMMA. Interactions between polymer surface and plasma species form polar groups such as COOH, CHO, C-OH and C-O leading to diminished water contact angle. Contact angle of PMMA membranes for different plasma gases at same discharge conditions is shown in Table-3. The contact angle was observed to decrease drastically from untreated PMMA membranes to plasma treated PMMA membranes. The surface hydrophilicity level of PMMA increased after  $O_2$  plasma which yielded the lowest contact angle of  $42^\circ$  and  $48^\circ$  in solution casted and compression moulded membranes, respectively. This change confirms the improvement of PMMA surface wettability necessary for the adhesion. During APTES treatment, the creation of surface hydroxyls and carboxyls produced due to plasma undergo condensation reaction with the silanols of 3-APTES and leaves an amine group available for further reaction [7]. In agreement with previous studies, the water contact angle was shown to increase significantly as the concentration of APTES was increased from 5% to 15%, indicating that the hydrophobicity of surface was enhanced [13]. As shown in Table-3, the effect of helium plasma followed

by 3-APTES treatment showed a remarkable increase of contact angle from  $92^\circ$ ,  $102^\circ$  to  $104^\circ$  for 5%, 10% and 15% APTES concentration in compression moulded PMMA.

**FTIR studies:** The extent of deposition of 3-APTES on the solution casted and compression moulded membranes was monitored by FTIR technique. Initially, comparison of FTIR data of untreated compression moulded and solution casted PMMA was done. As shown in Fig. 3, both the spectra showed characteristic peak at around  $1718\text{ cm}^{-1}$  attributing to the carbonyl stretching peak from the PMMA matrix for all the untreated surfaces. The peak at around  $2950\text{ cm}^{-1}$  in both the spectra was attributed to aliphatic methylene group asymmetric stretching vibrations while the peaks around  $1439\text{--}1435\text{ cm}^{-1}$  attributed to  $CH_3$  bending vibrations. Distinct spectral peak at  $1136\text{ cm}^{-1}$  was seen attributing to the presence of C–O–C stretching vibration. An additional peak at  $1670\text{ cm}^{-1}$  was observed in solution casted membranes attributed to the presence of DMF solvent traces compared to the compression moulded PMMA membrane.

Fig. 4a-c shows FTIR spectra of 3-APTES functionalized PMMA membranes at different APTES concentrations under different plasma gases. The characteristic absorption peak at  $3390\text{--}3470\text{ cm}^{-1}$  attributing to the amine groups was observed with more prominence in samples containing 10% APTES. On the other hand, the peaks at  $1573\text{--}1460\text{ cm}^{-1}$  (contributing

TABLE-3  
CONTACT ANGLE MEASUREMENTS OF UNTREATED SOLUTION CASTED AND COMPRESSION MOULDED PMMA MEMBRANES, AFTER ( $O_2$ ,  $N_2$ , AND He) PLASMA TREATMENTS AND AFTER PLASMA FOLLOWED BY 3-APTES TREATMENT AT DIFFERENT CONCENTRATIONS

Functionalization protocols	Water contact angle measurement after plasma		Water contact angle measurement after plasma and APTES					
	Solution casted PMMA membranes	Compression moulded PMMA membranes	Solution casted PMMA membranes			Compression moulded PMMA membranes		
			5%	10%	15%	5%	10%	15%
Untreated PMMA	$75^\circ$	$80^\circ$	-	-	-	-	-	-
Oxygen plasma	$42^\circ$	$48^\circ$	$56^\circ$	$81^\circ$	$95^\circ$	$60^\circ$	$87^\circ$	$111^\circ$
Nitrogen plasma	$67^\circ$	$69^\circ$	$72^\circ$	$81^\circ$	$93^\circ$	$71^\circ$	$86^\circ$	$102^\circ$
Helium plasma	$71^\circ$	$75^\circ$	$80^\circ$	$82^\circ$	$92^\circ$	$92^\circ$	$102^\circ$	$104^\circ$

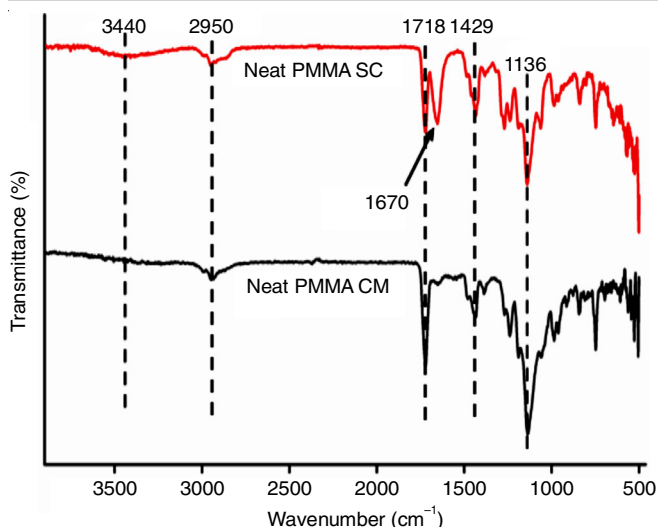


Fig. 3. FTIR spectra of untreated compression moulded and solution casted PMMA membrane

to NH bending vibration) appeared sharp in 10 % APTES in comparison to 5% and 15% APTES, stating that the addition of a high concentration of APTES stabilized the polymer membrane while excessive APTES may increase roughness of the surface of membrane, which leads to membrane deterioration. In addition, a shift of peak from 2938  $\text{cm}^{-1}$  in 5% APTES to 2905  $\text{cm}^{-1}$  and 2904  $\text{cm}^{-1}$  in 15% and 10% APTES, respectively is observed, indicating the shift of C-H stretching due to presence of APTES molecules on PMMA chains. Therefore, the 10% APTES is an optimized concentration in order to get maximum binding sites of APTES on the PMMA membrane. For the further characterization study, 10% APTES concentration was chosen since it offered sufficient amine groups while maintaining the topography of the surface.

Finally, the estimation of reactive amine groups on the 10% functionalized membranes was done by analyzing a reaction between the amine group and FITC molecules. Average mean intensity of the fluorescein group deposited on the PMMA membranes was calculated. Confocal microscopy on solution casted and compression moulded membranes before functionalization

(Fig. 5a-b) showed no fluorescence while Fig. 6a-f shows the confocal images of 10% APTES functionalized solution casted and compression moulded membranes under  $\text{O}_2$ ,  $\text{N}_2$  and He plasma. From Table-4, the average mean intensity of the fluorescein group calculated for both the membranes functionalized with plasma gases at 10% APTES can be seen. Although both solution casted and compression moulded membranes after plasma and APTES treatments resulted in functionalized membranes as demonstrated by rapid binding of FITC molecules, but the average mean intensity of fluorescein group in He plasma treated compression moulded membrane is two to ten times more than that obtained for  $\text{N}_2$  and  $\text{O}_2$  plasma. On the other hand, solution casted PMMA membrane treated with He plasma resulted in eight to fifteen times more average mean intensity value than other plasma solution cast membranes. Among the two fabricated PMMA, solution casted membrane showed twice more average mean intensity value on the surface in comparison to compression moulded membrane. This enhanced modification of both the membranes is attributed to the presence of high intensity of reactive species like OH, O,  $\text{N}_2$ ,  $\text{N}_2^+$  introduced on the membranes after treatment with He plasma as reported in literature [15].

## Conclusion

The study covers a method to fabricate and compare the stability of strongly bonded amine-functionalized PMMA films, which were synthesized differently but traversed similar modification techniques. Surface modification with varying plasma gas species and APTES concentrations to generate amine functionalities on PMMA membranes has been investigated. The SEM results showed morphology of compression moulded membrane to be smoother and uniform than solution casted membrane. Decreased water contact angle was obtained in both the PMMA membranes treated with  $\text{O}_2$  plasma prior to APTES treatment while after APTES treatment, water contact angle significantly increased in He plasma treated membranes. The role of plasma gas species in water contact angle (WCA) measurements showed an enhanced surface modification in membranes treated with He plasma followed by APTES while FTIR

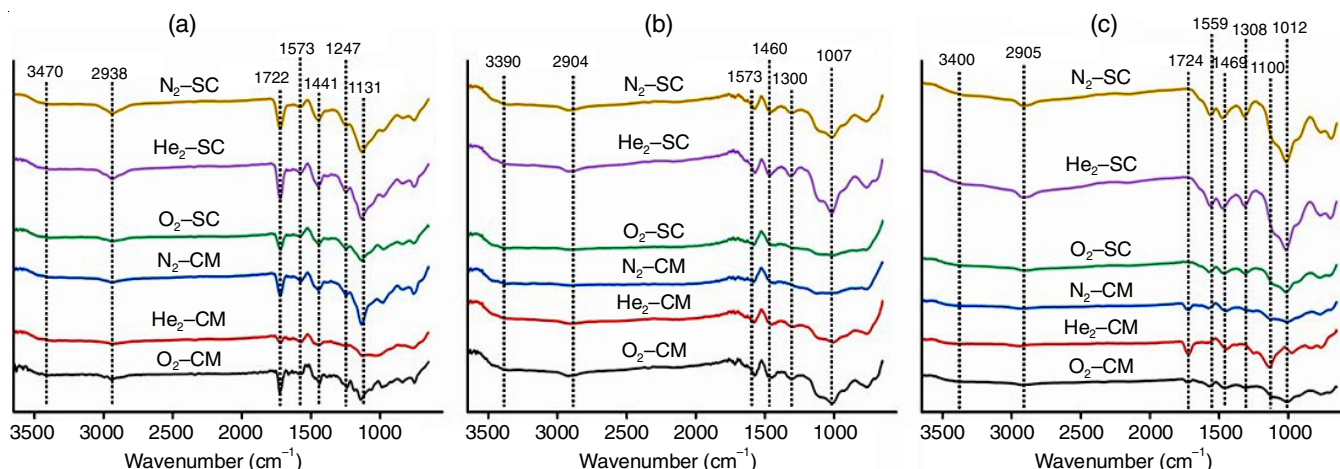


Fig. 4. FTIR spectra of 3-APTES functionalized PMMA membranes at different APTES concentrations (a) 5% APTES (b) 10% APTES and (c) 15% APTES



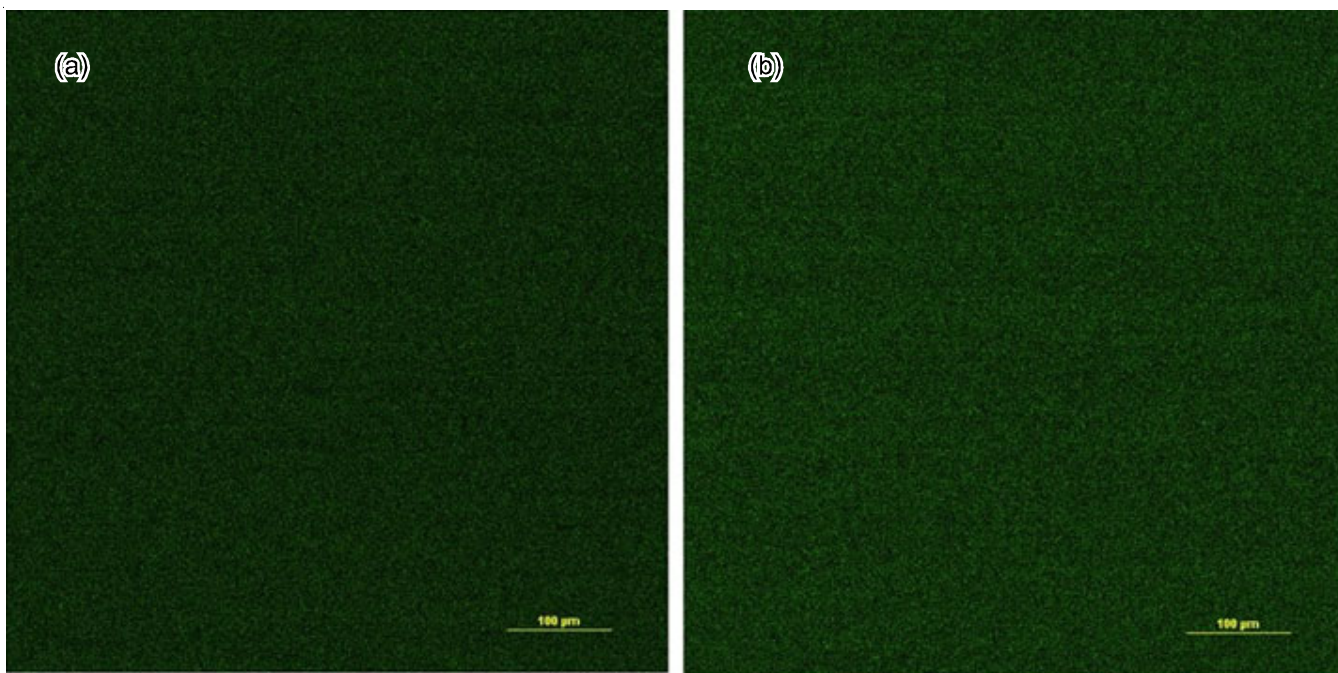


Fig. 5. Confocal images (a) untreated solution casted PMMA membrane (b) untreated compression moulded PMMA membrane

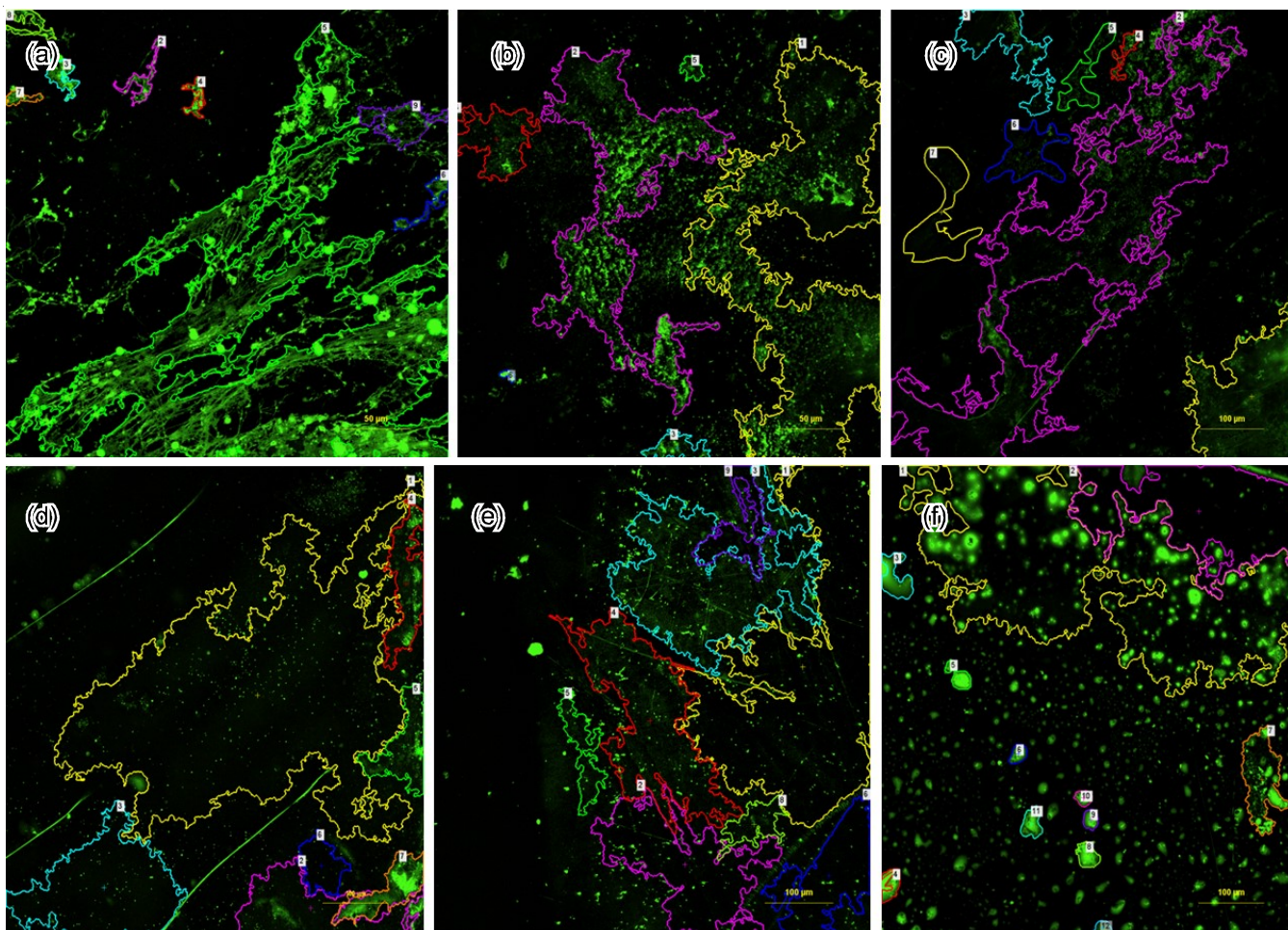


Fig. 6. Confocal images of functionalized PMMA (a) oxygen plasma + 10% APTES compression moulded PMMA (b) nitrogen plasma + 10% APTES compression moulded PMMA (c) helium plasma + 10% APTES compression moulded PMMA (d) oxygen plasma + 10% APTES solution casted PMMA (e) nitrogen plasma + 10% APTES solution casted PMMA (f) helium plasma + 10% APTES solution casted PMMA

TABLE-4

AVERAGE MEAN INTENSITY OF THE FLUORESCHEIN GROUP CALCULATED FOR THE CONFOCAL IMAGES OF COMPRESSION MOULDED AND SOLUTION CASTED PMMA MEMBRANES TREATED WITH O<sub>2</sub>, N<sub>2</sub> AND He PLASMA FOLLOWED BY 10 %APTES

Surface treatment on solution casted membranes	Average mean intensity of fluorescein group	Surface treatment on compression moulding membranes	Average mean intensity of fluorescein group
Oxygen plasma + 10% APTES	10.80	Oxygen plasma + 10% APTES	10.45
Nitrogen plasma + 10% APTES	20.27	Nitrogen plasma + 10% APTES	52.49
Helium plasma + 10% APTES	155	Helium plasma + 10% APTES	84.96
Untreated	N.D.*	Untreated	N.D.*

\*N.D. = not detected (&lt;1.0)

analysis showed effective deposition of APTES in membranes treated with 10% APTES after plasma. Further, confocal analysis concluded that both solution casted and compression moulded PMMA membranes were functionalized efficiently using He plasma and 10% APTES in comparison to the other treatments. However, among the two membranes, the solution casted membrane yielded twice more reactive amine groups on the surface in comparison to the compression moulding membrane. Such plasma-APTES treated PMMA films can immobilize a variety of biomolecules including DNA and therefore, these are expected to find wide applications as biosensors in biomedical and pharmaceutical analysis, clinical diagnostics, environmental monitoring and forensic investigations.

#### ACKNOWLEDGEMENTS

Author acknowledges the resource help for this work from Indian Institute of Technology, Delhi, India. We would also like to thank Nikon India Private limited, Gurgaon, Haryana, India for providing resource and guidance in the use of confocal microscopy.

#### CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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