International Journal of Advanced Biochemistry Research

ISSN Print: 2617-4693
ISSN Online: 2617-4707
NAAS Rating (2025): 5.29
IJABR 2025; 9(8): 249-254
www.biochemjournal.com
Received: 15-06-2025
Accepted: 29-07-2025

Dr. Namita Dash
Assistant Professor, Physics
College of Basic Science and Humanities, OUAT, Bhubaneswar, Odisha, India

Corresponding Author:
Dr. Namita Dash
Assistant Professor, Physics
College of Basic Science and Humanities, OUAT, Bhubaneswar, Odisha, India

Effect of low pressure dc glow air plasma of different thickness on PMMA film

Namita Dash

DOI: https://www.doi.org/10.33545/26174693.2025.v9.i8d.5157

Abstract
The intensities of all the functional groups decrease as the thickness increases for the plasma treated with constant powers. However, the intensities for higher thickness films show no further decrease and remain same**.** The transmittance increased for increase in thickness that decreased the smoothing of the surface from SEM micrograph**.**

Keywords: High brilliance, grafting, RF plasma, DC plasma, transmittance, solvent casting

Introduction
Poly methyl methacrylate (PMMA) is one of the best organic optical materials widely used to make a variety of optical devices, such as optical lenses [1,2]. Moreover, PMMA matrix is most preferred for designing components because of its better resistance to hydrolysis and its good outdoor weather resistance [3]. Surface modification of polymers involves altering the physical, chemical, mechanical or biological properties of a surface in order to better control the interactions and responses of a specific application [4]. Out of several surface modification techniques, perhaps the preferred method is low-pressure plasma processing. Plasma delivers exceptional results for manufacturers in many fields. Plasma treatment of polymer has been utilized broadly in surface modification to increase material adhesion and improve compatibility [5]. Plasma treatment can improve wettability, oxidize the surface, and enhance cell growth and adhesion [6]. Plasma generated in a vacuum environment influences the surface of the polymer to make it suitable for a specific application. A plasma treatment provides manifold possibilities to refine a polymer surface, enabled by the adjustment of parameters like gas flows, power, pressure and treatment time. Too many manipulative parameters for plasma treatment of polymer samples therefore create difficulties in optimization of the technique.
In this work, the effect of plasma treatment on the structural and optical properties of PMMA has been studied. At first, introduction and applications of PMMA is given in context to its structural and optical properties. Then a short description of low pressure DC glow discharge plasma followed by the literature review related to the present work is given. The objectives of the thesis then fixed from the above literature followed by the organization of the same.

PMMA (Poly Methyl Methacrylate)
PMMA was discovered in the early 1930s by British chemists, Rowland Hill and John Crawford, followed by its first application by a German chemist, Otto Rohm, in 1934[7].
PMMA is a polymer and an acrylic. It is an amorphous thermoplastic which is optically transparent, high brilliance, hard, rigid, brittle, refractive index is 1.49 unaffected by moisture, and offers a high strength-to-weight ratio. PMMA has good mechanical strength, acceptable chemical resistance and extremely good weather resistance [8].
Acrylics offer high light transmittance with a Refractive Index of 1.49 and can be easily heat-formed without loss of optical clarity. Prolonged exposure to moisture or even total immersion in water, does not significantly affect the mechanical or optical properties of acrylic. Most commercial acrylics have been UV stabilized for good weather ability and resistance prolonged sunlight exposure [9]. Acrylics are unaffected by aqueous solutions of most laboratory chemicals, by detergents, cleaners, dilute inorganic acids, alkalis and aliphatic hydrocarbons. Acrylics are easily sawed, drilled, milled, engraved, and finished

with sharp carbide-tipped tools [10]. Cut surfaces may be readily sanded and polished. They are also readily bend or thermoformed at low temperature and solvent bonding of properly fitting parts produces a strong, invisible joint. Acrylics are available in colorless. PMMA is available in both in liquid and solid [11].

PMMA is used in various applications such as drug delivery, automobiles, sensors, molecular gels, semiconductor, catalysts, environmental and industrial applications, store fixtures and displays, lenses and lighting fixtures, light pipes, windows and skylights, sight gauges, furniture, outdoor signs, Sculpture, Aircraft window as a glass replacement, Bone cement of orthopedic surgeries.

DC glow discharge air plasma

Plasma is a state of matter in which an ionized gaseous substance becomes highly electrically conductive to the point that long-range electric and magnetic fields dominate the behavior of the matter. Plasma is an electrically neutral medium that contains ions, free radicals, excited molecules and UV light [12,13]. When a gas under partial pressure is exposed to a high-voltage energy source (such as microwave), it becomes a mixture of ions, radicals, free-electrons and other types of molecular "fragments." The resultant plasma treatment can completely remove virtually all organic contamination to promote better adhesion. Plasma is frequently used to treat the surface of metals, polymers, glass, elastomers and ceramics to clean and improve "bonding" [14].

Uses of plasma in various fields:

It used in industries-surface properties, aerospace, automobiles, electronics, food packaging, glass, marine, medical, military, satellite application, nanopowders, supercomputers, nuclear fuel, pulsed plasma thruster, optics, paint, paper, plastics, textiles, polymers, laser, plasma lamps, ozone generation, plasma displaces[15].Uses of plasma treated on polymer: Polyethylene, polypropylene, polyacetylene, poly ethylene glycol, pyrrole, PVC(poly vinyl chloride),Teflon, terephthalate, PET, PC, PS, EPDM, PVDF, etc.

In the case of polymers, the surface should be compatible to the biological system, which can be effectively modified by the plasma. Plasma treatment can improve wettability, oxidize the surface, and enhance cell growth and adhesion. Absolute treatment affects the optical properties of the polymer. In addition to above, one can summarize the various effects of plasma on a polymer surface as follows: (a) surface modification, (b) grafting, (c) film deposition [16].

There is different type of plasma like microwave plasma, RF plasma, DC plasma, passive and active plasma, high energy density plasma etc.

Low-pressure plasma (or vacuum plasma or glow discharge plasma) process takes the cleaning and surface preparation of materials to the next level.

Primarily, a plasma treatment provides manifold possibilities to refine a polymer surface, enabled by the adjustment of parameters like gas flows, power, pressure and treatment time.

Depending on the gas composition and plasma conditions, ions, electrons, fast neutrals, radicals and UV radiation contribute to the polymer treatment, resulting in etching, activation and/or cross-linking [17].

Literature Survey

Effects of low-intensity UV treatment on the optical constants of red BS dye-doped poly methyl methacrylate (PMMA) film including refractive index, extinction coefficient, real and imaginary parts of dielectric constant, band gap energy and refractive index dispersion parameters are measured and calculated [18]. A study on aging of PMMA polymer treated on oxygen plasma on different temperature was studied. The aging rate of the sample was significantly lower at low temp. than the sample stored at high temperature [19]. PMMA shows poor adhesion for evaporated inorganic coatings. The DC and microwave plasma treatments can considerably increase free surface energy but an improvement of coating adhesion is, according to our results, only possible by the DC process. ATR spectroscopy has been applied to investigate the changed chemical structure of DC plasma-treated PMMA. Samples treated by microwave plasma did not show ATR alteration while XPS analysis indicated surface oxygen enrichment [20]. The attenuation in light transmission through PMMA films of different layer thicknesses on SiO_2 substrates for solar cell applications using Fourier transform infrared (FTIR) and ultraviolet visible and near infrared (UV-Vis-NIR) spectroscopy. The results show that, film thickness decreases as rotational speed increased and light transmission decreases as film thickness increases [21]. Poly (methyl methacrylate) (PMMA) has been modified via a dc pulsed oxygen plasma for different treatment times. The modified surfaces were characterized by X-ray photoelectron spectroscopy (XPS), optical profilometer, zeta potential, and advancing contact angle measurements [22]. Low power RF plasma can change surface properties and improve the wettability of PMMA surface. Optical constants and properties as well as band gap energy of PMMA don't change effectively by the applications of RF plasma [23]. Poly (methyl methacrylate) (PMMA) films filled with various mass fractions of $MnCl_2$ were prepared by a casting method. The structural and electrical properties were investigated using the following techniques, IR (200-4000 cm−1), UV/VIS (200-800 nm), X-ray diffraction (XRD), dc electrical resistivity, dc magnetic susceptibility and electron spin resonance (ESR) [24]. Effects of thermal aging on electric properties of poly methyl methacrylate (PMMA) polymer are reported in this paper. PMMA samples are submitted to successive heat-cooling cycles (T_{max} = 45 °C and T_{min} = 20 °C) in the ambient air. Different complementary techniques are thus employed to investigate structural modifications, conduction processes and dielectric relaxations. These are the Fourier Transform Infrared (FTIR) spectroscopy, impedance spectroscopy and current-voltage technique. Results are discussed in terms of FTIR bands intensities, relaxation frequencies and electrical conductivity [25]. Freshly prepared CdS-quantum dots (QDs) in DMF (clear pale solution) when loaded in poly methyl methacrylate (PMMA) lead to excellent optical properties. The tuning of the absorption and emission wavelengths via experimentally control parameters is considered novel and significant. The absorption band for CdS was observed at about 370 nm in polymeric matrix [26, 27].

Experimental Details

PMMA films were prepared by various methods solvent casting, self-assembly, layer by layer, in situ polymerization etc. Here, the solution casting method has been used to prepare three PMMA films of varying thickness. This method is unique in the sense that it does not require conventional extrusion or injection molding technologies. This process also allows other components to be incorporated into the structure of the part during layering process. The steps followed by the method are depicted in the Fig. 1.

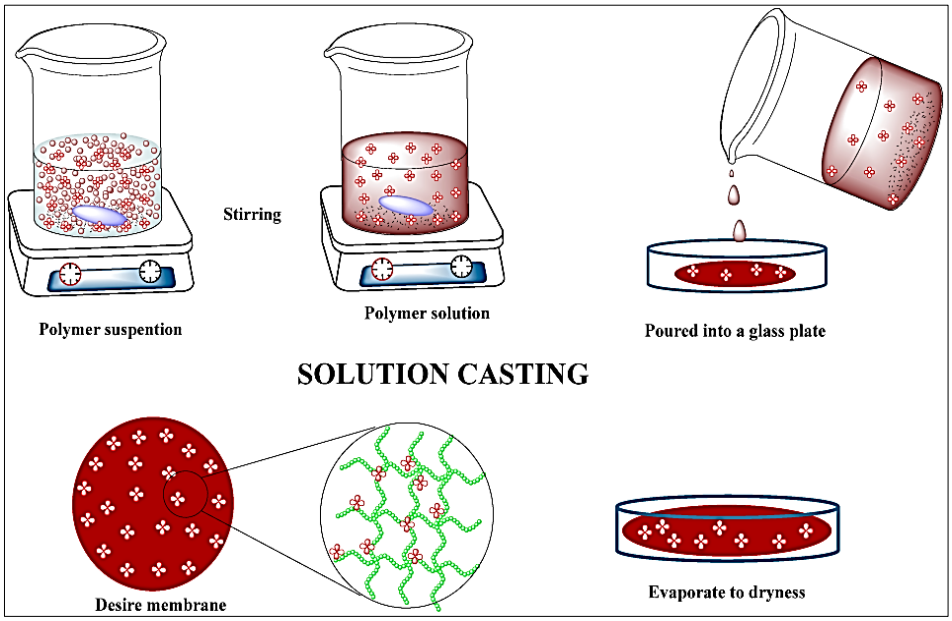

Fig 1: Schematic diagram for solvent casting method

PMMA films of different thicknesses were synthesized by solvent casting method followed by hot pressing. PMMA (Alfa Aesar) and Toluene (Merck, Research grade) were used as received without further purification. To 30 ml of Toluene (solvent), 3.9015 gm (15 wt%) of PMMA granules were added in a beaker and kept for stirring at 50 °C on magnetic stirrer with hot plate for 24hrs. until formation of slurry or viscous transparent solution. Then the solution was casted in to a petridish and solvent casted PMMA film having non-uniform thickness was obtained after all the solvent get evaporated. The above film was cut in to 4 pieces and hot pressed at 120 °C and different pressures (1 tonn,2 tonn,3 tonn) with the help of Table-top Hydraulic Hot-press to obtain films of different thicknesses.

Plasma treatment of PMMA films

The details of the plasma unit are as follows. The unit consists of a cylindrical glass chamber with two circular stainless electrodes. One of the electrodes is grounded and another one (cathode) is connected to a variable DC power supply (0 to -5 kV).

The base pressure can be achievable up to 10^{-3}mBar (measured with the help of pirani gauge) using Rotary vacuum pump. Out of the four as prepared PMMA sample, three were treated in DC air plasma at low pressure (5 X 10^{-2}mBar). The three films having different thicknesses were treated with plasma for 10mins each with power of the DC power supply with 20 Watt. During the treatment the inter electrode distance was fixed around 15 mm.

Table 1: Specification of samples

Sample Name	Specification
S_0	Hot pressed at 2 tonn(0.12 mm) and Untreated
S_1	Hot pressed at 3 tonn(0.06 mm) and Plasma Treated
S_2	Hot pressed at 2 tonn(0.12 mm) and Plasma Treated
S_3	Hot pressed at 1 tonn(0.21 mm) and Plasma Treated

Characterization techniques

UV Visible spectroscopy

The alterations in energy occurred in between atoms is recorded by electronic spectroscopy. The energy alterations occurred in within molecules are due to rotation, bending, stretching vibrations of bonds. A spectrum is formed due to these motions within the range of 200-700 nm wavelengths.

Tauc plot Methods

If absorbance or transmittance parameter is varied with wavelength, then this method is adopted. The band gap is estimated from the expression given below:

$$(\alpha h\nu)^{1/n} = A^{1/n}(h\nu - E_g)$$

(n= integer for type of transition A =absorbance and E_g= band gap).

The absorption coefficient α is calculated from the formula:

$$\alpha = \frac{1}{t} 2.303 log(100/T)$$

(t= thickness of the sample used)

The indirect band gap of the film is measured by plotting a graph between $(\alpha h\nu)^{1/2}$ and (hν). This equation seems to be straight line equation for which the slope is $A^{1/2}$ and the y-intercept is $A^{1/2}E_g$. Thus, band gap E_g is the ratio of slope and y-intercept. Similarly, direct band gap of the film is measured by plotting a graph between $(\alpha h\nu)^2$ and (hν).

In the present study the UV-Vis spectrum of the films were obtained by using UV-Vis spectrophotometer (UV-2600 from Shimadzu UV-Visible Spectrophotometer) at room temperature within wavelength range of 200- 700 nm (Fig. 2).

Fourier transform infrared spectroscopy

FTIR is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. FTIR spectrometer simultaneously collects high-spectral-resolution data over a wide spectral range. Here, in the present study the FTIR (Nicolet 1S5 Mid Infrared) is measured at room temperature. The samples analyzed must not be more than 20micrometre and should not be less than 1micrometre.

Scanning electron microscope

Scanning electron microscope (SEM) uses a focused beam of high energy electrons to generate a variety of signals at the surface of solid specimen. The signal that drive the electron reveal information about the sample including external morphology (texture), chemical composition and crystalline

structure and orientation of material making of the sample. The SEM is also capable of performing analysis of selected point locations on the sample; this approach is especially useful in qualitatively or semi qualitatively determining chemical composition (using EDS), crystalline structure and crystal orientation (using EBSD).

Results and Discussion

Surface structure analysis by FTIR

The most important characteristics of surface of samples are determined by functional groups. Fig. 2 shows FTIR spectra of PMMA of varying thickness after plasma treatment in the range of 500 to 2500 cm^{-1}. The inset shows the spectra of untreated film (of thickness = 0.12 mm). The peaks at 729cm^{-1},986cm^{-1},1145cm^{-1},1270cm^{-1},1386cm^{-1},1483cm^{-1},1729cm^{-1}correspond to the C-H, C-H, C-O, C-O, CH3, CH2, C = O bonds respectively are present in all the samples [28,29]. No new peaks and no peak shifts are observed in the spectra as the result of plasma treatment on films of different thickness. This signifies that no new bonds were formed in the PMMA surface due to the interaction of plasma reactive species with it.

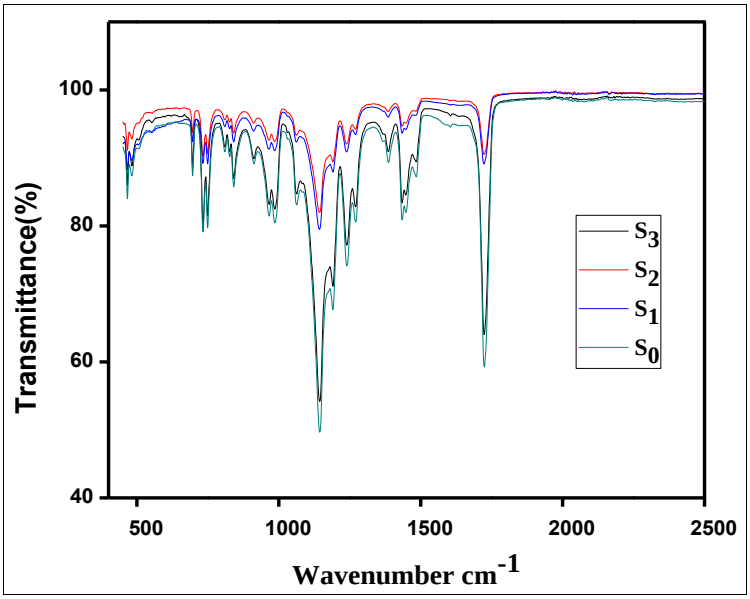

Fig 2: FT-IR spectra of plasma treated films of varying thickness

The intensities of all the functional groups decrease as the thickness increases for the plasma treated with constant powers. However, the intensities for higher thickness films show no further decrease and remain same. This noticeable change in various bands were due the decrease in number of bonds as a result of interaction of electrons, ions and radicals etc., present in the plasma medium with film surfaces [30]. Also, most synthetic polymers degrade after exposure to UV radiation in the plasma due to the presence of photosensitive impurities and/or abnormal structural moieties which are introduced during polymerization [31].

Optical properties analysis by uv-visible spectroscopy

UV-Vis spectrophotometer is a simplest tool to probe the optical properties and to estimate band gap energy of various materials. The transmission spectra of the plasma treated films were recorded as a function of thickness in the wavelength range of 200-800 nm and shown in the Fig. 3. The inset shows a comparison of untreated and plasma treated spectra of a film of equal thickness (thickness = 0.12mm).

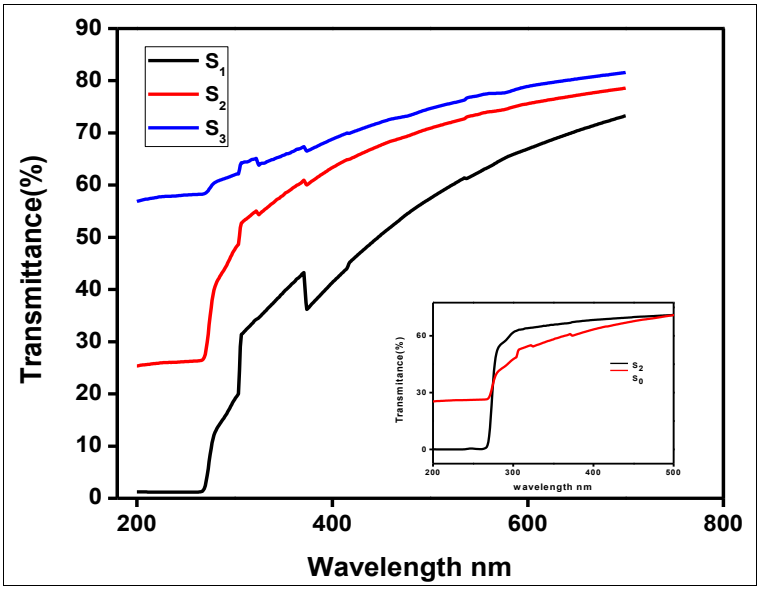

Fig 3: UV-Vis transmittance spectra of plasma treated films of varying thickness. The inset is the comparison of untreated and plasma treated spectra of a particular film (thickness = 0.12mm)

The inset of the Fig.3 depicts slight decrease in the transmittance percentage after plasma treatment for a particular film of thickness 0.12 mm. The same trend of decrease in transmittance percentage is observed for the film of thickness 0.06mm. However, the transmittance percentage increases for the films with highest thickness (0.21mm) even for the same plasma treatment. These slight changes in transmittance percentage can be understood from the fact that the treatment did not change the surface morphology and/or roughness much as observed in SEM micrographs (Fig.3) [32].

The optical band gap is the value of optical energy gap between the valance band and the conduction band. The direct and indirect optical band gaps of the samples is determined from the transmission spectra using Tauc plot and shown in the Fig. 3 (a) and (b), respectively. The values are shown in the table 2.

Table 2 shows decrease in band gap with increase in thickness of the films after plasma irradiation of constant power and for equal time period. This reduction in band gap values may be due to increase in the concentration of PMMA as increase in the thickness of the films [3].

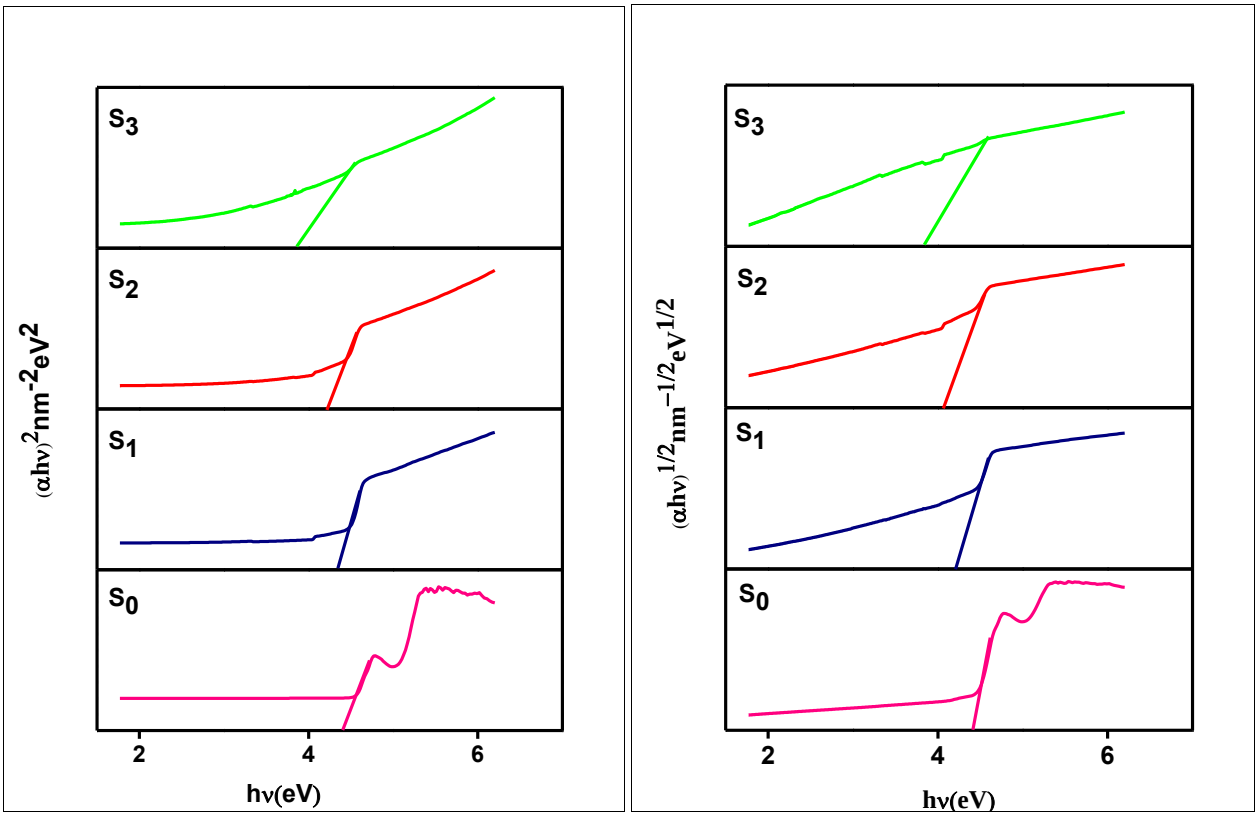

Fig 3: (a) direct optical band gaps and (b) indirect optical band gaps of the samples (using Tauc plot)

Table 2: Direct and indirect band gap values

PMMA type	Direct E_g(eV)value	Indirect E_g(eV)value
S_0	4.56	4.46
S_1	4.48	4.22
S_3	4.23	4.08
S_3	3.92	3.82

Surface morphology by SEM micrographs

To investigate the effect of plasma irradiation on the surface morphology of the PMMA films, untreated and plasma-treated PMMA surfaces were imaged with SEM and the results are shown in Fig. 4. The micrographs were taken with same magnification of 30 µm for all the samples. Fig.4 (a) shows the untreated film of thickness 0.12 mm, (b) shows the plasma treated film of thickness 0.12 mm and (c) shows the plasma treated film of thickness 0.21 mm.

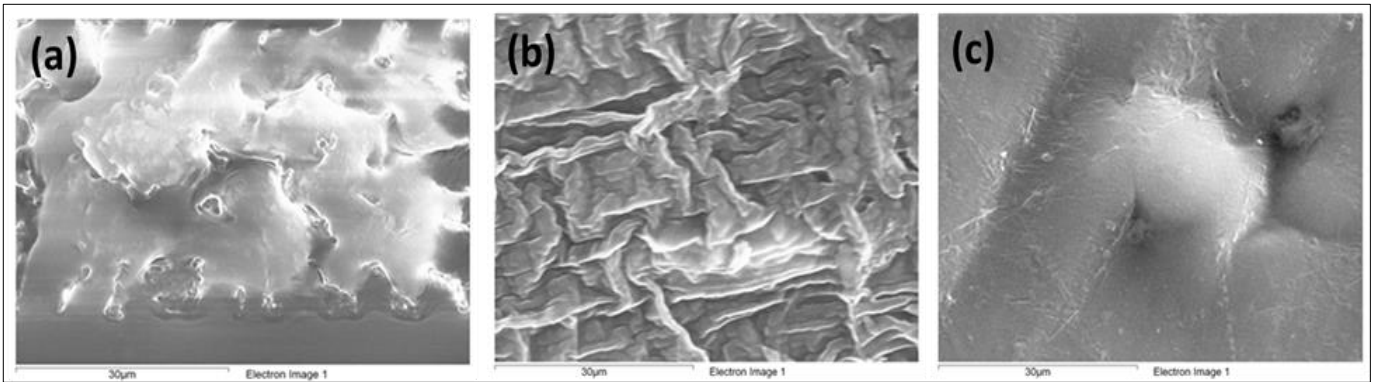

Fig 4: (a) The untreated film (0.12 mm), (b) the plasma treated film (0.12 mm) and (c) the plasma treated film (0.21 mm)

The relatively smooth surface of untreated sample becomes rod shaped after plasma treatment for the same thickness. However, as the thickness increased to the highest value the sample surface remain unaffected. This small change in plasma interaction with film surfaces supports the transmittance percentage data, where the transmittance decreases and then increases due to smoothness of the surface.

Conclusion

In this sample no peak shifts are observed in FTIR spectra after plasma treatment i.e. no new bonds are formed. For varying the thickness of the sample the number of bonds decreased as we increased the thickness but for higher thickness case the intensity remains same for constant power supply. The transmittance increased for increase in thickness that decreased the smoothing of the surface from SEM micrograph. Direct and indirect band gap decreased as we increased the thickness from UV-Vis spectroscopy.

References

1. Wochnowski C, Metev S, Sepold G. UV-laser-assisted modification of the optical properties of polymethylmethacrylate. Appl Surf Sci. 2000;154-155:706-711.
2. Baker AK, Dyer PE. Refractive-index modification of polymethylmethacrylate (PMMA) thin films by KrF-laser irradiation. Appl Phys A. 1993;57(6):543-534.
3. Ma H, Jen AK-Y, Dalton LR. Polymer-based optical waveguides: materials, processing, and devices. Adv Mater. 2002;14(19):1339-1365.
4. Roach P, Farrar D, Morgan H. Modern biomaterials: a review—bulk properties and implications of surface modifications. J Mater Sci Mater Med. 2007;18(7):1263-1277.
5. Blois S. Magnetic methods. In: Physical Techniques in Biological Research: Physical chemical techniques. Vol. 2. 1956. p. 393.
6. Lee JH, Park JW, Lee HB. Cell adhesion and growth on polymer surfaces with hydroxyl groups prepared by water vapour plasma treatment. Biomaterials. 1991;12(5):443-448.
7. Brydson J. Plastics Materials. London: Butterworths; 1989.
8. Berins ML. Plastic Materials/Properties and Applications. In: SPI Plastics Engineering Handbook of the Society of the Plastics Industry, Inc.. Boston, MA: Springer; 1991. p. 47-78.
9. Mohammed MF, Abd MM. Effect of temperature on lubricating oil and poly(methyl methacrylate) additive. Diyala J Eng Sci. 2012;5(1):205-220.
10. Marouf AAR. Characterization of Polymethyl Methacrylate and Silicon Photovoltaic Cells after Processing by Laser Direct Writing Technique [dissertation]. Sudan: Sudan University of Science and Technology; 2015.
11. Unknown author. Testing of a new PMMA-hA bone cement versus conventional PMMA cement *in vitro*. J Biomater Sci Polym Ed. 2003;14(11):1283-1298.
12. Liston EM, Martinu L, Wertheimer MR. Plasma surface modification of polymers for improved adhesion: a critical review. J Adhes Sci Technol. 1993;7:1091-1127.
13. Fozza AC, Klemberg-Sapieha JE, Wertheimer MR. Plasma surface modification of polymers. Plasmas Polym. 1999;4:183-198.
14. Grace JM, Gerenser LJ. Plasma treatment of polymers. J Dispersion Sci Technol. 2003;24(3-4):305-341.
15. Xu Q, Czernuszka JT. Controlled release of amoxicillin from hydroxyapatite-coated poly(lactic-co-glycolic acid) microspheres. J Control Release. 2008;127:146-153.
16. Zhao C, Xue L, Ran Q, Liu X, Zhao J, Chen H. Effect of film thickness on the antifouling performance of poly(hydroxy-functional methacrylates) grafted surfaces. Langmuir. 2011;27(8):4906-4913.
17. Hegemann D, Brunner H, Oehr C. Plasma treatment of polymers for surface and adhesion improvement. Nucl Instrum Methods Phys Res B. 2003;208:281-286.
18. Rashidian M, Dorranian D. Low-intensity UV effects on optical constants of PMMA film. J Theor Appl Phys. 2014;8(2):121.
19. Vesel A, Mozetic M. Surface modification and ageing of PMMA polymer by oxygen plasma treatment. Vacuum. 2012;86(6):634-637.
20. Schulz U, Munzert P, Kaiser N. Surface modification of PMMA by DC glow discharge and microwave plasma treatment for the improvement of coating adhesion. Surf Coat Technol. 2001;142:507-511.
21. Chiromawa N, Ibrahim K. Effects of poly(methyl methacrylate) (PMMA) film thickness on light transmission through SiO_2 for applications in solar cell technology. Int J Eng Innov Technol. 2015;5(1):125-131.
22. Chai J, Lu F, Li B, Ng T, Wang D. Wettability interpretation of oxygen plasma modified poly(methyl methacrylate). Langmuir. 2004;20(25):10919-10927.
23. Jofre-Reche JA. Optimization of the surface properties of polydimethylsiloxane by plasma treatment for adhesion improvement and durability to acrylic adhesive for medical applications [thesis]. 2014.
24. Tawansi A, El-Khodary A, Al-Hadeethi Y, Abdel-Aziz M. The effect of $MnCl_2$ filler on the optical window and the physical properties of PMMA films. Polym Test. 2002;21(4):381-387.
25. Namouchi F, Mhiri H, Bessais B, *et al*. Investigation on electrical properties of thermally aged PMMA by combined use of FTIR and impedance spectroscopies. J Alloys Compd.
26. Khanna PK, Singh N. Light emitting CdS quantum dots in PMMA: synthesis and optical studies. J Lumin. 2007;127(2):474-482.
27. Kasih TP. Development of novel potential of plasma polymerization techniques for surface modification [PhD thesis]. Gunma University; 2007.
28. Haris M, Kathiresan S, Mohan S. FT-IR and FT-Raman spectra and normal coordinate analysis of polymethylmethacrylate. Der Pharma Chemica. 2010;2:316-323.
29. Dorranian D, Rashidian M. Optical properties of PMMA thin films irradiated by low-intensity UV. J Theor Appl Phys. 2012;6:1.
30. Ahmed RM. Optical study on poly(methylmethacrylate)/poly(vinyl acetate) blends. Int J Photoenergy. 2009;2009:150389.
31. Ahmed RM. Optical study on poly (methylmethacrylate)/poly(vinyl acetate) blends. Int J Photoenergy. 2009;2009:150389.
32. Raja V, Sarma AK, Narasimha Rao VR. Optical properties of pure and doped PMMA-co-P4VPNO polymer films. Mater Lett. 2003;57:4678-4683.