Study of surface structure and optical properties of PMMA films treated for different time in DC glow discharge (air) plasma

Submitted By

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Under the Guidance of

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CERTIFICATE – I

This is to certify that the thesis entitled, ***"Study of surface structure and optical properties of PMMA films treated for different time in DC glow discharge (air) plasma"*** *is submitted in partial fulfillment of the requirements for the award of the degree of* ***Master of Science*** *in* ***Physics*** *of the* ***Odisha University of Agriculture and Technology, Bhubaneswar*** *is a faithful record of bonafide research work carried out by* ***Debadutta Acharjya*** *under my guidance and supervision and that no part of this thesis has been submitted for any other degree or diploma or published in any form.*

It is further certified that the help and sources of information availed of during the course of study have been duly acknowledged.

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Dept. of Physics	Advisory Committee
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CERTIFICATE-II

*This is to certify that the thesis entitled, “***Study of surface structure and optical properties of PMMA films treated for different time in DC glow discharge (air) plasma***” submitted in partial fulfillment of the requirements for the award of the degree of Master of Science in Physics of the* **Odisha University of Agriculture and Technology, Bhubaneswar** *is a faithful record of bonafide research work carried out by* **Debadutta Acharjya** *under my guidance and supervision that no part of thesis has been submitted for any degree or diploma or published in any form.*

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*I hereby declare that the project work entitled submitted “***Study of surface structure and optical properties of PMMA films treated for different time in DC glow discharge(air) plasma***” by me for the partial fulfillment of the master of science to the* **CBSH, Odisha university of agriculture and technology, Bhubaneswar** *is my own original work and has not been submitted earlier to OUAT or to any other institution for the fulfillment of the requirement for any course of study. I also declare that no chapters of this manuscript in whole or in part in lifted and incorporated in this report from any earlier work done by me or others.*

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ABSTRACT

In this paper PMMA films were prepared by solution casting method and were subjected to DC glow discharge (air) plasma treatment for different intervals of time(2.5 min ,5 min ,7.5 min). The films were then characterized through techniques like FTIR, UV-Vis, SEM to study their surface structure and optical properties. FTIR analysis revealed that there were no new peaks or peak shift observed in the treated films. While the characteristic intensity decreased with increase in treatment time which is due to decrease in no. of bonds and interaction of PMMA film surface with the electron, ion, radical and UV radiation of plasma.

Study of UV-Vis analysis showed us that there was an increase in the transmittance percentage during shorter time treatment (2.5 min) because surface impurities were reduced and hydroxyl groups were reduced. But during longer time treatment (5 min, 7.5 min) transmittance decreased due to generation of electrons on PMMA surface due to the effect of plasma. There were no significant changes in bandgaps of the films reported due to low power plasma treatment which was confirmed from other researchers.

The SEM micrographs indicated that the roughness of films increased with increase in treatment time. This result also confirmed the result of transmittance of UV-Vis analysis.

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CHAPTER-1

INTRODUCTION

1.1 Introduction

Glass products, in recent years have been replaced by optical polymers like PMMA in many optical applications where low weight, chemical inertness, high impact resistance, flexible formability and relatively low cost are of major importance [1]. PMMA is a representative polymer with excellent optical transparency. PMMA matrix is most preferred for designing components because of its better resistance to hydrolysis and its good outdoor weather resistance. It is a thermoplastic and can be molten and molded into anything we want. 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, anti-reflecting coatings etc. The desirable bulk properties of polymers are often compromised by their unfavorable surface characteristics, such as low hardness, low resistance to abrasion and scratching, and low surface energy, which generally leads to low wettability and poor adhesion [2]. Low pressure plasma treatment has been successfully used as a dry process to alter the surface properties of polymers by many researchers across the globe. It involves the interaction of the plasma-generated excited species with a solid interface and results in a physical and/or chemical modification of the first few molecular layers of the surface, while maintaining the properties of the bulk. Plasma treatment can improve wettability, oxidize the surface, and enhance cell growth and adhesion. Absolute treatment affects the optical properties of the polymer. The various effects of plasma on a polymer surface may be categorized as: (a) surface modification, (b) grafting, and (c) film deposition [3].

However, the effect of plasma treatment depends on parameters such as the kind of plasma (DC, radio frequency (RF) or microwave (MW)), the discharge power density, the pressure and flow rate of the gas or gas mixture, as well as the treatment time .

In this work, therefore, the effect of time of plasma treatment on the structural and optical properties of PMMA has been studied. At the outset, 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 work are then fixed from the above literature followed by the organization of the same.

1.2 Poly(methylmethacrylate) (PMMA)

Structure of PMMA:

PMMA, an ester of methacrylic acid (CH2=C[CH3]CO2H), belongs to the important acrylic family of resins. In modern production it is obtained principally from propylene, a compound refined from the lighter fractions of crude oil. Propylene and benzene are reacted together to form cumene, or isopropylbenzene; the cumene is oxidized to cumene hydroperoxide, which is treated with acid to form acetone; the acetone is in turn converted in a three-step process to methyl methacrylate (CH2=C[CH3]CO2CH3), a flammable liquid. Methyl methacrylate, in bulk liquid form or suspended as fine droplets in water, is polymerized (its molecules linked together in large numbers) under the influence of free-radical initiators to form solid PMMA. The structure of the polymer repeating unit is

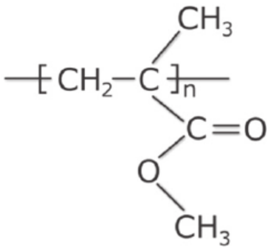

Fig: 1 Structure of PMMA.

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 [1].

Properties of PMMA:

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 [1].

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. 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. 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.

Molar mass varies, density 1.18 gm/cm^3 , melting point is 160 degree. PMMA has low cost, light weight. PMMA has water absorption ratio 0.3-0.4. Tensile strength increases with decrease in water absorption ratio. Coefficient of thermal expansion is high. It has low cost and is biocompatible in nature [13].

1.3 DC glow discharge air plasma and its irradiation effect

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 [9]. 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.”

Uses of plasma in various fields:

It is 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.

Treatment of plasma on polymer:

Polyethylene, polypropylene, polyacetylene, polyethylene 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 summarizes the various effects of plasma on a polymer surface as follows: (a) surface modification, (b) grafting, and (c) film deposition [4].

There are 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.

1.4 Literature survey

Surface properties of AT-BN incorporated PVDF/PMMA blend system which was air plasma treated were studied by E.Dhanumalayan and Co. Changes in the surface chemistry of polymer complexes was exposed after air plasma treatment [5].The surface properties of PMMA due to DC glow discharge air plasma treatment were observed by Olrike Schulz and Co. Surface energy of the PMMA samples increased leading to improvement in coating adhesion [6].Change in surface morphology and chemical composition of atmospheric plasma treated PMMA were studied by Tomas Homola and Co. Surface energy increased due to enhancement of oxygen containing polymer groups. But there were no changes reported on surface morphology by plasma treatment. Hydrophilic property was also achieved by this treatment but after a longer duration [7].PMMA films modified by atmospheric pressure non thermal plasma were studied by Zhi fang and Co. It was observed that after plasma treatment the surface of PMMA films was etched and O_2 containing polar groups were introduced on to the surface. Due to this there was a decrease in water contact and surface energy and surface property was improved. Hydrophobicity of films is achieved which depends on treatment of time [8].DC glow discharges Atmospheric pressure air plasma method was studied by Zdeno Machala. In this method electron densities was increased and due to which large volumes of plasma was obtained [9].

Low power oxygen and nitrogen plasma were used to modify PMMA surfaces to study its optical and surface properties by Dorramian D and Co. It was seen after treatment that roughness of sample is affected more by N_2 plasma compared to O_2 plasma while the molecular structure was affected by O_2 plasma. With increase in time of treatment surface energy is decreased. Contact angle is also decreased. The bandgap of the sample is not affected [10].Changes in the surface properties of PMMA treated with air plasma were examined by Diana Rymuszka.Wettability of the sample increased due to increase in surface energy. Increased surface roughness leads to increased hydrophobicity of PMMA [11]. Atmospheric pressure plasma technology a review paper by U Kogelschatz.Various applications of the plasma technology was given. One of them was to see the changes it made on the surface and optical property of polymers [12].Studies on development in Plasma surface modification technique with special emphasis on low energy or soft plasma was given by Z.Zhang. It was reported that there was an improvement of elasticity with reversible characterization [13].Studies on the surface of high density PMMA treated with O_2 & N_2 plasma by Gonzales lead to results that when rapid oxidation occurs it leads to increase in contact angle and hydrophilicity [14].The synthesis & properties of plasma polymerized PMMA with the help of plasma polymerization technique was studied by Choon-Sang Park. There was more amount of hydrophobicty then hydrophilicity observed in the sample. The surface is homogenous and amorphous in nature [15].

1.5 Motivation and Objectives

PMMA is an interesting representing polymer with good optical transparency. From the above literature studies, it is revealed that the plasma treatment of polymer samples can change various properties including its optical properties. However, too many manipulations in the parameters of the plasma cause difficulties in optimizing the process parameters. In this thesis, therefore, we have taken the low pressure DC glow discharge plasma for treatment purpose and defines the following objectives:

- To irradiate PMMA films of constant thickness by dc glow air discharge plasma of steady power by varying the time of treatment.
- Study of structural and optical properties of treated PMMA films as function of the time of treatment

1.6 Organization of the thesis

After brief discussion on structure, properties and applications of PMMA and plasma treatment in chapter 1, the experimental setup is presented in chapter 2. Chapter 3 is devoted to results and discussion and chapter 4 discusses the conclusions drawn from the above work.

CHAPTER-2

EXPERIMENTAL DETAILS

In this chapter, the details of the experimental procedures of synthesizing and characterization techniques are discussed. At first, the procedures for preparing PMMA films are discussed followed by the detailed of the plasma unit used for treatment of the as prepared films. Then various characterization techniques like FTIR, UV-Vis and SEM used along with their specification are given. The results thus obtained from these characterizations are used for discussions in the next chapter.

2.1 Synthesis of PMMA films

PMMA ([CH2C(CH3)(COOCH3)]n) with average molecular weight of 15,000 g mol-1(Alfa Aesar) as the matrix polymer and toluene(Merck) as solvent was chosen for synthesis of PMMA thick films. Out of the various methods, solution casting method was used to prepare PMMA thick films. Solution casting method is the oldest technology in plastic film manufacturing; this process is becoming increasingly attractive for the production of films with extremely high quality requirements. The advantages of this process include maximum optical purity and extremely low haze. But there are many pre-requisites for this method:

- The polymer must be soluble in a volatile solvent (here toluene was used) or water.
- A stable solution with a reasonable minimum solid content and viscosity should be formed.
- Formation of a homogeneous film and release from the casting support must be possible.

Procedure followed during synthesis:

3.9g of PMMA granules was added to 30ml of Toluene in a beaker and kept under stirring for 24 hours at 50^{o}C on a magnetic stirrer with hot plate to get transparent viscous solution. Then the solution was casted in to a petridish and kept at room temperature until to get thick film after evaporation of all the solvent and hardening of PMMA solution. To obtain uniform thickness, the film was further hot pressed at 120^{o}C, 2 tonn pressure with the help of table top manual hydraulic polymer hot press for 10 minute. The film finally obtained was of 0.12mm thickness. All the above procedure followed during the experimental work shown in Fig. 2.1.

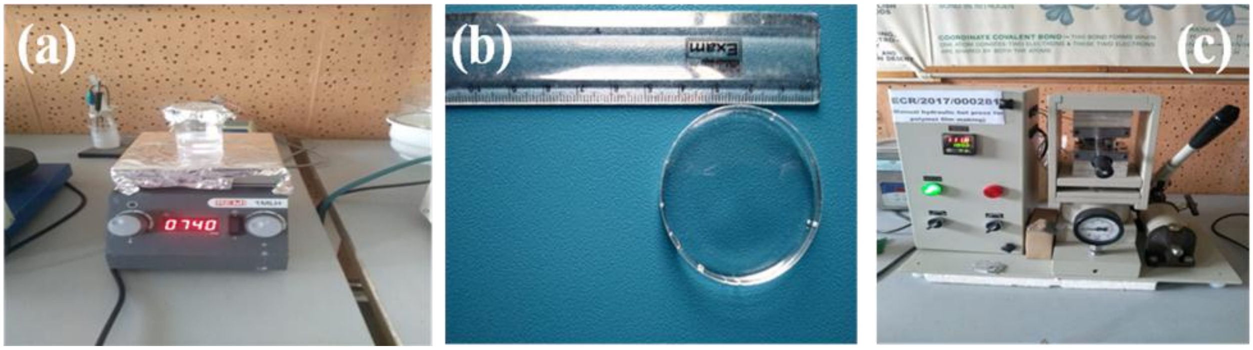

Fig: 2.1 (a) Solution of PMMA and toluene on the magnetic stirrer, (b) removed film after casted on a Petridis and (c) hydraulic machine for hot pressing the films to obtain desired thickness.

2.2 Plasma treatment of PMMA films

The schematic representation of mechanism associated with the plasma treatment of polymer film is represented in Fig 2.2. The DC glow discharge air plasma unit used in the treatment is shown in the Fig 2.3.

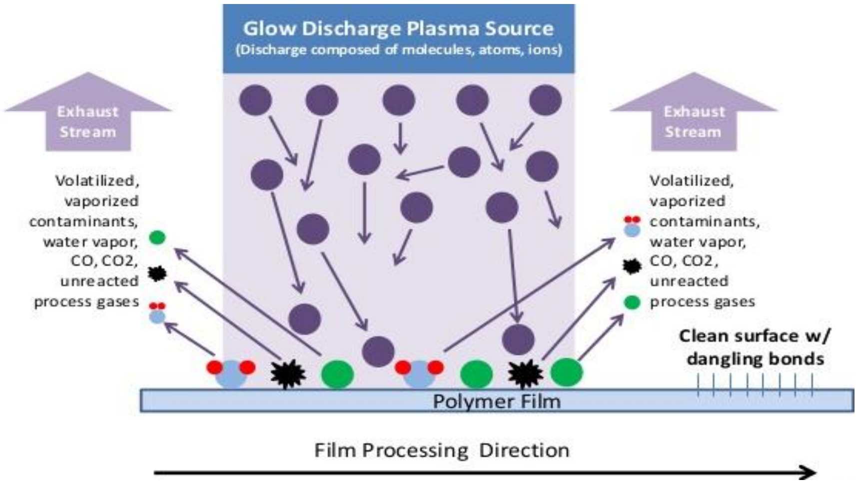

Fig: 2.2 Schematic representation of the process during plasma treatment.

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.

Fig: 2.3 Experimental set up for plasma treatment.

The PMMA films (of same thickness = 0.12mm) were kept under DC plasma in between two electrodes inside the plasma glass tube at constant input power (20W) and constant working pressure (5 X 10^{-2} mBar) for different time intervals. The gas in the chamber was air as no specific gases were supplied to the chamber through the feed through. Details of the samples thus obtained after DC glow discharge air plasma treatment for varying time of 2.5, 5 and 7.5 minutes were given in the Table: 1

Table 2.1 Detail of the samples obtained after synthesis and plasma treatment

Serial No.	Sample Name	Plasma Treatment Details
1	$\mathbf{S_0}$	Untreated PMMA film
2	$\mathbf{S_1}$	Plasma treated for 2.5 min
3	$\mathbf{S_2}$	Plasma treated for 5 min
4	$\mathbf{S_3}$	Plasma treated for 7.5 min

2.3 Characterization techniques used

2.3.1 FTIR (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. For chemical analysis IR instrumentation was discovered to be the first analytical technique and has been used since fifty years.

The design of FTIR is similar to conventional Michelson interferometer as shown in Fig 2.4.It consists of a beam splitter, a pair of mirrors ,a detector and a source .The beam splitter used is a semi-transparent material to IR and a thin layer of germanium is sandwiched in between KBr. The moving mirror (as shown in Fig 2.4) introduces a path difference between beams which gives rise to interferogram (plot of interference intensity as a function of optical path difference). The source gets radiated by inter-ferrogram. Then the detector (digital computer) receives interferogram signal converts it into IR spectrum (plot between wave number and intensity). The most attractive feature about it is that even gas samples can be characterized but special cells are required to contain them.

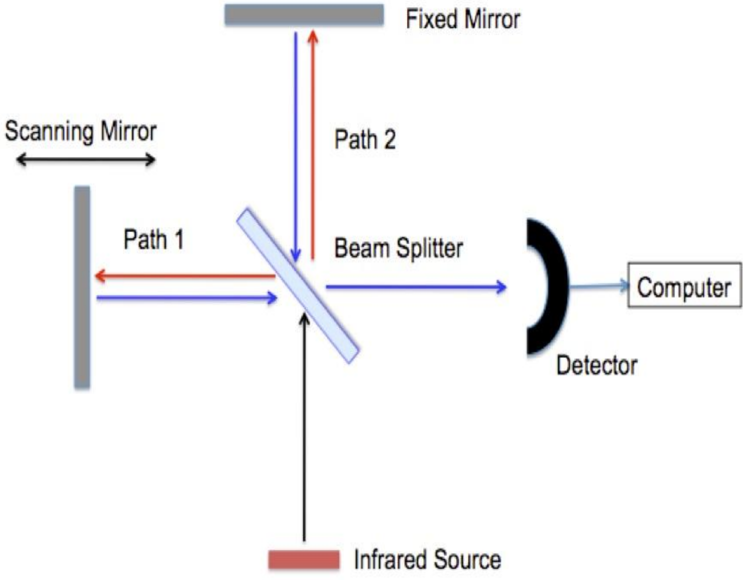

Fig: 2.4 Schematic of FTIR spectroscopy

Commercial FTIR was invented during 1970 as an advanced IR Spectroscopy in terms of capability and performance. FTIR is technique to detect the chemical bonds present in the sample by the spectrum produced on the absorption of IR radiation. It is considered as fingerprint of molecules. It has some advantages over dispersive IR spectroscopy. In IR Spectroscopy a spectrum is created by the collection of signals of IR at each wave number separately where as in FTIR spectrum over the whole range of wave number is generated simultaneously. Even signal to noise ratio is very less in comparison to IR.

Here, in the present study the FTIR spectra were recorded at room temperature using the Nicolet 1S5 Mid Infrared FTIR spectrophotometer (Fig. 2.5).

Fig: 2.5 Nicolet 1S5 Mid Infrared FTIR spectrophotometer used for analyzing the films

The samples analysed must not be more than 20micrometre and should not be less than 1micron. Because the excess thick samples can absorb more IR radiation and transmittance cannot be calculated. Similarly, for excess thin samples absorption is too weak to be determined. There are different sampling methods for different samples. Powder samples are mixed with mulling agent and liquid samples are sandwiched in between KBr for characterization process.

2.3.2 UV-Vis spectroscopy

Ultraviolet and visible (UV-Vis) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. The UV-Vis spectral range is approximately 190 to 900 nm. This spectroscopy is useful in characterizing the absorption, transmission, and reflectivity. The interaction of electromagnetic radiation with molecules is observed by UV-Vis spectroscopy. In this present work, the films were exposed to UV and the optical properties such as reflectance, absorbance and transmittance were studied by using UV-2600- Shimadzu (Fig 2.6) in the range (200-900) nm.

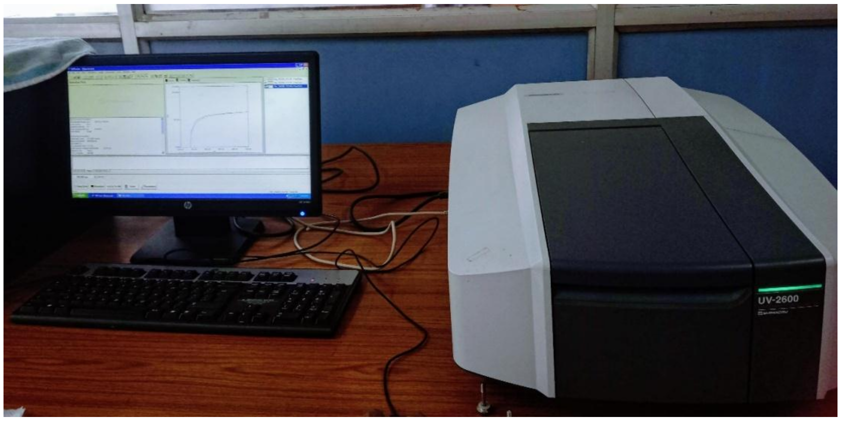

Fig: 2.6 UV/Vis spectrometer (UV-2600- Shimadzu)

When a molecule absorbs UV-Visible radiation generates transitions between electronic energy levels for which UV-Vis spectroscopy is also called electronic spectroscopy. These transitions can be helpful to determine the binding energy of the electron undergoing transition. It follows Beer–Lambert's law to determine the intensity of the absorbed light i.e.

$$\mathbf{I} = \mathbf{I_0 e^{-\alpha t}}$$

where, I=intensity of absorbed light, α=absorption coefficient, t=thickness of sample and I_0=intensity of incident light.

Absorbance can be calculated by taking the negative logarithm of the ratio of intensity of transmitted light and intensity of incident light. The observable parameters are transmittance, absorbance and reflectance The UV-Vis spectrum is the variation of absorbance with the increasing wavelength. From the spectrum the optical band gap can be calculated by the following Tauc plot method.

Tauc plot method:

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; n =1/2 direct and n=2 indirect A =absorbance and E_g= band gap)

The absorption coefficient α is calculated from the formula:

` $\alpha = \frac{2.303A}{t}$ (t= thickness of the sample used)

The thickness of the film is measured by using digital slide calipers to calculate absorption coefficient. Then graph was plotted in between $(\alpha h\nu)^{1/2}$ and (hν) for indirect band gap and $(\alpha h\nu)^2$ 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.

2.3.3 SEM (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.

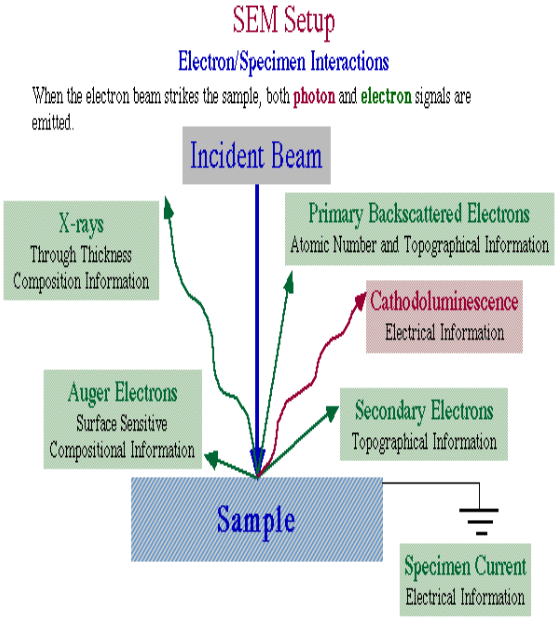

Fig: 2.7 Electron – Specimen interaction

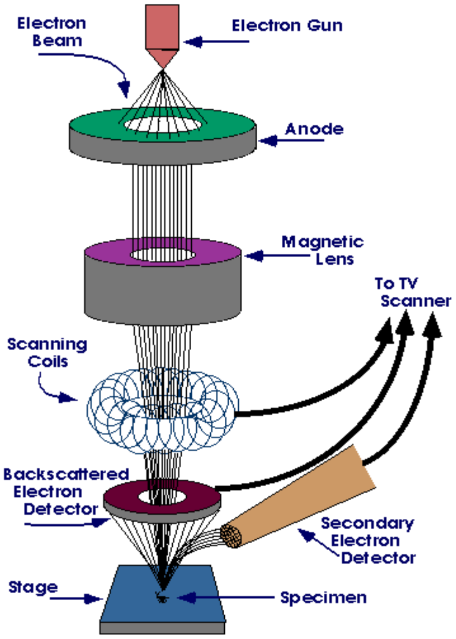

Fig: 2.8 Schematic of working of SEM

In most application, data are collected over selected area of surface up sample and a 2-dimensional image is generated that display spatial variations in these properties. The detail of the electron sample (specimen) interaction is shown in the Fig. 2.7 and the schematic of the working of the SEM instrument is given in Fig. 2.8.

Areas ranging from appr.1cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 2X to 30,000X spatial resolution of 50 to 100 nm). The instrument used for taking the micrographs of the samples is shown in the Fig. 2.8.

Fig: 2.9 SEM (Perkin Elmer spectrum two with UATR)

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).

CHAPTER-3

RESULTS AND DISCUSSION

In this chapter, the results obtained from various characterization techniques after successive synthesis of one untreated and three plasma treated PMMA films at varying time (specification given in table 2.1) is discussed. At first the surface structure and molecular vibrations of the composite films are discussed through FTIR techniques. The optical properties are then analyzed by recorded UV-Vis spectra followed by the band gaps calculated from the UV-Vis transmission spectra. Finally, the surface morphologies of the sample surfaces are investigated through SEM micrographs.

3.1 Surface structure analysis by FTIR

The FTIR spectra plotted in Fig 3.1 shows peak of both untreated and DC glow discharge plasma treated (at different times) PMMA films. Spectra reported in this work were taken with a spectrophotometer in the wave number region between 500 and 2000 cm^{-1}.

From the graph it is clear that the pattern of untreated and plasma treated films at different time exhibit similar FTIR characteristic bands. The multiple peaks between 1500 - 1400 cm^{-1} are interpreted as CH_3 and CH_2 deformation vibration. The highest intensity observed at 1724.13 cm^{-1} corresponding to stretching vibrations C=O and other at 1200-1100 cm^{-1} corresponds to stretching vibration C-O [11]. 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.

The highest intensity characteristic for C=O and C-O stretching vibration decreases with increasing the treatment time in the order of 2.5 min, 5 min, 7.5 min and shown in the in set of the Fig 3.1 . This noticeable change in various bands were due to the decrease in number of bonds as a result of interaction of electrons, ions and radicals etc., present in the plasma medium with

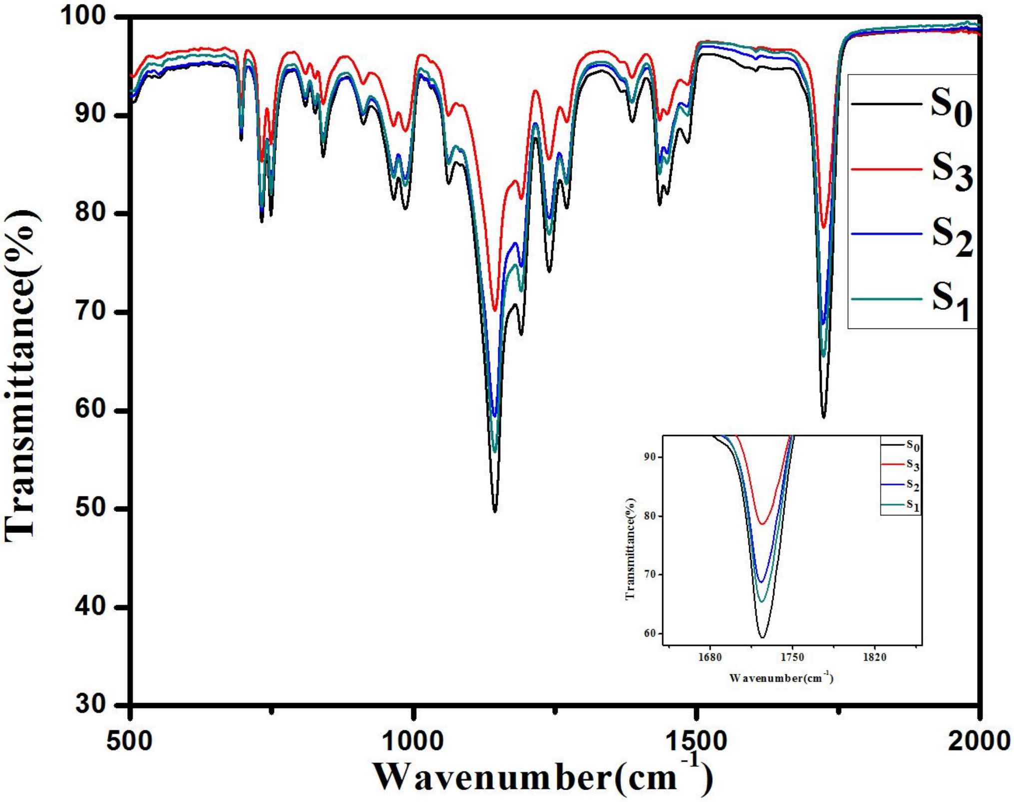

Fig: 3.1 FTIR of untreated and plasma treated PMMA samples. The in set shows variation of intensities with treatment time

film surfaces [4]. 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 [17].

3.2 Optical properties analysis by UV-Visible spectroscopy

The percentage of transmittance against wavelength of the untreated and plasma treated films at different exposure time were recorded in the wavelength range of 200–800 nm and shown in the Fig. 3.2. The figure depicts that the transmittance percentage increases for smaller treatment time of 2.5 min and then decreases for higher treatment times of 5 and 7.5 respectively. In pure PMMA electrons are strongly linked to their atoms through covalent bonds and there are no free electrons and the breaking of electron linkage and moving to the conduction band need photon with high energy [18]. This may be the reason for high transmittance of pure PMMA. The plasma treated sample showed lower transmittance for 5 and 7.5 min where interactions of energetic electrons, ions and other radicals present in the plasma with the surface bonding of PMMA films may add free electrons or help to generate free electrons at the surface thus, transporting to higher energy levels. On the other hand smaller treatment time may reduce the surface impurities, adsorbed hydroxyl groups, thus slight increase in transmittance percentage for this film.

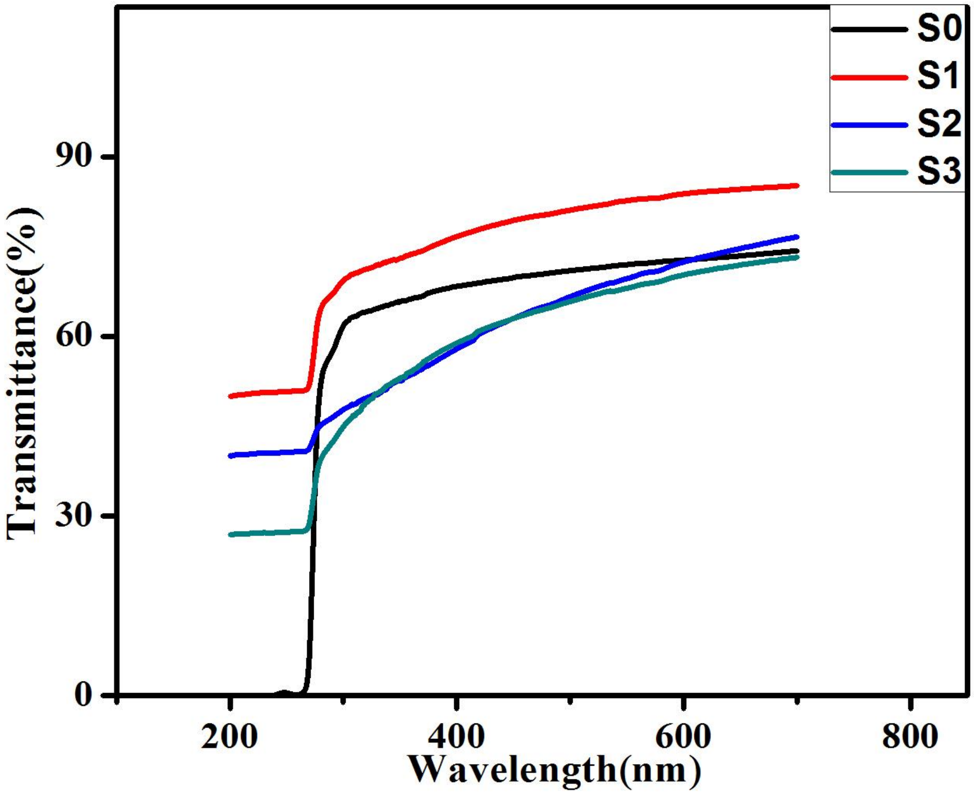

Fig: 3.2 UV-Vis transmittance spectra of untreated and plasma treated films of varied treatment time.

The Tauc plot method can be used for the investigation of the optically induced transitions and can provide information about type of band gap transition in in crystalline and noncrystalline materials. The direct and indirect optical band gaps of the samples are determined from the transmission spectra using Tauc plot and shown in the Fig. 3.3 (a) and (b), respectively. The in set in both the figures depicts the extrapolation of linear region of the graph to the energy axis (X-axis) and the values thus obtained are shown in the table 3.

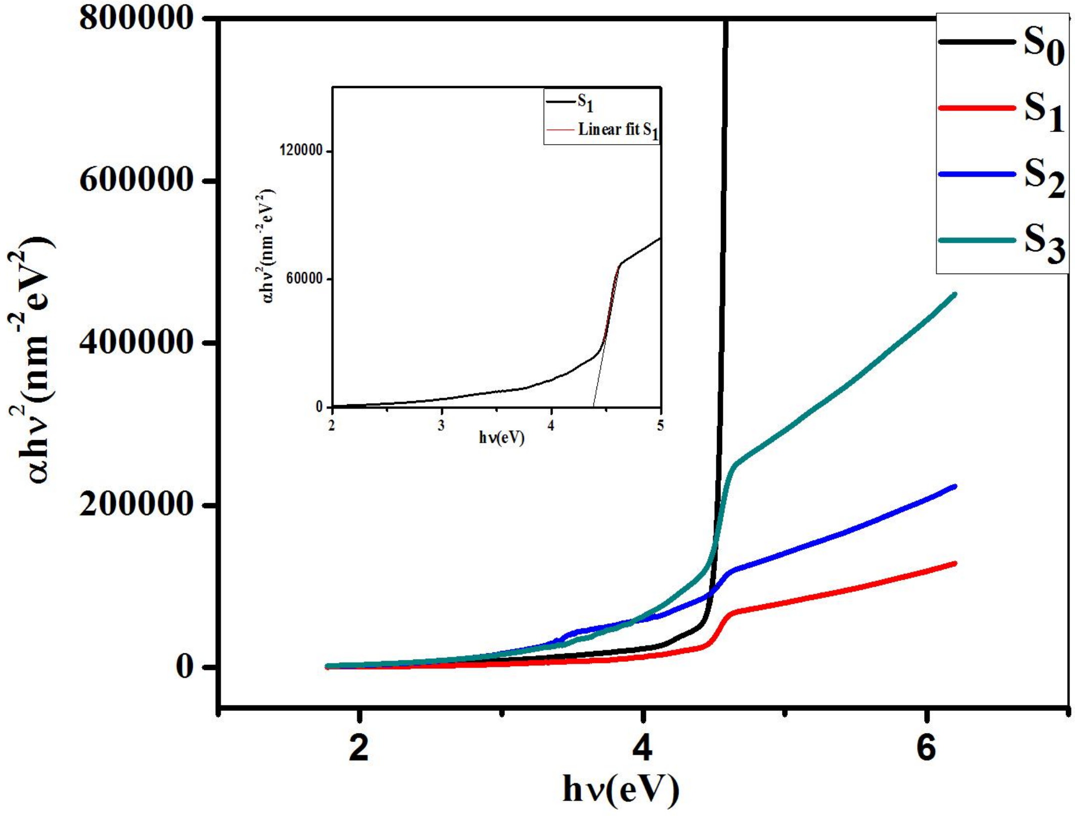

Fig: 3.3 Direct optical band gap of untreated and plasma treated PMMA samples. The inset shows the typical linear fitting.

Table 3.1 shows decrease in band gap after plasma irradiation of 2.5 and 5 min. But minute increase in the band gap was observed for the sample irradiated for 7.5 min. Same types of result has been reported by other researchers [10].

Table 3.1 Values of direct and indirect band gaps

PMMA Samples	Direct band gap (eV)	Indirect band gap (eV)
Untreated	4.570	4.395
2.5 min	4.389	4.145
5 min	4.099	3.352
7.5 min	4.297	3.906

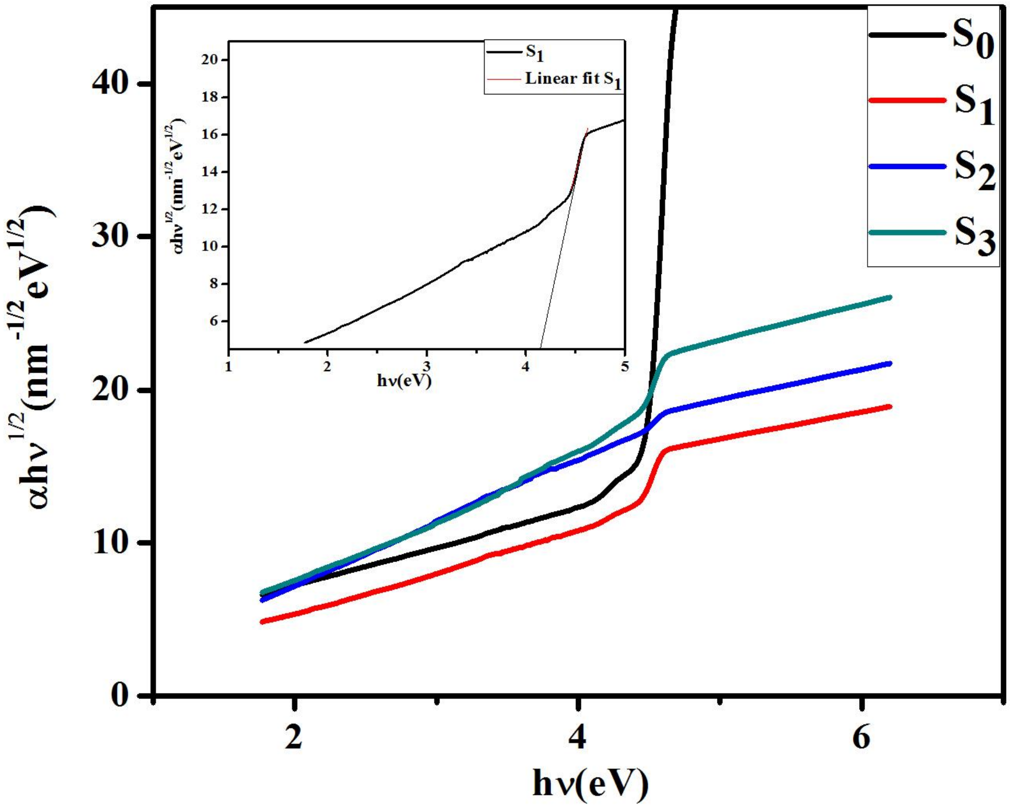

Fig: 3.4 Indirect optical band gap of untreated and plasma treated PMMA samples. The inset shows the typical linear fitting.

Decrease in band gap may be due to the increase in amorphousness in the sample as a result of plasma treatment which generally causes reduction in crystallinity [19]. This may be confirmed by taking the XRD pattern.

3.3 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 (for different times) surfaces were imaged with SEM and the results are shown in Fig. 3.4. The micrographs were taken with same magnification of 30 µm for all the samples. Fig. 3.4 shows the SEM micrographs of (a) untreated film (b) plasma treated film for 2.5 min (c) plasma treated film for 7.5 min.

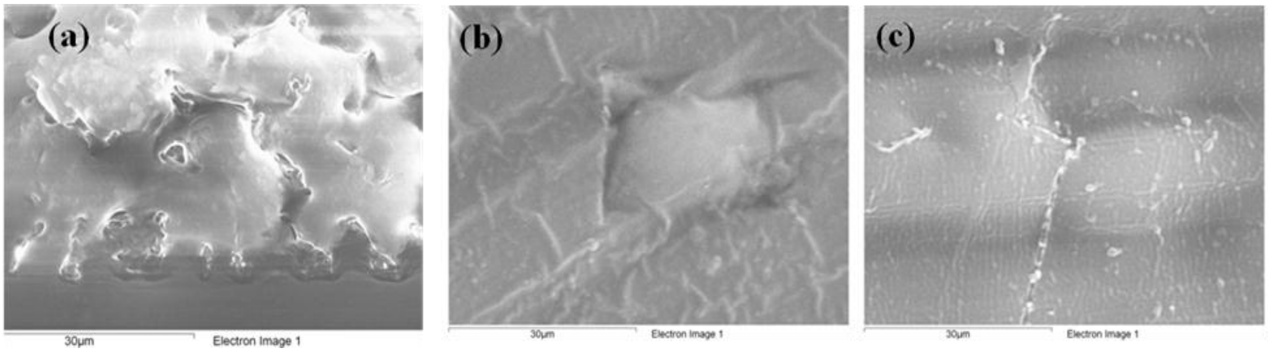

Fig. 3.5 Typical SEM micrographs of (a) untreated film (b) plasma treated film for 2.5 min (c) plasma treated film for 7.5 min.

The relatively uniform surface of untreated sample becomes rough (making deep cleavage) after more time of plasma treatment Fig. 3.3 (c). However, for smaller time treatment did not alter the surface much. This supports the UV-Vis transmittance result. As the smoothness decreases (or roughness increases) the transmittance decreases. 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.

CHAPTER-4

CONCLUSION AND FUTURE SCOPE

In this work PMMA films are prepared by solution casting method which are then treated at different time interval in DC glow discharge (air) plasma and are characterized using various techniques as FTIR, UV-Vis, and SEM. FTIR analysis reveals that no new peaks or peak shifts are observed in the spectra of PMMA after plasma treatment. While the characteristic intensity decreases with increasing the plasma treatment time. This is due to the decrease in the no. of bonds as a result of interaction of plasma electrons with the surface of PMMA. During UV-Vis analysis, we observed that there is an increase in transmittance percentage during shorter duration (2.5 min) treatment but it decreases during longer duration (5min, 7.5min) treatment. This is due to the interaction of electrons, ions, & radicals present in plasma with the surface of PMMA film. During shorter time interval there is not much greater interaction on the surface and there is reduction of hydroxyl groups, which increases transmittance. While in longer duration the interaction between electrons, ions, radicals and UV radiation present in plasma and PMMA film surface increases. Due to increase in concentration of electrons on surface of PMMA transmittance decreases. Subsequently absorbance increases. While the SEM micrograph shows that there is a gradual reduction of smoothness of surface on increasing the time of plasma treatment. Cleavage formation occurs on the surface and becomes more pronounced on increasing the treatment time. Thus transmittance of the sample decreases gradually confirming the UV-Vis results.

The future scope for the plasma treatment of PMMA films is that they can be used for optical applications and also in the field of biomedicine and airplane industries due to their improved surface structural and optical properties.

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