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Synthesis and Characterization of Plasma Treated TiO_2 Nano Composites Polymer Membranes

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Nano particles of TiO_2 are synthesized by chemical root and were used for nano composites polymer membranes. The absorption peak at 411 nm and TEM image of TiO_2 nanoparticles confirms spherical shape with particle size ranging from 8–15 nm. TiO_2 Nanocomposite membranes of polymethyl methacrylate (PMMA) were prepared by solution cast method. The low energy nitrogen plasma was achieved by DC glow discharge method and was used to expose these nanocomposite membranes. These membranes were characterized by different techniques such as Optical Microscopy, SEM-Scanning electron microscope, Raman spectroscopy. Response of electrical resistance at different frequencies is also recorded for the membranes before and after plasma treatment and found ≈ 30 times increase in electrical resistance after plasma treatment at low frequencies.

Keywords: PMMA Composite Membrane, N_2 Plasma Treatment, Raman Spectroscopy, SEM.

RESEARCH ARTICLE

1. INTRODUCTION

Polymers have become very important materials in modern manufacturing processes and offer wide varieties of chemical, mechanical and elastic properties, lightweight, flexibility and good processability applicable in numerous applications like electro-optical properties,[1] gas filtration,[2] bactericidal properties,[3] chemical,[4] electrical,[5] optical,[5] biological,[6] and mechanical applications[7] etc. PMMA is an interesting polymer for mechanical and optical applications due to its easy possibility and high transparency in the visible range. PMMA also has immobilization of activated sludge.

Nanocomposites in principle can be formed from clays and organoclays in a number of ways including various in situ polymerization,[8] solution and latex[9] methods. A number of experimental investigations on these materials have indicate that the polymer nanocomposites exhibit new and sometimes improved properties that are not displayed by the individual phases or by their conventional composite counterparts. Even a small addition of nano-particles has the potential to drastically transform the properties of the host polymer.[10]

Polymer nanocomposites have many diverse applications like flame resistance,[1] layer-by-layer self-assembled polymer films,[4] electrical/electronic properties,[5] composite reinforcement,[11] barrier properties,[12] dye-sensitized solar cells,[12] gas sensor,[2] nanomedicine,[13] cosmetic applications,[14] flammability resistance,[15] polymer blend compatibilization,[15] bound catalysts,[15] miniemulsion particles,[15] fuel cell electrode polymer,[16] polymer blends,[17] barrier properties.[18] Polymer nanocomposites represent a new alternative to conventionally filled polymers. As due to presence of nanoparticles, filler dispersion nanocomposites exhibit markedly improved properties, compared to the pure polymers or their traditional composites.[19]

Recent literature shows there are a lot of reports for TiO_2 because it has many interesting properties and gained great interests to scientists and researchers around the world because of the unique properties. TiO_2 can be simply used as the filler for coatings on plastics and rubbers resultant improved performance in UV-shielding, dynamic fracture toughness, flame retardant, optical transparency,[1] photo catalysis,[11] scratch resistance,[19] chemical resistance,[19] photo-electrochemical activity,[20] solar energy conversion,[21] mycobacterium activity,[22] UV detectors and ultrasonic sensors.[23] Environmental compatibility, non-toxicity, long-term stability, resistance to discoloration under UV light and low price are some typical advantages of TiO_2. It also has strong negative effect on the thermal stability of PVDF/PMMA because of its catalytic decomposition character. Hence TiO_2 has received most attention as nano composite for polymer because of these excellent properties.

PMMA nanocomposites with high refractive index can be made by incorporating the TiO_2 colloids into PMMA, with improve optical and electrical properties.[20] Solar cells based on nanocomposites of PMMA with TiO_2 showed

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some excellent photovoltaic cell efficiency.[21] PMMA-TiO_2 composites are also used as additives,[18] ultra fast optical nonlinearity measurements,[18] optical waveguide,[18] photovoltaic application,[19] semiconductor materials and for biomedical applications,[19] digestion breathing through lungs and grills,[30] discharge of sweat from skin,[24] urine in kidneys,[24] blood purification[24] environment protection and preservation[25] and to form a protective pigment kind of film to get opaque films.[26] Nonlinear optical properties such as fast response time and large third order nonlinearity ($x3$) of these materials are essential for several current and future optical device applications in optical computing, real time holography, optical correlators and phase conjugators. But these studies were mostly concerned with the measurement of the linear optical refractive index, nonlinear optical properties of nanohybrid thin films, biomedical applications of TiO_2 in PMMA.

Recently PMMA TiO_2 nanocomposites are receiving grate interest for synthesis of electrochemical sensors, electrochemical catalyst electrodes, ion-exchange membranes, microporous membranes, catalyst support coating of electrochemical sensors and modulation of redox condition of reactions with many other electrochemical applications. But to use these membranes in various electrochemical applications they required high permselective, semipermeable, surface functionalization and activation of polymer surface. Plasma treatment is a useful tool for modification of surface properties and can provide these required properties to the membranes.[27–32] Plasma surface treatment usually refers to a plasma reaction that either results in modification of the molecular structure of the surface, or atomic substitution.[32] As Kohma et al. has used plasma treated nanocomposite electrode for amperometric glucose sensor having high substrate selectivity without any permselective membrane.[33] Barge et al. has synthesized semipermeable membrane that can generate voltages and facilitate oxidation/reduction reactions on polymer surface by plasma treatment.[34] Lee et al. provides catalyst supports and surface functional group concentration to polymers by plasma treatment.[35] Fundamental studies of diffusionally restricted reactions, low sample volume analysis and cell membrane interactions for plasma treated membranes have deeply investigated by Wittenberg et al.[36] Low/high temperature plasma treated nanocomposite membranes were synthesized for polymer electrolyte fuel cell (PEFC) applications,[37] electro-analysis, electro-synthesis, and electrochemical-based energy storage devices,[38] semipermeable membranes, ultrastructure of bio-membranes, bio-membranes pertaining to Electrochemistry.[39] Still surface, chemical modification and modulation of electrochemical properties have not been yet fully explored for PMMA TiO_2 nanocomposites membranes.

In this paper, we have synthesized TiO_2 nano particle by chemical root and prepared 2% TiO_2 nano composite PMMA membrane by solution casting method.[19] These membranes are subjected to surface modification by treatment of glow discharge plasma. These membranes are characterized by Raman spectroscopy, optical microscopy and SEM to investigate the effect of plasma treatment on surface and chemical modification of nanocomposite membrane. Modulation of electrochemical properties was determined by measuring the response of electrical resistance at different frequencies for these membranes before and after plasma treatment.

2. EXPERIMENTAL DETAILS

Poly methyl methacrylate (PMMA) granules were used to prepare flat sheet membranes of 20 μm thick by solution cast method. They were obtained as commercial grade from Loxim Polymers, Jaipur-India. Dichloromethane of extra pure grade was used as a solvent for preparing polymer solution.

2.1. Synthesis of TiO_2 Nanoparticles

Synthesis of TiO_2 nanoparticles was carried out at room temperature using a simple chemical precipitation route as described by Borse and Kankate.[40]

2.2. Preparation of Membranes

Solvent casting method is one of the easiest and least time consuming methods for the preparation of polymer nanocomposites,[19] hence solution-casting method was used for preparation of membranes. Poly methyl methacrylate (PMMA) granules are weighed and dissolved in dichloromethane (CH_2Cl_2). This solution was stirred by magnetic stirrer to ensure the uniform dissolution and to enhance rate of dissolution. The process is carried out at room temperature for around 3 hours till a clear solution is formed then pour in flat-bottomed Petri-dishes floating on mercury to obtained uniform thickness membranes. The solvent was allowed to evaporate slowly over a period of 10–12 h. 2% TiO_2 nanocomposite. Poly methyl methacrylate (PMMA) membranes were also prepared by solution casting method. Poly methyl methacrylate (PMMA) solution was prepared in the same way as mentioned above for pristine membranes. TiO_2 nanoparticles were dispersed in the solvent dichloromethane using ultrasonicator. This dispersed solution was then added to the Poly methyl methacrylate (PMMA) solution and stirred for around 30 minutes then pour into flat-bottomed petri-dishes floating on mercury to obtained uniform thickness membranes. The solvent was allowed to evaporate slowly over a period of 10–12 hours. The films so obtained were peeled off using forceps.

2.3. Nitrogen Ion Plasma Irradiation

Plasma treatment consists of a source chamber with the complete power supply and connected to a vacuum system. The magnet is positioned to get a magnetic field inside the source chamber. Initially the chamber is evacuated to a base pressure of 10^{-10} torr and working pressure is maintained at 10^{-7} torr by admitting the N_2 gas. The N_2 gas used for generating plasma is admitted into source chamber using a flow controller and plasma is generated by applying high voltage DC power between two electrodes with magnetic field generates the DC glow discharge. The gas is then energized by DC power; the current in the upper and lower electrodes is maintained at few 2 mA and 1.5 KeV and gap between two electrode is maintained at 5 cm, hence 20 watt/cm^2 power is generated between two electrodes, this power is used to generate N^+ ions, as only 8.8 eV energy is required for dissociation of N_2 gas into N atoms and then conversion into N^+ ions by ionization of N atom, rest energy/power is used to accelerate ions between electrodes, these accelerated N^+ ion are used for plasma processing of nanocomposite polymer membrane. This glow discharge plasma is quite homogenous and magnetically confined at low-pressure was used for surface modification. The other energetic species like radicals, electrons and meta-stable photons in short-wave UV range can also present with nitrogen ions in this plasma.

2.4. UV Vis Spectroscopy

UV-Visible spectral analysis was done using a double beam UV-Vis spectrophotometer (Shimadzu 2100).

2.5. Transmission Electron Microscopy (TEM)

The particle size and morphology of TiO_2 NPs is determined by transmission electron microscopy (TEM). The imaging is performed using a Technika TEM instrument operating at 200 kV.

2.6. Raman Spectroscopy

Raman spectra are obtained by Nicolet Megna single beam green light raman spectrometer at University of Rajasthan, Jaipur. Raman spectrometer is used to gather information about the structure/chemical bonding of a compound and as an analytical tool to measure the purity of the compound. The 600 nm line of a laser source He—Ne with wavelength 633 nm served as excitation source. By using 100× objective lens of the microscope, the excitation volume was limited to a sphere of ~ 1 mm in diameter. Spectral resolution of the order of 1 cm^{-1} was used to analyze the structural/chemical changes of polymer surface.

2.7. Optical Microscopy and SEM

Optical microscope is fundamental tool for investigate surface structures. This gives a high resolution view for seeing object of higher dimension; here the surface modified by plasma treatment is primarily investigated by optical microscope to see the effect and level of plasma modification. LABOMED optical microscope is used for the imaging and micrographs (at 100× magnifications) are stored in computer through CCD camera which is attached to the computer with standard software (Pixel View). SEM analysis was done using scanning electron microscope (Carl ZEISS EVO^R-18) operated at 20 kV.

3. RESULTS AND DISCUSSION

The plasma is homogenous at a low-pressure glow discharge. Use of glow-discharge plasma technique is particularly useful for functionalization of surfaces as it is possible to modify outermost surface layer by this technique. The accelerated ion from the N_2 plasma has sufficient energy to induce cleavage of the chemical bonds in the membrane structure and to form macromolecule radicals, which subsequently initiate graft copolymerization (Fig. 1). For polymer surfaces, it has been recognized as a valuable tool to improve their adhesion properties. Additionally, weak boundary layers and surface contaminants are also removed during modification. These factors improve the adhesion properties of the surface.[10] Plasma treatment of polymer surface causes not only a modification during the plasma exposure, but also leaves active sites on the surfaces which are subjected to post-reaction.[30] Scheme in Figure 1 shows modification in surface properties of polymer materials by low pressure plasma treatment like formation of macromolecule radicals, increase in chemical reactivity, formation of sputtered particles and creation of active sites followed by graft copolymerization. Over the last few decades, polymers have been used successfully in many industrial applications, including adhesion, packaging, thin films, biomaterials, and coatings.[41] These plasma treated membranes has also vide range of application in modification of polymer nanocompsoite like in RO applications,[41] Hydrophilicity/hydrophobicity increases,[42] Surface charge decreases,[42] Higher flux,[43] Increased chlorine resistance.[43]

The UV-Visible absorption spectrum exhibited the characteristic surface plasmon resonance (SPR) peak of TiO_2 nanoparticles centered at 411 nm as shown in Figure 2, indicating reduction of $TiCl_3$ by NH_4OH and formation of TiO_2 nanoparticles. We suppose the size of nanoparticles are less than 15 nm as Liu et al. had reported similar study on nanoparticles synthesis and found nanoparticles of size 4–5 nm order for absorption peak at 412 nm.[44] Kandori et al. has reported the band gap of synthesized nanoparticle for 4.2 nm size having absorption peak 412 nm and found it as $E_g = 3.15$ eV while for bulk it is 3.0 eV. This yields a blue shift for the rutile nanoparticles of about 0.15 eV.[45]

The TiO_2 NPs are vacuum dried and re-dispersed in acetone by ultra-sonication, to ensure that there is no HCl present in the samples. Figure 3 shows TEM image of TiO_2 NPs synthesized having spherical shape and particle size ranging from 8–15 nm. Individual particles in TEM images can be identified easily this shows no aggregations of TiO_2 NPs particles.

Raman spectra of the pristine and 2% doped (untreated and plasma treated) membranes are as shown in the

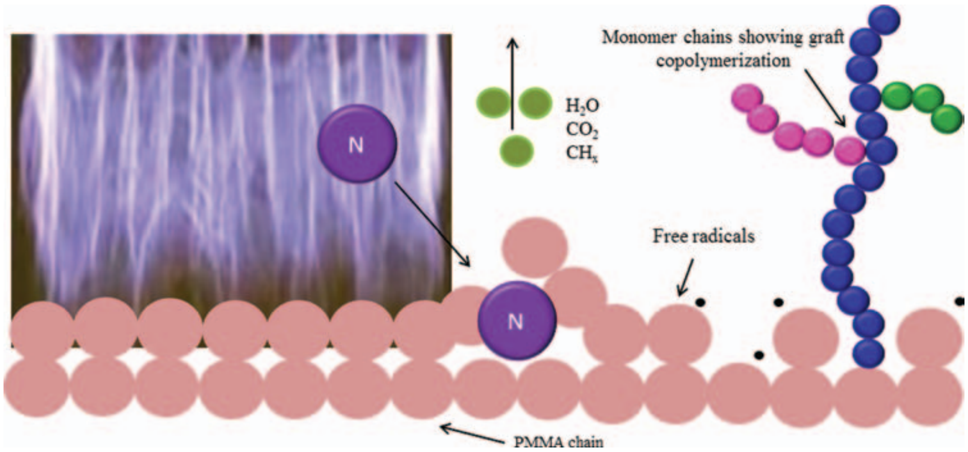

Fig. 1. Representation of types of modification on surface of polymer materials that can be induced by low pressure plasma treatment.

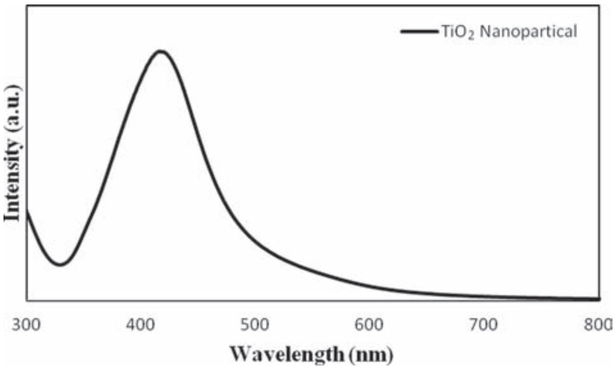

Fig. 2. UV Vis spectra of synthesized nanoparticles.

Figure 4. Compression of Raman spectra for these nanocomposite membranes give the clear picture of TiO_2 mixing and plasma treatment for these membranes, between 250–1225 cm^{-1} characteristic peak for PMMA appears at 450 cm^{-1} for O—H bonding, 670–710 cm^{-1} for C—O and C—H bonding, 978 cm^{-1} for C═O bonding.[46] TiO_2 mixing can be confirmed by characteristic peak[47, 48] of TiO_2 in PMMA at 1650 cm^{-1}, which is present only in nanocomposite membrans. Raman peak coming at 2165 cm^{-1} in both the plasma treated samples is due to saturation of unsaturated C═O bond present in PMMA and formation of C—N[49] bond after plasma treatment on the membrane surface. These characteristic peak indices change in chemical bonding and structure on the surface of the samples due to plasma treatment. Also the same characteristic peaks in the Raman spectra of plasma treated and untreated samples show that there is no change in the basic structure of the membrane bulk material. Similarly Jones et al. found increase in the surface concentration of chemical groups (C—N, C—OH and hydroxyl) and selective introduction of nitrogen-containing functionalities to polymer membranes by plasma treatment.[50]

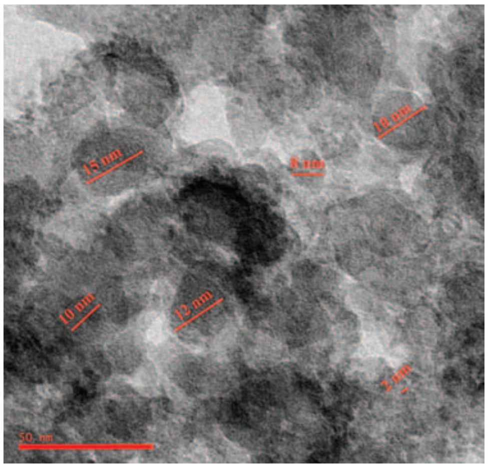

Fig. 3. Transmission electron micrographs (TEM) of TiO_2 NPs synthesized, having spherical shape and particle size ranging from 8–15 nm.

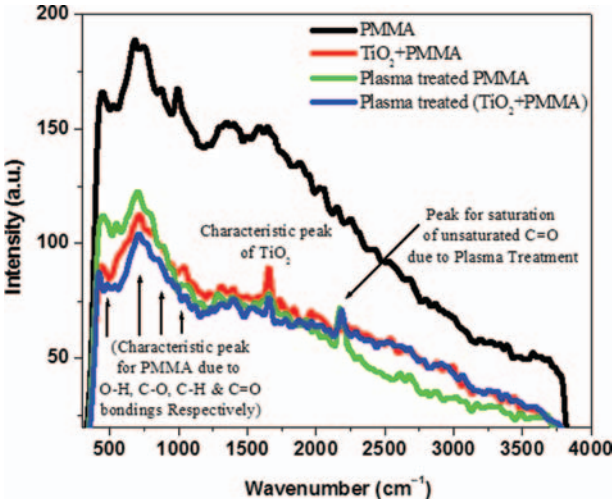

Fig. 4. Raman spectra of pristine and TiO_2 doped membranes both plasma treated and untreated.

The effect of plasma treatment/modification on the surface of membrane is primarily investigated by optical

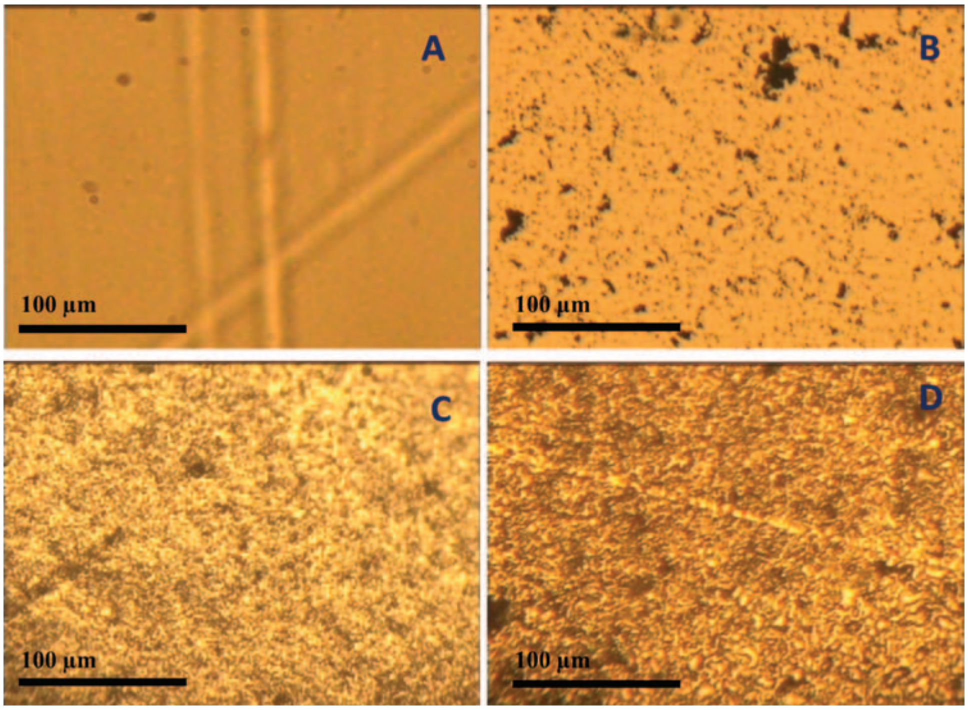

Fig. 5. Optical microscope images of (A) pristine PMMA (B) plasma treated PMMA, (C) 2% TiO_2 doped membrane (D) Plasma Treated 2% TiO_2 Membrane.

microscope at higher dimension (100× magnifications) as shown in Figure 5. It shows the surface morphology of pristine and TiO_2 nanocomposites membrane before and after plasma treatment.

It is clear from Figure 5 that surface becomes rough after plasma treatment of N_2 plasma at chosen conditions. A SEM image shown in Figure 6 also supports the previous conclusion drawn from microscopic images.

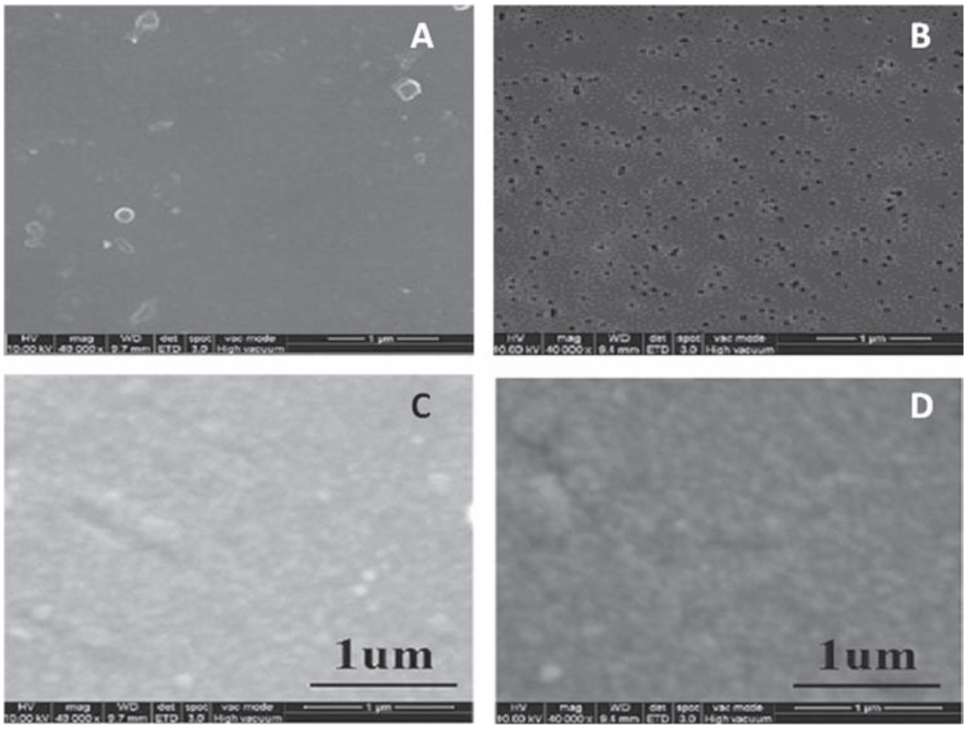

Fig. 6. SEM images of pristine and TiO_2 doped membranes both plasma treated and untreated.

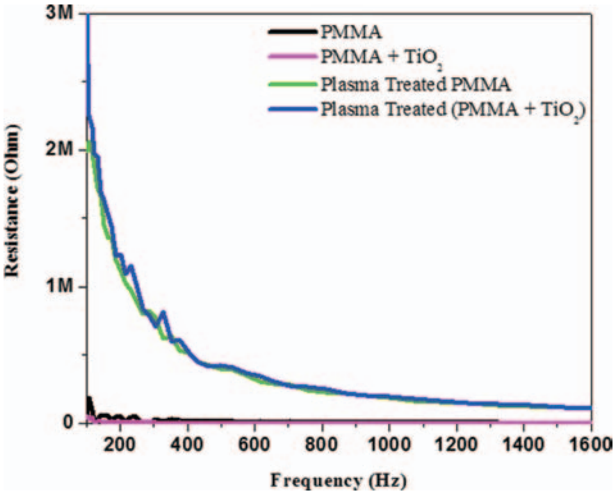

Fig. 7. Response of electrical resistance with frequencies for the TiO_2 nanocomposite PMMA membranes before and after plasma treatment.

This study and characterization shows that N_2 plasma increase roughness of polymer nanocomposite as well as create C—N bonding onto the membranes surface without affecting the bulk properties of polymers this shows increase in surface energy, activation and adhesion and functionalized nanocomposite polymer surface with nitrogen. Similar results were obtained when Timothy et al. grafted Vinyl-benzyl chloride onto PVDF polymer films for using such membranes in low temperature direct methanol fuel cells but PVDF based materials easily underwent an undesirable degradation, they have enhanced the performance of PVDF by plasma induced radiation-grafting methodology, it prevent degradation of films with good retention of ionexchange capacities.[37] Such as adhesion of diamond films was found increased on plasma modified GC surface films for synthesis of electrochemical sensors.[38]

Excellent corrosion resistance, semi-permeability and activated functionalized surface of plasma treated TiO_2 + PMMA nanocomposite membranes makes them suitable for synthesis of electrochemical sensors, electrodes for electrochemical catalization and other electrochemical applications. Hence we have recorded the response of electrical resistance with different frequencies before and after plasma treatment for nanocomposite membranes. Firstly a peace (2 cm × 2 cm) of each membrane was taken, than a circular thin film of aluminum of the order of 20 nm thickness and 1 cm diameter were deposited using thermal evaporation method on both side of each taken peace to act as a capacitor.[18] Measurement for electrical resistance with different frequencies was done using LCR meter at the step size of 5 Hz. Figure 7 shows behavior of electrical resistance with frequencies for the TiO_2 nanocomposite PMMA membranes before and after plasma treatment. Twenty five time increase in electrical resistance was found at low frequencies (100–400 Hz) for pristine membranes, while it was more than 30 times for nanocomposite membranes makes them suitable for synthesis of low frequencies electrodes for electrochemical catalization.

4. CONCLUSION

Nanoparticles of TiO_2 having spherical shape and particle size ranging from 8–15 nm are synthesized using chemical method. Pristine Poly methyl methacrylate (PMMA) membranes and its composite with TiO_2 nanoparticles are prepared by solution cast method. These membranes are exposed with N_2 plasma for improving the surface properties and activation. An increase in surface roughness, hydrophobicity, adhesion and functionalization has been observed after plasma treatment. This technique will help us to prepare nanocomposite membranes with desired surface properties for selective filtration and antibacterial applications. To use these membranes for synthesis of electrodes for electrochemical catalization, response of electrical resistance with different frequencies are determined and ≈30 times increase in electrical resistance after plasma treatment was found at low frequencies. Further development in this direction will be use of different nanoparticles of various sizes for nanocomposite membranes and systemic study after plasma treatment of N_2 and Ar.

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