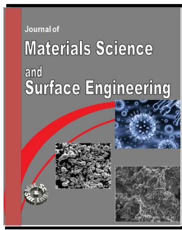

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Reactive Polymer Surfaces for Cell Colonization

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Abstract

Nano particles of TiO_2 are synthesized by chemicals and used as nano composites polymer membranes. Solution casting was used for preparation of nano composite polymeric membranes in the range of 20 micron and irradiated by air plasma. These membranes were characterized by technique such as optical microscopy, scanning electron microscope, Raman spectroscopy. Plasma irradiation modifies surface roughness, surface energy and surface reactivity of polymers; that helps to enhances bacterial cell colonization on nano composite polymer membranes.

Introduction

Polymers are receiving great interest in modern manufacturing processes and offer wide varieties of chemical and mechanical properties applicable in numerous applications[1-3]. It is well known that permanent bonding, coating, printing, etc. are difficult on many polymers without surface pre-treatment[4]. Therefore, after surface treatment of polymers these have significant benefits in the specific requirements of surface properties while retaining bulk mechanical properties. The physical and chemical surface modifications of polymeric materials without alteration of the bulk properties are of great interest in many applications[5-6]. Complex nature of plasma due to presence of ions, neutrals and radiation in the discharge makes low-temperature plasmas as a widely used process in developing a number of materials fabrication processes including etching of complex patterns and surface modifications of polymeric membranes[7-8].

Plasma surface treatment usually refers to a plasma reaction that either results in modification of the molecular structure of surface or atomic substitution[9]. Plasma treatment is a useful tool in the modification of surface properties. The accelerated ions from the plasma have sufficient energy to induce cleavage of the chemical bonds in the membrane structure and to form macromolecule radicals, which subsequently initiate graft copolymerization[10]. Various plasma components such as electrons, ions, radical etc are involved in this process. 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[11-12].

Glow-discharge plasma technique is particularly useful for functionalization of surfaces as it is possible to modify the outermost surface layer by this technique. The plasma is almost homogenous at a low-pressure glow discharge. This technique for polymer surfaces modification has been recognized as a valuable tool to improve their adhesion properties and surface energy[13]. Additionally, weak boundary layers and surface contaminants are also removed during modification. These factors improve the adhesion, surface energy and reactivity of surface[14-15].

Experimental

Nanoparticles of TiO_2 are synthesized under controlled aqueous hydrolysis $TiCl_4$. To obtain small and narrow particle size distributions of TiO_2 NPs, all optimized parameter like reaction time, temperature, concentration of Ti precursor and other experimental condition were kept constant. The $TiCl_4$ was cooled at −20 °C in deep freezer, then 5 ml of this solution was taken into a caped stopping funnel and added drop wise into 300 mL of de-ionized Milli-Q water under vigorous stirring. The synthesis was done using a 1:60 $\{TiCl_4{:}H_2O\}$ volume ratio with a resulting TiO_2 concentration of ≈14.0 gL^{-1}. To avoid aggregation of particles PH of the solution was maintained at 2 using PH meter. The reaction mixtures were undergo vigorous stirring for 24 hrs on magnetic stirrer at 0°C, for complete removal of HCl gas and to obtained white uniformly dispersed TiO_2 nanoparticle suspension[14-15]. Polycarbonate (PC) granules were used to prepare flat sheet membranes by solution cast method and dichloromethane of extra pure grade was used as a solvent. Polycarbonate granules are weighed and dissolved in dichloromethane (CH_2Cl_2) to prepare a 10% solution[16]. The solution is stirred by magnetic stirrer to ensure the uniform dissolution and to enhance the rate of dissolution[17-18]. The process is carried out at room temperature for around 2-3 hours till a clear solution is formed then pour in flat-bottomed Petri-dishes floating on mercury to ensure a uniform structure of the membranes. The solvent was allowed to evaporate slowly over a period of 10 –12 h.

TiO_2 nano composite polycarbonate membranes with doping concentrations 2% were prepared by solution casting method. Polycarbonate solution was prepared in the same way as mentioned above for pristine membranes. TiO_2 nanoparticles were dispersed in the solvent dichloromethane using ultra-sonicator. This dispersed solution was mixed with the polycarbonate solution and

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stirred for around 30 minutes then pour into flat-bottomed Petri-dishes floating on mercury to ensure a uniform structure of the membranes. The solvent was allowed to evaporate slowly over a period of 10-12 hours. The films so obtained were peeled off using forceps.

Plasma irradiation set up at Department of Physics, University of Rajasthan consists of source chamber with complete power supply and connected to a vacuum system. Air used for generation of plasma is admitted into source chamber using a flow controller and applying DC power between two electrodes in magnetic field. The confined plasma in chamber is used for surface modification. Applying a high voltage between two electrodes with magnetic field generates the DC glow discharge. The chamber is evacuated to a base pressure of 10^{-10} torr and working pressure is maintained at 10^{-7} torr by admitting the appropriate gas. The current in the upper and lower electrodes is maintained at few mA and 1.2 KeV.

The plasma is almost homogenous in a low-pressure glow discharge. The reaction chamber is evacuated and refilled with low-pressure air to create glow discharge. Energetic species in this plasma include ions, radicals, electrons and meta-stable photons in short-wave UV range.

Results and Discussion

LABOMED microscope is used for recording optical images. Images are stored in computer through CCD camera, attached to computer with standard software (Pixel View). Images show that pristine membrane have very smooth surface but plasma treatment has increased its roughness. Nano composite membrane is comparatively having high porosity but plasma treatment again increases its roughness (Figure 1).

Raman spectra are obtained on raman spectrometer. In present case, Nicolet Megna single beam green light raman spectrometer is used. Raman spectrometer is used to gather both information about structure/chemical bonding and modification after plasma treatment as an analytical tool to measure chemical reactivity of compound. Raman Spectra of the pristine and 2 % doped (un-irradiated and plasma irradiated) membranes are shown in the Figure 2.

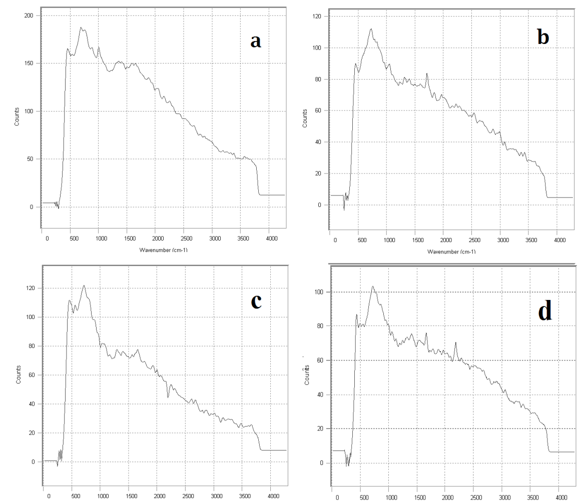

Figure 2: Raman spectra of pristine and TiO_2 doped membranes before and after plasma irradiation (a) Pristine membrane, (b) 2 % TiO_2 doped membrane, (c) Plasma treatment pristine membrane (d) Plasma Treated 2 % TiO_2 Membrane.

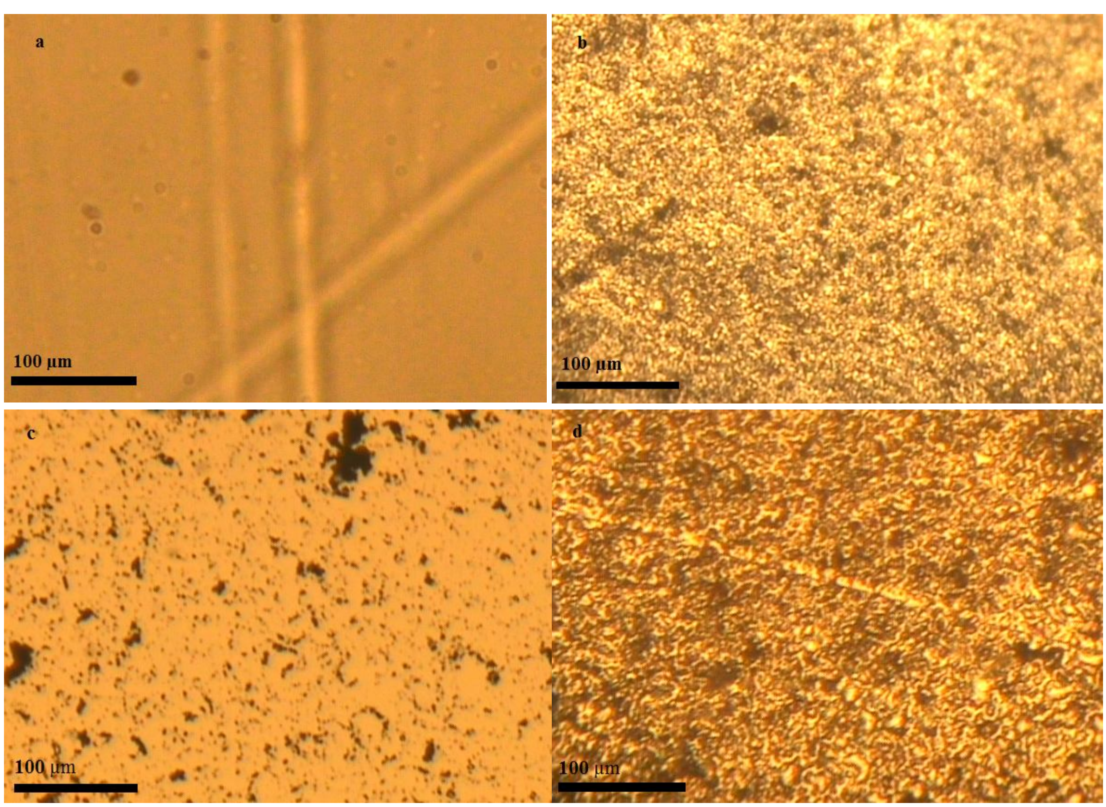

Figure 1: Optical micrographs of pristine and TiO_2 doped membranes both before and after plasma irradiation (a) Pristine membrane, (b) 2 % TiO_2 doped membrane, (c) Plasma treatment pristine membrane (d) Plasma Treated 2 % TiO_2 Membrane.

Results show characteristic differences in peaks between pristine and TiO_2 casted membranes due to presence of TiO_2 bonding in samples. Also we observed some N_2 bonding peaks (as it is a major component of air) and shift in few peaks after plasma treatment for these membranes. These wavelengths are indicators of change in the chemical bonding and structure of samples due to plasma treatment. Also the mostly similar characteristic peaks in raman spectra of treated and untreated samples determined that there was no change in the basic structure of the membrane material. Only surface material and its properties got modified while bulk properties remain unchanged (Fig. 2).

Surface morphologies of TiO_2 Nano composite polycarbonate membranes were investigated before and after plasma treatment using SEM. SEM images of films are shown in Figure 3. It was observed that porosity and roughness of plasma treated membranes increased.

To study the effect on bacterial cell colonization on plasma irradiated samples, E.coli bacteria was chosen because it was relatively easy to handle, nontoxic, readily available and shows the clear colonies within 72 hrs. The autoclaved membrane was mounted on the liquid nutrient Agar (Autoclaved) media by streaking and spreading and few drops of bacteria solution was spread on membranes. The membranes were kept at 37º C in the incubation chamber for 48 hrs.

The membranes were studied under optical microscope. In this study the media is supported with the polymer membrane of poly-carbonate of thickness 20 micron. For the polymer film without plasma treatment it is non-porous, this polymer film was acting as a passive layer between base support and food (media). This results into no growth on the surface of polymer film but TiO_2 casted films show little growth of bacteria due to some porosity present in membranes. But when polymer film is made porous by plasma treatment and experiment is repeated to compare the bacterial growth on porous polymer films as separating media for support and food. It is found that the growth enhance with the porosity (figure 4). This shows enhancement in bacterial cell colonization on polymer membranes after plasma irradiation.

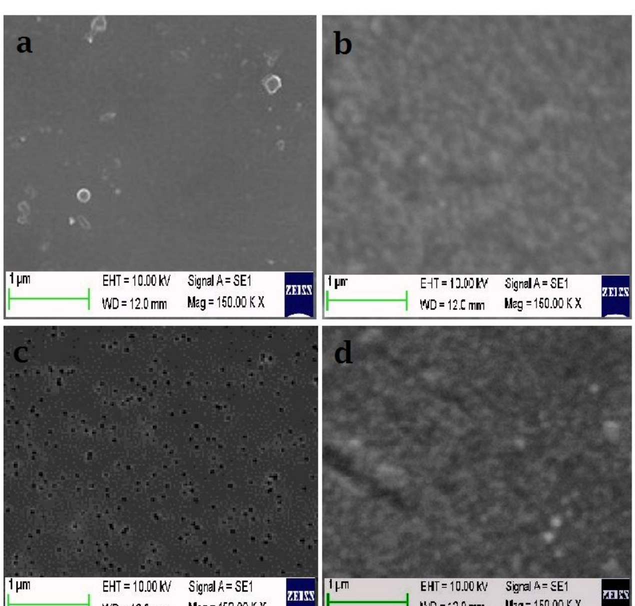

Figure 3: SEM images of pristine and TiO_2 doped membranes before and after plasma irradiation (a) Pristine membrane, (b) 2 % TiO_2 doped membrane, (c) Plasma treatment pristine membrane (d) Plasma Treated 2 % TiO_2 Membrane.

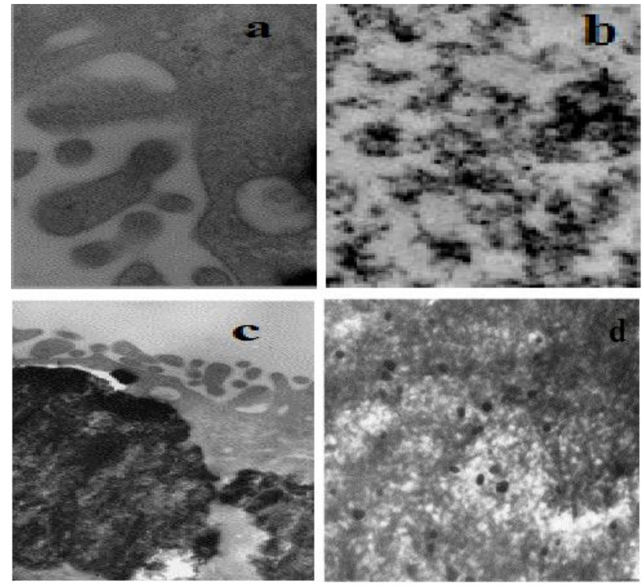

Figure 4:Optical microscope images for bacterial cell colonization on polymer membranes before and after plasma irradiation (a) Pristine membrane, (b) 2 % TiO_2 doped membrane, (c) Plasma treatment pristine membrane (d) Plasma Treated 2 % TiO_2 Membrane.

Conclusions

Pristine polycarbonate membranes and polycarbonate membrane doped with 2 % TiO_2 nanoparticles were prepared by solution cast method. These membranes were subjected to surface modification techniques i. e. air plasma treatment was done. Plasma treatment techniques applied here have shown considerable improvement in surface morphology. Plasma treatment has helped in increasing flux whereas doping has modified the surface properties. Raman results shows modification in chemical properties of polymer membranes due to TiO_2 NPs casting as well as plasma irradiation. An increase in surface roughness has been observed after plasma treatment by SEM and optical microscope images. So plasma irradiation resulted in surface roughness and chemical modification of polymer membranes, i. e., surface energy and reactivity of membranes got increased after plasma treatment. This increase in surface energy as well as reactivity allows starting bacterial cell colonization on membrane that can be explained by natural cell membrane mechanism.

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