

Surface modification of nanocomposite polymer membranes by ion plasma irradiation for improving biocompatibility of polymer

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ABSTRACT

Polymers are receiving great interest due to their increasing applications in various fields, especially for synthesis of biomaterial. Biomaterials are nonviable materials used in medical devices, intended to interact with biological systems. To use polymer as biomaterial they required properties like antibacterial, antimicrobial, high adhesion and wettability. Low temperature plasma treatment can offer these properties to polymers. Hence a systematic study was carried out for determining the effect of ion plasma treatment on nanocomposite polymer membranes. TiO₂ nanoparticles having particle size 10-16 nm were synthesized by chemical method and used for preparation of nanocomposite polymer membranes. Argon ion plasma was used for modified polymer surface. These membranes were characterized by different techniques to identify surface and chemical modification. FTIR results shown significant modification in chemical properties, while SEM images shows increase in surface roughness of nanocomposite polymer membranes after plasma treatment. Bacterial cell adhesion and wettability were also found to be increased after plasma treatment. Copyright © 2014 VBRI press.

Keywords: Biomaterial; nonviable material; antibacterial activity; adhesion and wettability.



Narendra Kumar Agrawal received his M. Sc. in physics from Department of Physics, University of Rajasthan in 2009. Currently I am pursuing my Ph. D degree from Department of Physics, Malaviya National Institute of Technology, Jaipur under the supervision of Professor K. C. Swami and co- supervision of Professor Y. K. Vijay. My area of research includes Synthesis and enhancement of biocompatibility of bio-materials in controlled manner so that they can be used as biomedical devices or implants using the principles & applications of Plasma Physics, Neuroscience, Nanotechnology, Biotechnology, Computer/Computational Science, Information technology.



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Introduction

Any substance or combination of substances, other than a drug, synthetic or natural in origin, can be used for any period of time, as whole or part of biological system, which can treat, augment or replaces any tissue, organ or function of the system is called biomaterial. These biomaterials are nonviable materials used in medical devices, intended to interact with biological systems. Hence the subject can only be explored by considering/measuring the biological response of materials [1].

Polymers have become very important materials in modern manufacturing processes due to their wide varieties of chemical, mechanical and elastic properties, lightweight, flexibility and good process-ability, applicable in numerous fields like gas filtration [2], bactericidal properties [3], electrical [4], optical [5], mechanical applications [6] etc. Physico-chemical properties of polymers like surface free energy [7], hydrophilicity [3], surface morphology and cell-polymer interactions [8] makes them widely useable material for synthesis of nano-biomaterials, bio-devices and bio-sensors [9]. Recently polymers having unique surface properties like low surface energy, hydrophilicity, specific surface morphology, higher cell/protein adhesion are receiving great interest for synthesis of artificial skin diaphragm, valves for heart, kidney, lenses for eyes and other biomedical devices [10-11].

Biomaterials in contact with biological body have optimal combination of mechanical and surface characteristics so that they results superior performance in biological environments [12]. In general no polymers directly possess surface-interface and chemical properties needed for biomedical applications like low surface energy, hydrophilicity, surface morphology, chemical functionality, antibacterial and antimicrobial properties, adhesion and peeling strength and blood compatibility [13, 14].

Nanomaterials or plasma irradiation plays a crucial role in incorporating these problems [13, 14]. Plasma irradiation of nanocomposite polymers produces chemical and surface modification in controlled fashion [15], chemical functionalization [14], scaling up antibacterial & antimicrobial properties in ecofriendly nature [14], high adhesion & peeling strength [16] and blood compatibility [17]; makes them biocompatible extremely suitable for many biomedical applications and nano-biomaterial synthesis [4].

In this paper we have synthesized polymer nanocomposite membranes (PNCM) using polymethyl methacrylate (PMMA) and TiO₂ nanoparticles (NPs) and irradiated with low temperature Ar ion plasma for surface and chemical modification [13]. PMMA is chosen because, due to its good processability it is receiving great interest for synthesis of bone cement, intraocular lenses, contact lenses and fixation of articular prostheses from last few decades [18], whereas TiO₂ become widely acceptable biomaterial due to its good corrosion resistance, excellent fatigue strength, good machinability and low-density. It can also increase wettability of polymers and can decompose organic dust [19-24]. Ar ion plasma irradiation of these PNCM leads to two competitive reactions, namely modification and degradation [25]. When modification effect dominates, properties of polymer will change due to

ion beam interaction, plasma-graft co-polymerization and plasma polymerization. When degradation is prominent, etching will take place on polymer surface. At suitable ion energies both surface and chemical modification occurs on PNCM [25]. These modified PNCM were characterized by FTIR, SEM and XRD to identify chemical and surface modifications. Bacterial cell adhesion and wettability were also determined for these modified membranes.

Experimental

Synthesis of TiO₂ nanoparticles were carried out at room temperature using a simple chemical precipitation route as described by Agrawal et al. [26]. TiO₂ NPs thus synthesized were characterized by TEM to determine particle size.

Polymethyl methacrylate (PMMA) granules used to prepare 25µm flat sheet membranes were obtained as commercial grade from Loxim Polymers, Jaipur-India. Benzene of extra pure grade was used as a solvent for preparing polymer solution. Solvent casting method is one of the easiest and least time consuming methods for the preparation of PNCM [25, 27], hence solution-casting method was used for preparation of membranes. PMMA granules were weighed and dissolved in benzene by continuous stirring till a clear solution is formed and 3 weight% TiO₂ nanoparticles were dispersed in benzene using ultrasonicator [28]. This dispersed solution was added to 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.

Ar Plasma irradiation set up at University of Rajasthan consists of a source chamber with complete power supply and vacuum system was used for plasma irradiation. To get uniformly distributed plasma, initially chamber was evacuated to a base pressure of 10⁻⁹ torr and working pressure is maintained at 10⁻⁵ torr by admitting Argon gas using flow controller. Ar ion plasma was generated by applying high voltage DC power between two electrodes and ions were accelerated using DC power. The electrodes were kept at 5 cm distance, current in upper and lower electrodes were maintained at few mA while acceleration voltage was maintained at 3.5 KeV; hence 40 watt/cm² power is generated between two electrodes. These accelerated Ar⁺ ion were used for surface and chemical processing of NCPM [25].

Particle size and morphology of TiO₂ NPs was characterized using Technika 200 transmission electron microscopy (TEM) instrument operating at 200 kV and conformed using scanning electron microscope (Carl ZEISS EVOR -18) operated at 15kV. The same SEM (Carl ZEISS EVOR -18) instrument was used to characterize surface modification on NCPM before and after plasma treatment. Chemical modifications before and after plasma treatment were characterized by Fourier transform infrared spectroscopy (FTIR) IRAffinity-1 (SHIMADZU). Crystalline structure of NCPM were recorded by X'Pert Pro x-ray diffractometer (PAN analytical BV, The Netherlands) operated at a voltage of 45kV and current of 40mA with Cu k(α) radiation of wavelength 1.54059 Å, at

grazing angle X-ray diffraction. Scanning was done in region of 2θ from 5° to 60° at 0.030° per step at time step as 5 s. UV-Visible spectral analysis was also done to identify the effect of plasma treatment on optical properties of NCPM using a double beam spectrophotometer (UV-1800 ENG240V SOFT SHIMADZU).

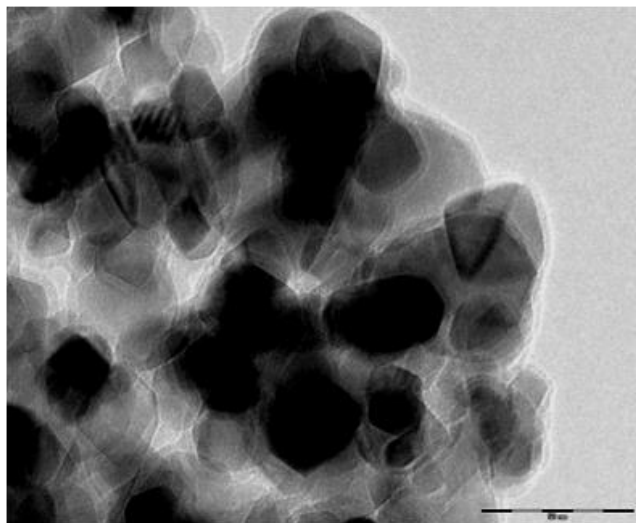


Fig. 1. Transmission electron micrographs (TEM) of synthesized TiO_2 NPs, having spherical shape and particle size ranging from 10-16 nm.

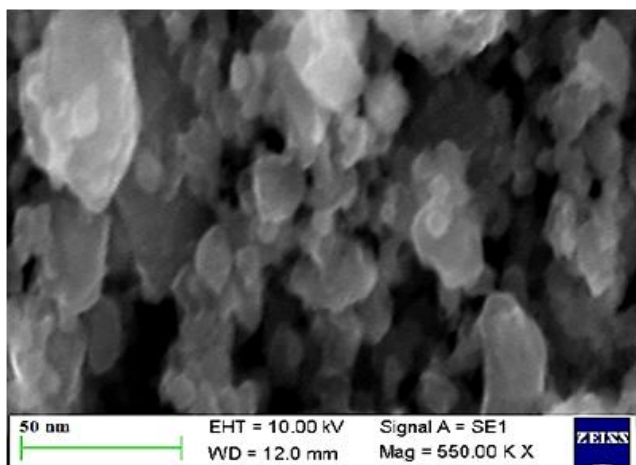


Fig. 2. SEM image of synthesized TiO_2 NPs, as individual TiO_2 NP can easily be identified from image showing no aggregation in NPs even at higher sampling concentrations.

Results and discussion

The TiO_2 NPs were dispersed in acetone by ultra-sonication and used for particle size analysis by TEM and SEM. TEM image (**Fig. 1**) shows spherical shape, 10-16 nm TiO_2 nanoparticles. As particle boundary of individual TiO_2 NP can easily identified from image, i.e. nanoparticles are well dispersed without any aggregation. For present study where particle size and shape of NPs are only concerned, TEM image is best indicator of particle size and shape. But to determine aggregation present at higher sampling concentrations, we have also analyzed TiO_2 NPs by SEM. SEM image in **Fig. 2** shows particle size and morphology of the TiO_2 NPs. As individual TiO_2 NP can easily be

identified from image showing no aggregation in NPs even at higher sampling concentrations.

At applied low pressure and DC power accelerated Ar^+ ions has sufficient energy to produce surface and chemical modification i.e. induce cleavage of chemical bonds, graft copolymerization, modify polymer surface, functionalization, improve adhesion properties and wettability [25]. The effect of Ar^+ ion irradiation on the surface of NCPM membrane was investigated by SEM (**Fig 3**). **Fig. 3** clearly shows that surface roughness of NCPM was increased after plasma treatment, is responsible for higher adhesion and wettability.

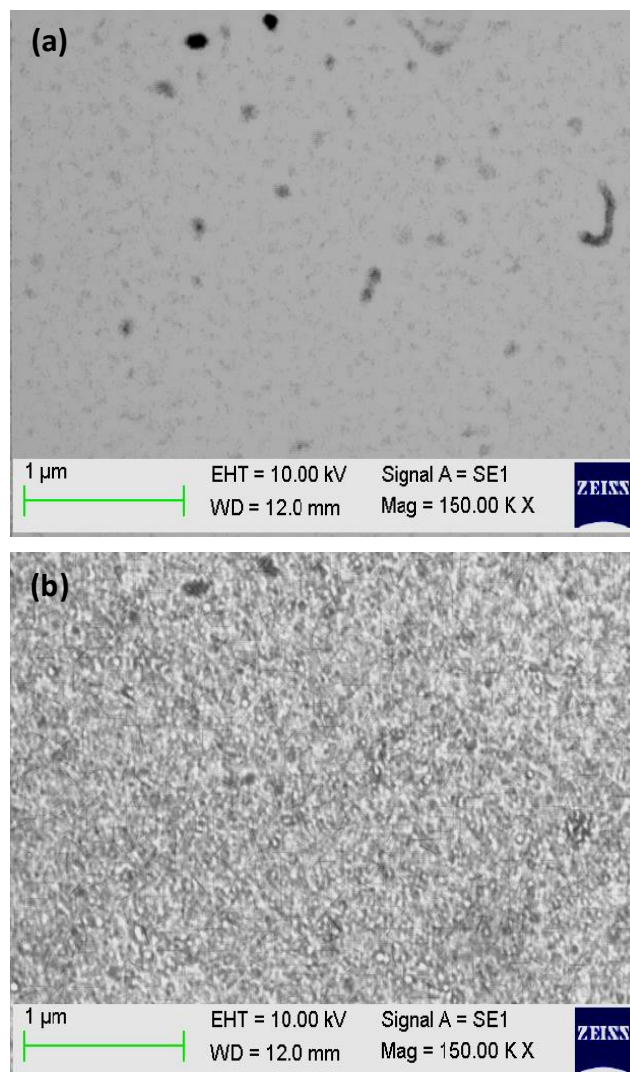


Fig. 3. SEM images of NCPM (a) before and (b) after plasma treatment, showing increase in surface roughness after Ar^+ ion plasma irradiation.

Chemical modifications on NCPM after plasma treatment were determined by FTIR measurements. **Fig. 4** shows FTIR spectra of untreated and treated NCPM. Absorption bands as obtained from untreated membranes are classified as (a) C-O stretching vibration at 1030 cm^{-1} (b) C=O stretching vibrations at 1770 cm^{-1} (c) CH_3 stretching vibration at 2890 cm^{-1} and (d) C-C, & C-H stretching vibration of aromatic compound at 3070 cm^{-1} , absorption corresponding to TiO_2 NPs are also observed in finger print region ($250\text{-}750\text{ cm}^{-1}$) of FTIR spectra. 4.5% absorption was found to increase after plasma treatment,

epically in absorption bands of C-O and C=O. Plasma irradiation also separated C-C and C-H bands between 3070 cm^{-1} to 3190 cm^{-1} due to dissolution/breaking of C-H bond and formation of C-C bonds, shows crosslinking in polymer. Hence longer polymer chain formation starts i.e. crosslinking phenomenon enhanced during plasma irradiation (Fig. 4).

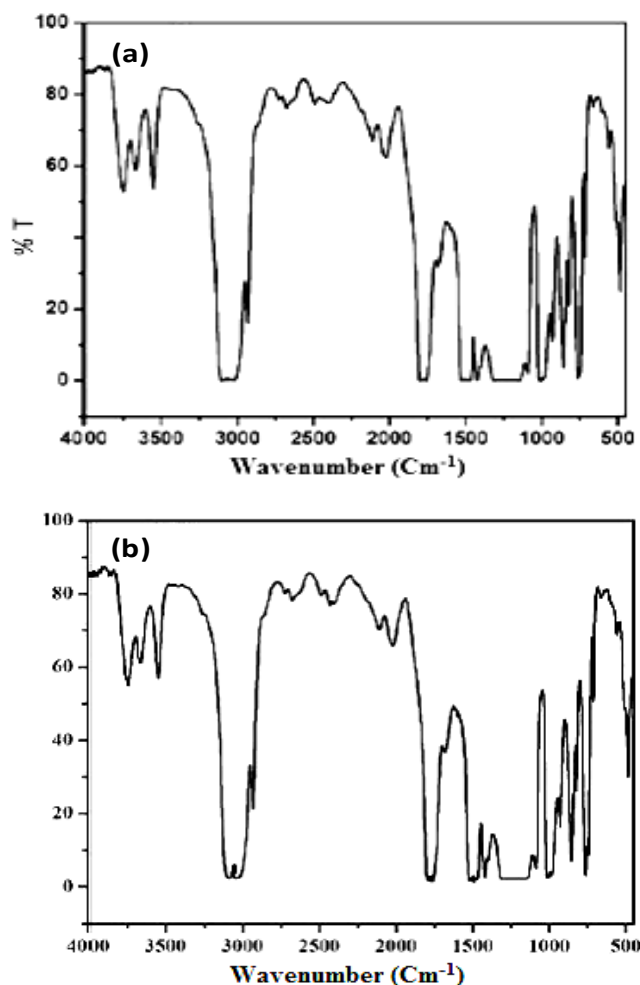


Fig. 4. FTIR spectra of NCPM (a) before and (b) after Ar^+ ion plasma irradiation.

XRD patterns were recorded to identify the effect of Ar^+ ion plasma irradiation on the crystalline nature of NCPM. Fig. 5 shows XRD spectra of untreated and treated NCPM. The strongest peak for TiO_2 NPs in NCPM was observed for lattice plane A (1 0 1) at reflection angle $2\theta = 25.3^\circ$, having a particle size of 15.2 nm, calculated using the Scherrer equation [29] (JCPDS files for anatase (No. 21-1272)). Other lattice planes were obtained at 30.9° , 36.8° and 54.9° , which show TiO_2 NPs of sizes 13.8, 15.7, and 17.2 nm, respectively. A broad diffraction peak between $2\theta = 10\text{--}20^\circ$ corresponds to the amorphous pattern of PMMA.

After plasma treatment, the same crystalline sites/planes were observed for TiO_2 NPs, but the intensity of the peaks increased due to etching of PMMA from the surface of NCPM, hence the TiO_2 content on the surface of NCPM increased after plasma irradiation. Small variations found in the amorphous hump of PMMA indicate modulation of PMMA properties due to the crosslinking phenomenon.

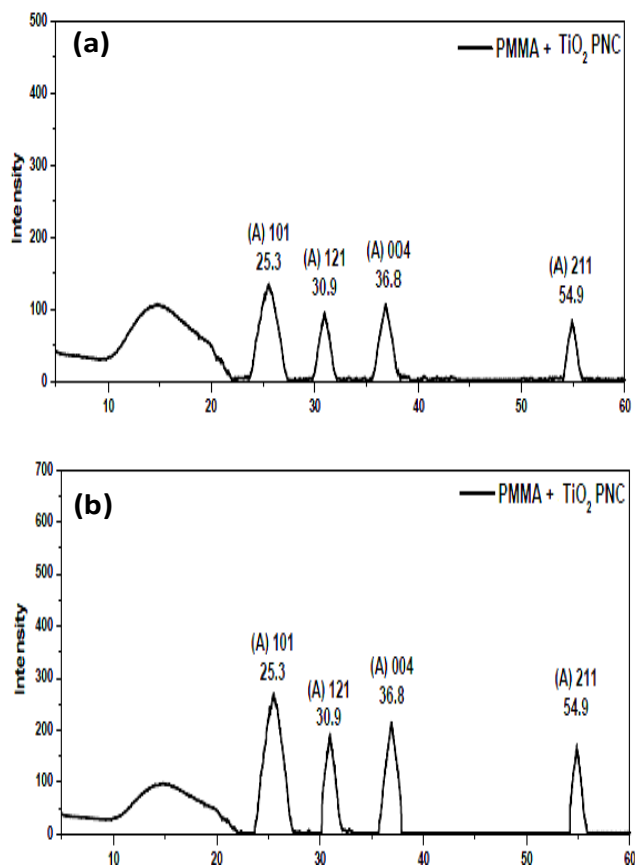


Fig. 5. XRD spectra of NCPM before and after Ar^+ ion plasma irradiation.

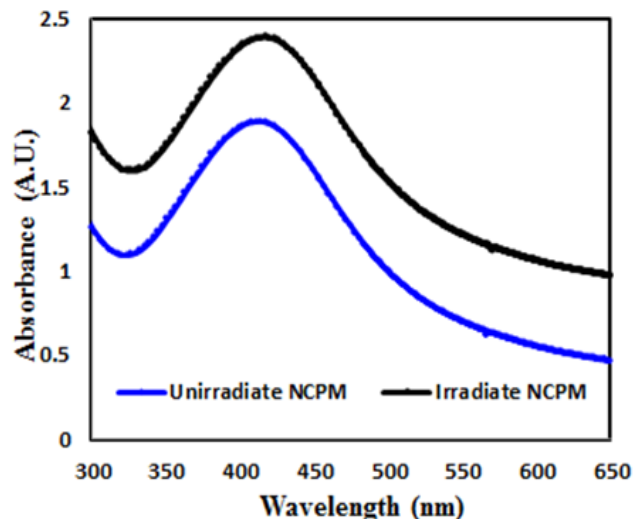


Fig. 6. UV-Vis spectra of NCPM before and after Ar^+ ion plasma irradiation.

UV-visible absorption spectra were recorded to identify the effect of plasma irradiation on the optical properties of NCPM (Fig. 6). The Surface Plasmon Resonance absorption for NCPM comes at 410 nm ($E_g = 3.02\text{ eV}$) corresponds to the absorption of TiO_2 NPs before and after plasma irradiation. There was no change in the absorption edge, but the total absorbance was found to be increased after plasma treatment, showing that NCPM became more opaque after plasma treatment. Similar results were also

observed in FTIR spectra where % transmission was decreased after plasma treatment.

PMMA TiO₂ nanocomposites are receiving great interest for synthesis of catalyst electrodes [7], ion-exchange membranes [30], microporous membranes [31], permselective membranes [32], semipermeable membranes [33] and modulator of redox condition with many other bio-medical applications. All these applications required high porosity, electrochemical properties as well as high concentration of NPs on surface of NCPM. XRD and SEM results show that plasma irradiation improves porosity and concentration of NPs on surface of NCPM. Hence we have measured current vs. voltage characteristic of NCPM before and after plasma treatment (Fig. 7), and found increment in conductivity up to at least two orders of magnitude. Represents that plasma irradiation effectively etch-out PMMA to increase TiO₂ content on NCPM surface, i.e. helps in achieving better electrical properties of NCPM.

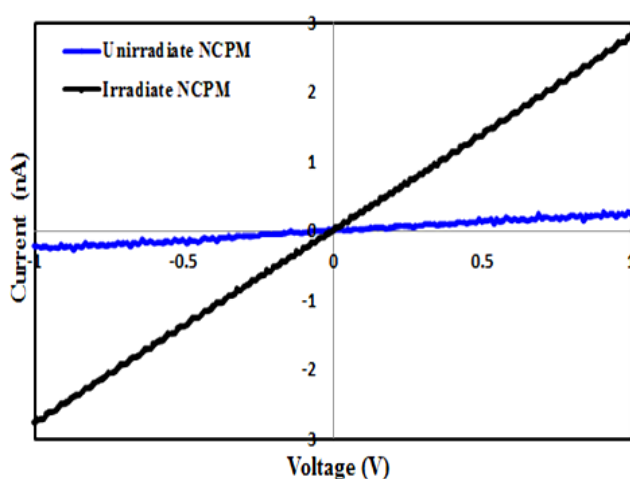


Fig. 7. Current vs. Voltage characteristic of NCPM before and after Ar⁺ ion plasma irradiation.

Bacterial cell adhesion and wettability

Objective of this work is to increase bio-compatibility of polymers. An increase in cell adhesion and wettability are best indicator for higher bio-compatibility of polymers, hence test for bacterial cell adhesion and wettability was also performed using these NCPM.

Bacterial cell adhesion on membranes were investigated using *E. coli* bacteria as it is relatively easy to handle, nonpathogenic, readily available and shows clear colonies within 24 hrs. Standard *E. coli* (≈ 100 cfu/mL) inoculums were inoculated in 50 mL sterilized normal saline for 24 hrs. and its few drops were put on autoclaved NCPM (irradiated and un-irradiated) and kept at 37 °C in incubation chamber. Clear colonies of bacteria were observed after 24 hrs. These membranes were washed in running water for 10 minutes and then studied under optical microscope. High bacteria content was found on Ar⁺ ion plasma irradiated NCPM comparative to un-irradiated NCPM (Fig. 8), i.e. bacteria/cells adhered/attached poorly to control/un-irradiated surface and are found to be better adhered to Ar⁺ ion plasma irradiated NCPM.

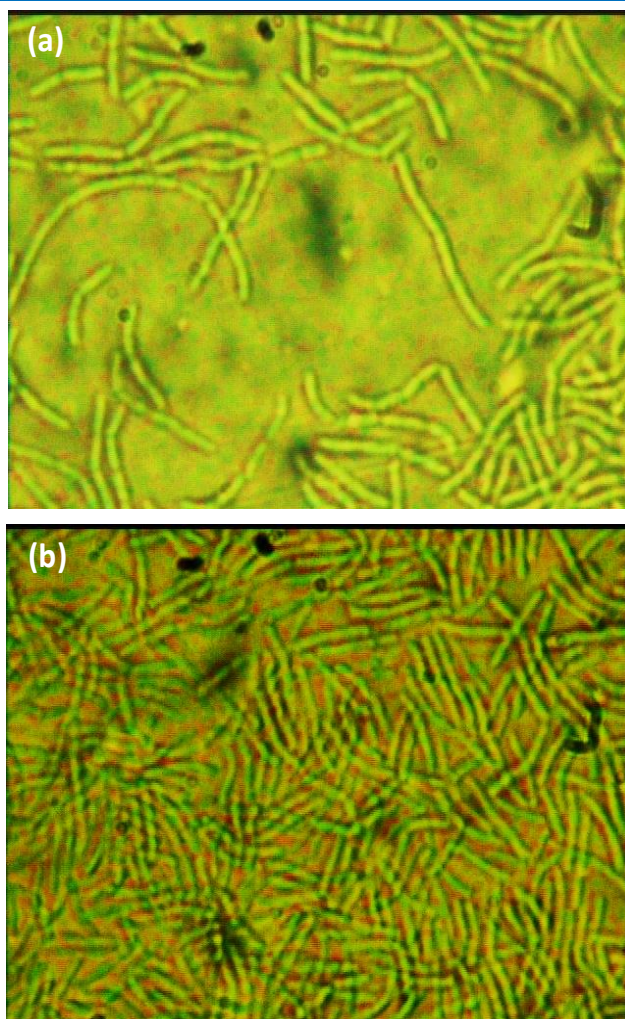


Fig. 8. Bacterial cell adhesion/attachment on NCPM (a) before and (b) after Ar⁺ ion plasma irradiation.

This may be due to the fact that Ar⁺ ion plasma irradiation generate hydroxyl group on NCPM surface. These hydroxyl groups makes hydrogen bonding with polar groups on bacterial cell surfaces resulting better adhesion and hydroxylation properties of these NCPM after plasma irradiation.

Hydrophobic materials are not favorable for blood cell adhesion, bacterial attachment and proliferation over surface. Hence most of biomaterial requires high wettability and high surface energy that can be determined by measuring water contact angles for NCPM. Here a 3 μ l droplet of ultra-pure water (Milli Q) was placed on a horizontal NCPM surface and contact angle were determined. Water contact angles for un-irradiated membrane was recorded 118°, which changes to 48° for Ar⁺ ion plasma irradiated NCPM (Fig. 9), i.e. Ar⁺ ion plasma irradiation also increases wettability of NCPM. Polar and dispersion components of surface energy were calculated using Owens–Wendt method [34]. Un-irradiated NCPM has almost non-polar surface with a polar component $\gamma_s^p = 0.8$ mJ/m² and dispersion component $\gamma_s^d = 19.2$ mJ/m² which makes its surface energy $\gamma_s = 20.0$ mJ/m². But after Ar⁺ ion plasma irradiation polar component becomes $\gamma_s^p = 8.0$ mJ/m² and dispersion component $\gamma_s^d = 20.0$ mJ/m², i.e. its total surface energy becomes $\gamma_s = 28.0$ mJ/m². Such Ar⁺

ion plasma irradiation not only increases wettability of NCPM but also significantly increases polar component of surface energy and polarity.

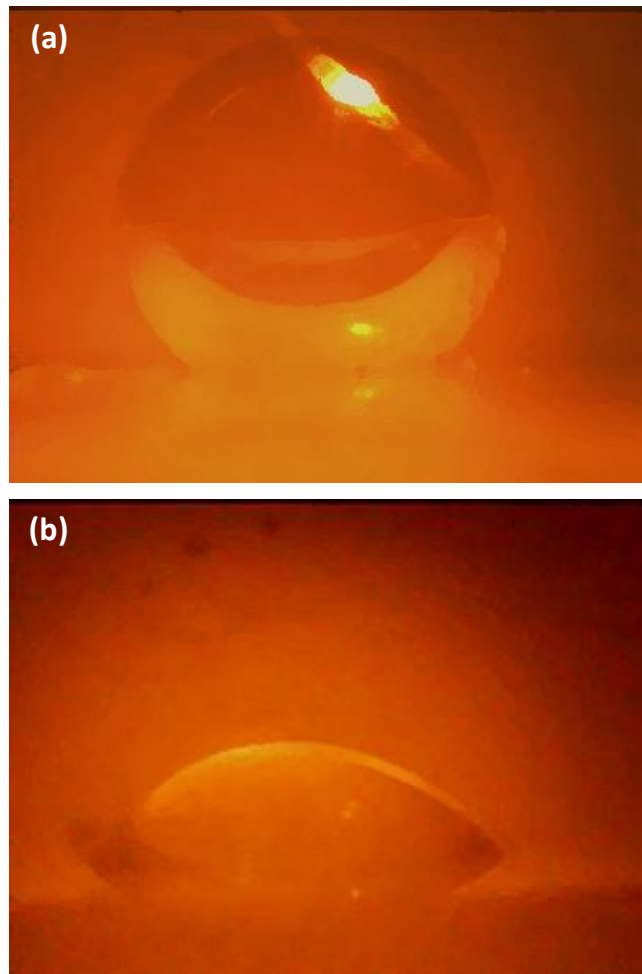


Fig. 9. Wettability study on NCPM before and after Ar^+ ion plasma irradiation.

Conclusion

Polymers are becoming ideal material to use as bio-material, but to use any material as bio-material it requires higher bio-compatibility. Nanomaterials and ion plasma irradiation can improve bio-compatibility of polymers by increasing cell adhesion, surface energy and wettability.

Here spherical shape, 10-16 nm sized TiO_2 NPs were synthesized using chemical method and used as nanocomposite for PMMA. NCPM having 3 wt % TiO_2 NPs in PMMA are prepared by solution casting method. Low temperature Ar^+ ion irradiation has been performed for these NCPM with homogeneous, glow discharge plasma for 10 minute for modulation of surface and chemical properties. An increase in surface roughness, porosity and functionalization has been observed after Ar^+ ion plasma irradiation. Ar^+ ion plasma irradiation for NCPM also increases absorption in UV-Vis region, improves I-V characteristic up to at least two orders of magnitude by selective etching of polymer without effecting bulk properties of material. Chemical modifications identified by FTIR shows Ar^+ ion plasma irradiation initiate cross linking by dissolution/braking of C-H bond and initiating

crosslinking between C-C. These surface and chemical modifications in NCPM leads to formation of hydroxyl groups and increase surface energy resulted in higher cell adhesion and high wettability. Thus Ar^+ ion plasma treatment makes NCPM bio-compatible.

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Reference

- Oehr, C.; *Ionizing Radiation and Poly.* **2003**, *208*, 40.
DOI: [10.1016/S0168-583X\(03\)00650-5](https://doi.org/10.1016/S0168-583X(03)00650-5)
- Vijay, Y. K.; Acharya, N. K.; Wate, S.; Avasthi, D. K.; *Int. J. Hydrogen Energy.* **2003**, *28*, 1015.
DOI: [10.1016/S0360-3199\(02\)00166-0](https://doi.org/10.1016/S0360-3199(02)00166-0)
- Sunada, K.; Watanabe, T.; Hashimoto, K.; *J. Photochem. and Photobio. A: Chem.* **2003**, *156*, 227.
DOI: [10.1016/S1010-6030\(02\)00434-3](https://doi.org/10.1016/S1010-6030(02)00434-3)
- Chua, P. K.; Chena, J. Y.; Wanga, L. P.; Huang N.; *Mater. Sci. Eng.* **2002**, *36*, 143.
DOI: [10.1016/S0927-796X\(02\)00004-9](https://doi.org/10.1016/S0927-796X(02)00004-9)
- Yu, S.; Liu, X.; Liu, J.; Wu, D.; Liu, M.; Gaoc, C.; *Separation and Purification Technol.* **2011**, *76*, 283.
DOI: [10.1016/j.seppur.2010.10.017](https://doi.org/10.1016/j.seppur.2010.10.017)
- Bagra, B.; Pimpliskar, P.; Agrawal, N. K.; *AIP Conf. Proc.* **2014**, *1591*, 189.
DOI: [10.1063/1.4872539](https://doi.org/10.1063/1.4872539)
- Gao, L.; Zhang, Q. H.; *Scripta Mater.* **2001**, *44*, 1195.
DOI: [10.1016/S1359-6462\(01\)00681-9](https://doi.org/10.1016/S1359-6462(01)00681-9)
- Mohammadia, M. R.; Fray, D. J.; Cordero-cabrera, M. C.; *Sensor. & Actua. B, Chem.* **2001**, *124*, 74.
DOI: [10.1016/j.snb.2006.11.048](https://doi.org/10.1016/j.snb.2006.11.048)
- Agarwal, R.; Agrawal, N. K.; Singh, R.; *Mater. Focus*, **2014**, *3*, 267.
DOI: [10.1166/mat.2014.1177](https://doi.org/10.1166/mat.2014.1177)
- Baylay, H.; Jayasinghe, L.; *Mol Membr Biol.* **2004**, *21*, 209.
DOI: [10.1080/09687680410001716853](https://doi.org/10.1080/09687680410001716853)
- Kedawat, G.; Gupta, B. K.; Kumar, P.; Dwivedi, J.; Kumar, A.; Agrawal, N. K.; Kumar, S. S.; Vijay, Y. K.; *ACS Appl. Mater. Interfaces*, **2014**, *6*, 8407.
DOI: [10.1021/am501307h](https://doi.org/10.1021/am501307h)
- Oganov, A. R.; Glass, C. W.; Lyakhov, A. O.; Stokes, H. T.; Zhu, Q.; Agarwal, R.; Dong, X.; Pertierra, P.; Raza, Z.; Salvado, M. A.; Dong, D.; Qian, G. R.; Zeng, Q.; Raktin, M.; USPEX: Universal Structure Predictor: Evolutionary Xtallography, <http://uspe.x.stonybrook.edu>, Manual Version 9.3.9, Volume 1, Stony Brook University, New York (**2014**).
- Gomathi, N.; Sureshkumar, A.; Neogi, S.; *Current Science*, **2004**, *90*, 148.
DOI: [10.1002/app.30691](https://doi.org/10.1002/app.30691)
- Agrawal, N. K.; Agarwal R.; Vijay Y. K.; Swami K. C.; *Journal of Material Science and Surface Engineering*, **2013**, *1* (1), 4.
- Ramalingam, M.; Tiwari, A. *Adv. Mat. Lett.* **2010**, *1*, 179.
DOI: [10.5185/amlett.2010.9160](https://doi.org/10.5185/amlett.2010.9160)
- Goyal, A.; Sharma, V.; Sharma, A.; Agarwal, R.; Sharma, K. B.; Kothari, S. L.; *J. of Nano-and Electronic Phys.* **2011**, *3* (1), 254.
DOI: [81.05.Dz81.07.Be81.16.Be](https://doi.org/10.1051/Dz81.07.Be81.16.Be)
- De, S.; Sharma, R.; Ali, N.; Mazumder, M. K.; *IEEE*, **2004**, *5*, 932.
DOI: [10.1109/IAS.2004.1348524](https://doi.org/10.1109/IAS.2004.1348524)
- Listona, E. M.; Martinub, L.; Wertheimer, M. R.; *J. of Adhesion Science and Technol.*, **1993**, *7*, 1091.
DOI: [10.1163/156856193X00600](https://doi.org/10.1163/156856193X00600)
- Agrawal, N. K.; Agarwal, R.; Vijay, Y. K.; Swami, K. C.; *J. Mat. Sci. Surf. Eng.* **2014**, *1* (1), 23.
- Agrawal, N. K.; Agarwal, R.; Vijay, Y. K.; Swami, K. C.; *J. Bionanosci.* **2014**, *8*, 108.
DOI: [10.1166/jbns.2014.1207](https://doi.org/10.1166/jbns.2014.1207)
- Lee, K. M.; Hu, C. W.; Chen, H. W.; Ho, K. C.; *Solar Energy Mater. & Solar Cells*, **2008**, *92*, 1628.
DOI: [10.1016/j.solmat.2008.07.012](https://doi.org/10.1016/j.solmat.2008.07.012)

22. Agarwal, P.; Mehta, A.; Kachhwaha, S.; Kothari S. L.; *Adv. Sci. Eng. Med.* **2013**, 5 (7), 709.
DOI: [10.1166/asem.2013.1307](https://doi.org/10.1166/asem.2013.1307)
23. Agarwal, R.; Agrawal, N. K.; Singh, R.; *Adv. Sci. Eng. Med.* **2014**, 6 (2), 203.
DOI: [10.1166/asem.2014.1474](https://doi.org/10.1166/asem.2014.1474)
24. Wang, Y. Q.; Zhang, H. M.; Wang, R. H.; *Coll. and Surfaces B: Biointerfa.* **2008**, 65, 190.
DOI: [10.1016/j.colsurfb.2008.04.001](https://doi.org/10.1016/j.colsurfb.2008.04.001)
25. Agrawal, N. K.; Awasthi, K.; Vijay, Y. K.; Swami, K. C.; *Adv. Electrochem.* **2013**, 1, 98.
DOI: [10.1166/adel.2013.1017](https://doi.org/10.1166/adel.2013.1017)
26. Agrawal, N. K.; Singh, M.; Vijay, Y. K.; Swami, K. C.; *Adv. Sci. Eng. Med.* **2014**, 6(5), 595.
DOI: [10.1166/asem.2014.1535](https://doi.org/10.1166/asem.2014.1535)
27. Saxena S.; Dubey, R.; *Adv. Sci. Eng. Med.* **2014**, 6, 704.
DOI: [10.1166/asem.2014.1564](https://doi.org/10.1166/asem.2014.1564)
28. Agrawal, N. K.; Agarwal, R.; Vijay, Y. K.; Swami, K. C.; *Adv. Sci. Eng. Med.* **2014**, 6 (6), 698.
DOI: [10.1166/asem.2014.1565](https://doi.org/10.1166/asem.2014.1565)
29. Pimpliskar, P.; Bagra, B.; Gautam, A. K.; Khandelwal, S.; Agrawal, N. K.; *AIP Conf. Proc.* **2014**, 1591, 481.
DOI: [10.1063/1.4872646](https://doi.org/10.1063/1.4872646)
30. Langford, J. I.; Wilson, A. J. C.; *Journal of Applied Crystallography* **1978**, 11, 102.
DOI: [10.1107/S0021889878012844](https://doi.org/10.1107/S0021889878012844)
31. Agrawal, N. K.; Agarwal, R.; Vijay, Y. K.; Swami, K.C.; *Journal of Material Science and Surface Engineering*, **2014**, 1 (2), 32.
32. Wagner, E. M. V.; Saglea, A. C.; Sharmab, M. M.; Lac, Y. H.; Freeman, B. D.; *J. Membrane Sci.* **2011**, 367, 273.
DOI: [10.1016/j.memsci.2010.11.001](https://doi.org/10.1016/j.memsci.2010.11.001)
33. Sairam, M.; Patil, M. B.; Veerapur, R. S.; Patil, S. A.; Aminabhavi, T. M.; *J. Membrane Sci.* **2006**, 281, 95.
DOI: [10.1016/j.memsci.2006.03.022](https://doi.org/10.1016/j.memsci.2006.03.022)
34. Ma, G. Q.; Liu, X. N.; Huang, D. H.; Yuan, X. B.; Sheng, J.; *Appl. Surface Sci.* **2009**, 255, 7483.
DOI: [10.1016/j.apsusc.2009.03.066](https://doi.org/10.1016/j.apsusc.2009.03.066)

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