# Materials Today: Proceedings 30 (2020) 137-144



Contents lists available at ScienceDirect

# Materials Today: Proceedings



journal homepage: www.elsevier.com/locate/matpr

# Tuning of TiO<sub>2</sub> nanoparticles incorporation in poly methyl methacrylate for synthesis of polymer nanocomposites for promising biomedical application

Narendra Kumar Agrawal<sup>a,b</sup>, Ravi Agarwal<sup>a,c,\*</sup>, Priti Agarwal<sup>d</sup>

<sup>a</sup> Samnvya, The Information Management System, Jaipur 302033, India

<sup>b</sup> Department of Physics, St. Wilfred's College For Girls, Jaipur 302020, India

<sup>c</sup> Centre for Converging Technologies, University of Rajasthan, Jaipur 302004, India

<sup>d</sup> Department of Botany, University of Rajasthan, Jaipur 302004, India

## ARTICLE INFO

Article history: Received 6 March 2020 Received in revised form 6 May 2020 Accepted 7 May 2020 Available online 8 June 2020

Keywords: Biomaterials Polymer Nano-Composites (PNC) Wettability Percolation Bacterial Response Surface Morphology Surface Energy Polymer Nano-Composites Membrane (PNCM)

# ABSTRACT

Polymer Nano-Composites (PNC) exhibit advanced applications that depend on the surface characteristics and physicochemical properties of materials. These physical and physicochemical properties of materials can be modified for the use of nanomaterials as fillers in a polymer matrix with some appropriate mixing or incorporation. Hence, it is a critical and crucial task to identify the apt amount of the filler that is suitable for most of the applications. Hence, to identify the apt amount that is suitable for various applications, we had synthesized the PNC using TiO<sub>2</sub> Nano-Particles (NPs) as filler in various amounts in Poly-methyl-methacrylate (PMMA). As synthesized PNC was characterized for their optical, surface and electrical properties. The results are compared in such a manner to find out the apt amount of TiO<sub>2</sub>, which can give the best performance as PNC for various applications. The study illustrates that less than 2% of TiO<sub>2</sub> incorporation is insufficient as the total surface contact is very less that is not suitable for most of the applications. While for the incorporation of more than 5% of TiO<sub>2</sub> NPs, particles get start to agglomerate during the synthesis of PNC that limits the applications of PNC that is generated due to nano-phase of the material. The focused aim of this study is to enhance the properties of polymers in such a manner that they can be used as biomaterials. Hence, we have also explored the wettability and bacterial response of the PNC. Here 3% - 4% incorporation of TiO<sub>2</sub> NPs provides excellent results to PNC, so at these incorporation amounts of  $TiO_2$  in PMMA, this modified PNC can be used as a biomaterial. The technique explores the use of nanotechnology for the new class of PNC with modified properties. © 2020 Elsevier Ltd. All rights reserved.

Selection and Peer-review under responsibility of the scientific committee of the International Conference on Advancement in Nanoelectronics and Communication Technologies.

# 1. Introduction

Biomaterials or biomedical devices are the substances or the combination of substances other than drugs, synthetic [1] or natural [2] in origin that can be used for any period, which augments or replaces partially or any tissue, organ or function of the body to maintain or improve the quality of living beings. The gold was the first material that had been used as a biomaterial for various dentistry purposes [3]. Current advancement and state of the biomedical field show the growing need for the development of materials that can be used as a biomaterial [4]. As these materials

\* Corresponding author. *E-mail address:* agarwal.ravi.cct@gmail.com (R. Agarwal). The gold was teresis, diffusivity and easy processing increases the use of polymers for the synthesis of lightweight materials and biological applications [15–17]. Biological response of the polymeric biomaterial is complex and it depends on surface characteristics, wetta-

age bags [5–14], etc.

bility, chemistry and morphology of the material used [18–21]. No polymer, in general, has these particular properties to be used for various biomedical and other applications [21]. Hence, it shows the growing need for the development of such materials that can

have to be used for the synthesis of various biological implants and materials, such as ear replacement, tendon & knee prosthesis, hip

prosthesis, ocular prosthesis, artificial heart & lungs, synthetic skin,

cardiac valve, tube for Neuron regeneration, catheters, blood stor-

Mechanical and chemical properties like tensile strength, hys-

https://doi.org/10.1016/j.matpr.2020.05.202

2214-7853/© 2020 Elsevier Ltd. All rights reserved.

Selection and Peer-review under responsibility of the scientific committee of the International Conference on Advancement in Nanoelectronics and Communication Technologies.

be used for various biomedical and other applications. Recently Agarwal et al., shown an innovative approach for modulation of physical, chemical and surface properties of polymers using nanos-tructured materials in the polymer matrix [22,23]. Attractive forces between polymeric chains and the tendency of polymerization provide them unique qualities while reinforcing polymers by employing organic [24] and inorganic nanoparticles that causes the surface tuning, abrasion, cross-linking and the modification of the chemical properties in a controlled manner [25–29].

Presence of nanoparticles as filler dispersion in nanocomposites exhibits remarkably improved properties, compared to the pure polymers or their traditional composites [22]. The smaller/ nano size of the filler material provides more area for interaction with the polymer matrix [30]. The interaction area between filler and polymer matrix composite is used in controlling properties of PNC, which make these polymer nano-composite materials special for use in particular applications. PNC represents a new alternative to conventionally filled polymers with diverse applications like flame resistance, conducting properties, composite reinforcement, barrier properties, solar cell applications, gas sensor, biomedical sensors, cosmetics, bound catalysts, fuel cell electrode, polymer blends, high-performance fabrics, ballistic protection, actuators, diffusion barriers, refractive index tuning, corrosion and scratch-resistant [31–37].

Hence, in this study, we have optimized the incorporation amount in the PMMA matrix, applicable in various industries to the synthesis of various biomedical applications. TiO<sub>2</sub> nanoparticles provide vast utility in numerous applications like biomedical imaging, antibacterial activities, sensing, optics, adhesives, printing inks, water purifiers, food colourant and photo catalyzation, solar cell application, sunscreen lotions, organic dust decomposition. Incorporation of TiO<sub>2</sub> NPs in PMMA amends the properties of PMMA drastically, such as synthesis of high refractive index materials with improved optical and electrical properties [20]. PMMA-TiO<sub>2</sub> composites are also used as additives, ultrafast optical nonlinearity measurements, optical waveguide, photovoltaic application, semiconductor materials for biomedical applications, discharge of sweat in artificial skin, urine in kidneys, environment protection and preservation and to form a protective pigment kind of film to get opaque films [35-39]. For the synthesis of TiO<sub>2</sub>-PMMA nano-composite, TiO<sub>2</sub> Nanoparticles have been synthesized by the chemical route and mixed in PMMA in various percentages for the preparation of nano-composite polymer membranes by solution casting method. These membranes are characterized by XRD, SEM, AFM and UV-Vis spectroscopy for the determination of physical and surface characteristics. The electrochemical response of membranes has been determined by measuring I-V characteristics. A study of the bacterial response of these membranes has been determined using E. coli bacteria and wettability has been determined by measuring the water contact angle of the membranes. The results of the analysis are compared simultaneously to determine the best performance of polymer nanocomposites.

## 2. Materials and methods

Synthesis of colloidal TiO<sub>2</sub> NPs had been accomplished using a simple chemical precipitation method as described by Verma et al. [40–42]. TiO<sub>2</sub> NPs were prepared by aqueous hydrolysis of TiCl<sub>4</sub>. The TiCl4 (99.5% pure) was cooled at -20 °C in a deep freezer, then 10 ml of TiCl<sub>4</sub> was taken into stopping funnel and added dropwise into 400 ml of deionized water at the reaction temperature of 0° ± 0.2 °C, under rigorous stirring conditions for 48 h. A white coloured precipitate thus obtained was filtered and washed with

distilled water. These NPs were dried and characterized by TEM and XRD.

Particle size and morphology of the TiO<sub>2</sub> NPs were determined using a Technika TEM instrument operating at 200 kV. The dried NPs were dispersed in acetone by ultra-sonication and a drop of this stable particle dispersion was kept and dried on a carboncoated copper TEM grid, for TEM measurements. Phase and particle size of the TiO<sub>2</sub> NPs were obtained using X'Pert Pro X-ray diffractometer (PAN analytical BV, The Netherlands) operated at 45 kV and 40 mA current. 1.54059Å copper K $\alpha$  radiation was used as a primary source of X-ray. Scanning was done for 20 from 5° to 60° with a step size = 0.01° and time per step = 1.1 s. Particle size was determined by the Debye-Scherer formula and crystalline phases were determined using Powder X high Score Plus software.

PMMA granules were used to prepare 20 µm membranes by a solution casting method. PMMA granules were obtained as commercial-grade from Loxim Polymers, Jaipur-India. Dichloromethane of the extra pure grade was used as a solvent for preparing a polymer solution. PMMA granules were weighed and dissolved in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) using a magnetic stirrer to ensure uniform dissolution and to enhance the rate of dissolution. The process was carried out at room temperature for around 3 h until a clear solution formed then pour it in flat-bottomed Petridishes floating on mercury to obtained uniform thickness membranes. 0.1, 0.5, 1.0, 2.0, 3.5, 5.0 and 8.0 wt% TiO<sub>2</sub> nanocomposite, PMMA membranes were also prepared by solution casting method. For the synthesis of Polymer Nano-Composites Membrane (PNCM), separate PMMA solutions were prepared in the same way as mentioned above for pristine membranes. The appropriate quantity of TiO<sub>2</sub> nanoparticles was dispersed in dichloromethane using ultra-sonicator. These dispersed solutions were then added to the PMMA solutions and stirred for around 30 min then pour into flat-bottomed Petri-dishes floating on mercury to obtained uniform thickness membranes. After the complete evaporation of dichloromethane, membranes were peeled off using forceps.

XRD measurements on synthesized PNCMs were carried out using similar X'Pert Pro X-ray diffractometer (PAN analytical BV, The Netherlands), used for characterization of TiO<sub>2</sub> NPs operating at similar conditions. Topography and effect of TiO<sub>2</sub> casting on surface characteristics of PMMA membranes were carried out using a Scanning electron microscope (Carl ZEISS EVOR –18) operated at 20 kV. Emendation of surface characteristics and surface roughness due to the presence of TiO<sub>2</sub> NPs in polymer membranes were also characterized using Nanosurf Easy Scan-2 Atomic force microscopy. The dual-beam UV–Vis Spectrophotometer (Shimadzu 2100) determined alteration and optical properties of PMMA membranes due to TiO2 incorporation. We have also determined the I-V characteristics of the NC membranes using Keithley Nanovoltmeter.

As these polymer NC membranes can be used for various applications including biomaterial synthesis, hence wettability and antibacterial properties of this material turn out to be an important investigation. Wettability of these PNC had been determined by measuring water contact angle, a 5 µl droplet of double distilled water had been clanged on to horizontal PNC membrane surface and contact angle was determined. Nanoparticles of TiO<sub>2</sub> show admirable catalytic and antibacterial activity against various microorganisms under UV illumination. Hence, the bacterial deactivation rate also investigated for these PNCs using E. coli bacteria. A set of eight pieces (1 cm X 1 cm) were taken from each PNC membrane and used for this investigation. The standard E. coli inoculums were prepared as described by Agarwal et. al. [40] and 10% of these fresh standard inoculums of E. coli (~115 cfu/ml) were inoculated in 100 ml sterilized normal saline, and then 20 µl of this solution was positioned on each piece of PNC and illuminated by UV light. A piece from each set was taken after 1 h then dissolved in dichloromethane and investigated using Spectrophotometer.

# 3. Results and discussion

In this study, we have preferred TiO<sub>2</sub> NPs, as they have a vast range of applications including advance biomaterial synthesis. The synthesized NPs had been characterized by TEM and XRD to confirm the aspect and crystalline phase/ size of the material. The x-ray diffraction pattern of TiO<sub>2</sub> NPs is shown in Fig. 1. The anatase phase TiO<sub>2</sub> NPs were obtained having crystalline planes as A (101), A (121), A (004) and A (211) at the 20 reflection angle of 25.3°, 30.9 °, 36.8 °, and 54.9°, respectively. Crystalline sizes were determined using the Debye-Scherer formula appeared as 5 nm, 5.5 nm, 5.6 nm, and 5.3 nm, respectively. The peak analysis, fitted by the Gaussian curve method of XRD pattern and comparison with JCPDS files (no. 21-1272 and 29-1360) shows the anatase phase of TiO<sub>2</sub> NPs and absence of other reflection planes confirm the absence of other types of contamination with the particles. Particle size and morphology of TiO<sub>2</sub> NPs are obtained by TEM (Fig. 2). TiO<sub>2</sub> synthesized having a spherical shape, narrow particle size distribution and particle size ranging from 5 nm to 10 nm. Distinct particles in the TEM image show no aggregation of TiO<sub>2</sub> NPs.

These NPs were further used for the synthesis of polymer nanocomposites, but it is very important to use the apt amount of NPs in polymers composites. As at the lower amount of NPs in PNC, surface concentration/content of NPs are very low that cannot tender superior performance in various applications while the higher amount of NPs can cause the agglomeration of NPs during the synthesis of PNC that can lead to hindrance/encumbrance of properties generated due to the nanophase of material. Hence, to identify the apt amount of TiO<sub>2</sub> NPs that can give the best performance of PNC in various applications, we had synthesized 0.1, 0.5, 1.0, 2.0, 3.5, 5.0 and 8.0 wt% TiO<sub>2</sub> - PMMA nanocomposite membranes. A pristine membrane of PMMA was also synthesized to use as a control.

The membranes were characterized by XRD to probe the nanocomposite structure and behaviour/state of the NPs in the course of the PNC synthesis. For this particular investigation, monitoring of intensity can give the information about the surface contents of the NPs (for a higher amount of NPs on the surface gives higher



Fig. 1. XRD pattern of TiO<sub>2</sub> nanoparticles synthesized using wet chemical methods.



Fig. 2. TEM micrograph of  $TiO_2$  NPs, showing particle size and their distribution between 5 and 10 nm.

XRD intensity) while diffraction planes at different angles, can give the information about the crystallinity of the PNC and particle size of the NPs in PNC (calculated using Debye-Scherer formula). Fig. 3 shows the XRD patterns of all synthesized polymer membranes and Table 1 elucidates the particle size of the TiO<sub>2</sub> NPs for each PNC. In all the XRD patterns, the crystalline planes for TiO<sub>2</sub> NPs are at a similar position as observed for the synthesized PNC with a similar phase and all parameters. A broad peak corresponding to the amorphous pattern of PMMA was also obtained between 10° -22°. A significant conclusion can be drawn by comparing all the XRD patterns simultaneously. It shows that as the concentration of the TiO<sub>2</sub> NPs incorporation increases the relative intensity of TiO<sub>2</sub> NPs in PMMA also increases, indicating a higher amount of NPs onto the PMMA surface. Whereas by the comparison of the data given in Table 1, we can conclude that particle size remains almost constant up to 3.5 wt% TiO2 incorporation in PMMA but as the percentage increases further, the particle size of NPs also get increased drastically in course of the synthesis of membranes



**Fig. 3.** XRD pattern of various polymer nanocomposites having 0.0, 0.1, 0.5, 1, 2, 3.5, 5, 8 wt% TiO<sub>2</sub> NPs incorporated in PMMA. The spectra clearly show an increase in the relative intensity of TiO<sub>2</sub>, with the increase of TiO<sub>2</sub> incorporation of PMMA.

#### Table 1

Average crystalline sizes for TiO<sub>2</sub> NPs in polymer nanocomposites having different TiO<sub>2</sub> incorporation.

	20 (degree)	FWHM	Size (nm)	Average (nm)
PMMA	_	_	_	-
PMMA + 0.1% TiO <sub>2</sub> PNC	25.3	1.2	7.1	
	30.9	1.1	7.5	7.3
	36.8	1.2	7.4	
	54.9	1.6	7.3	
PMMA + 0.5% TiO <sub>2</sub> PNC	25.3	1.2	7.1	
	30.9	1.1	7.5	7.4
	36.8	1.3	7.2	
	54.9	1.5	7.8	
PMMA + 1.0% TiO <sub>2</sub> PNC	25.3	1.1	7.3	
	30.9	1.2	7.2	7.5
	36.8	1.2	7.4	
	54.9	1.4	8.2	
PMMA + 2.0% TiO <sub>2</sub> PNC	25.3	1.3	7	
	30.9	1.2	7.2	7.7
	36.8	1.1	8.1	
	54.9	1.3	8.8	
PMMA + 3.5% TiO <sub>2</sub> PNC	25.3	1	7.9	
	30.9	1.1	7.5	8.8
	36.8	1.1	8.1	
	54.9	1	11.6	
PMMA + 5.0% TiO <sub>2</sub> PNC	25.3	0.6	14.4	
	30.9	0.5	16.5	15.0
	36.8	0.8	13.3	
	54.9	0.8	15.8	
PMMA + 8.0% TiO <sub>2</sub> PNC	25.3	0.3	32.1	
-	30.9	0.2	40.2	38.0
	36.8	0.2	41.1	
	54.9	0.3	38.9	

(dissolution, incorporation, and drying), indicates for higher amount  $TiO_2$  incorporation, they start losing their properties occurred due to nanoscale. It should be noted that best efficiency generally obtained for the nano-scale phase separations [40]

The morphology and state of NPs in the course of PNC synthesis has also been investigated by SEM (Fig. 4). The topography of PNC shows that TiO<sub>2</sub> NPs were closely packed with PMMA, confirming powerful contact formed between PMMA and TiO<sub>2</sub> NPs. The images show TiO<sub>2</sub> NPs covering the PMMA particles such as connected to form a conductive TiO<sub>2</sub> network in the interstitial space between PMMA particles that can enhance the conductivity of the PNC. The results are in well agree with the results of the study done by Mizuno et. al. showing that 3 wt% titania nanofibers are well dispersed and homogeneously distributed without any phase separation in the polymer matrix. The  $n-TiO_2$  also shows excellent adhesion and strong interfacial bonding to the PMMA [17].

It is well known that the surface roughness/properties are very crucial for biomedical applications and biomaterial synthesis and usually no polymer has the surface properties required for biomedical material synthesis but the incorporation of NPs can offer the desired surface property to the polymers that have been the premier objective of this work. Hence, the influence of the TiO<sub>2</sub> NPs incorporation into the PMMA onto the membrane morphology and surface roughness has been investigated using atomic force microscopy (Fig. 5). The RMS surface roughness values were calculated in Table 2. A significant variation of 45 nm– 486 nm was observed in the surface roughness with the increase of TiO<sub>2</sub> concentration in polymer membranes. The images clearly show that



Fig. 4. SEM micrograph of polymer nanocomposites having 2 and 3.5 wt% TiO<sub>2</sub> NPs incorporated in PMMA.



Fig. 5. AFM micrograph of various polymer nanocomposites having 0.0, 0.1, 0.5, 1, 2, 3.5, 5, 8 wt% TiO<sub>2</sub> NPs incorporated in PMMA.

# Table 2 Average roughness of PNCM determined through AFM imaging.

Samples	Surface Roughness (nm)
PMMA PMMA + 0.1% TiO <sub>2</sub> PNC PMMA + 0.5% TiO <sub>2</sub> PNC PMMA + 1.0% TiO <sub>2</sub> PNC PMMA + 2.0% TiO <sub>2</sub> PNC	45 nm 74 nm 135 nm 185 nm 210 nm 225 nm
PMMA + 3.5% TiO <sub>2</sub> PNC PMMA + 5.0% TiO <sub>2</sub> PNC PMMA + 8.0% TiO <sub>2</sub> PNC	235 nm 296 nm 486 nm

the surface roughness is increasing with the increase of NPs concentration and for up to 3.5% of TiO<sub>2</sub> incorporation, NPs can easily be identified but for the higher concentration of particles, surface roughness increases drastically.

Variation of nanoscale phenomena can also be characterized by the optical properties of the material, as the particle size of the material decreases the band-gap of the material increases. Hence, to determine the effect of different amounts of TiO<sub>2</sub> NPs incorporation in PMMA can also be investigated through UV–Visible spectroscopy. The UV–Visible spectrum of all PNCs has shown in Fig. 6. With the increase of TiO<sub>2</sub> NPs incorporation in PNC, the absorbance of PNC also was increased and the characteristic peak



Fig. 6. UV–Vis spectra of PNCM showing an increase in absorbance of PNC with the increasing  $TiO_2$  incorporation.

of  $TiO_2$  shows a slight redshift with increasing  $TiO_2$  NPs amount, this represents the particles being agglomerated at higher concentrations during the synthesis of PNC.

PMMA is a non-conducting polymer and normally it behaves as an insulator, hence it is used for fabrication of switches and other insulation materials in the electrical industry, while TiO<sub>2</sub> is a semiconductor material but sometimes it shows good conducting properties too. The SEM investigation in Fig. 4 shows that at a level of 3.5% incorporation of TiO<sub>2</sub> NPs, TiO<sub>2</sub> particles are distributed in such a channel view that they are crossing the percolation threshold to convert non-conducting PMMA into conducting PNC. This is due to the TiO<sub>2</sub> NPs connected to form a conducting TiO<sub>2</sub> network in the interstitial space between PMMA; hence, we have also investigated the I-V characteristic of PNC (Fig. 7). The measurement shows that up to the 1% TiO<sub>2</sub> composite PNC, a very small current less than 20nA flows through the membrane that is because there is no TiO<sub>2</sub> conducting channel available to transport the current through PNC. For 2% TiO<sub>2</sub> composite PNC the current amount increase to 200nA but for further increase in TiO<sub>2</sub> incorporation, significantly increase in the passing current was observed (2.1  $\mu$ A, 3.8  $\mu$ A and 4 $\mu$ A for 3.5%, 5% and 8% TiO<sub>2</sub> incorporated PNC) through PNC, due to the manifestation of large TiO<sub>2</sub> channelling in PNC. These results reveal that the PNC having more than 3% incorporation of TiO<sub>2</sub> NPs can extensively use as conducting PNC and fabrication of various organic solar cell devices, as TiO<sub>2</sub> NPs are very absorber of solar UV radiation to convert them in electron-hole pairs (Fig. 8).

TiO<sub>2</sub> NPs have the potential to disengage bacteria under the illumination of UV light has the incorporation of TiO<sub>2</sub> in PMMA proexcellent antibacterial vides properties for biomedical applications. The photocatalytic activity of TiO<sub>2</sub> including successful extermination of bacteria, viruses, and fungi enhanced for the particles below 20 nm. E. coli can be completely killed under UV illumination on TiO<sub>2</sub> film after an hour but only 0.25gm/L nanophase titania to completely exterminate all the E. coli in 10 min. As XRD and SEM result shows that TiO<sub>2</sub> NPs incorporated in the membranes retain its nanophase (<20 nm) for up to 3.5% TiO<sub>2</sub> PMMA PNC. XRD results also indicate that the surface content/ availability of TiO<sub>2</sub> increase with the increase of incorporated TiO<sub>2</sub> amount in PNC. Hence, we had investigated the rate of E. coli survival on these PNC under UV illumination. Eight pieces (1 cm X 1 cm) were taken from each PNC membrane and divided into eight sets such that each set contains a piece of each PNC, then we positioned 20 µl as prepared solution of E. coli on a piece of each membrane. Each set was dissolved after 1 h in dichloro-



**Fig. 7.** I–V characteristic of PNCM, showing higher conductivity for PNCM having 3.5% or more TiO<sub>2</sub> incorporation, as due to these incorporations large manifestation of TiO<sub>2</sub> channelling occurs in PNC to achieve percolation threshold.



**Fig. 8.** A bacterial survival study performed on synthesized PNCM under UV illumination, showing the highest bacterial deactivation efficiency for the 3.5% TiO<sub>2</sub> incorporated membrane.

methane and Optical density (OD) was recorded at 532 nm using Spectrophotometer. Interesting results were found from this investigation that all the membranes show the negative bacterial survival/growth rate (-0.5, -0.8, -1.2, -6.3, -10.2, -15.1, -10.1 and -3.4% per hour for pristine, 0.1%, 0.5%, 1.0%, 2.0%, 3.5%, 5.0% and 8.0% respectively) under UV illumination but the PNC having 3.5% TiO<sub>2</sub> NPs was the best suitable for the extermination of the bacteria as almost all the bacteria were get exterminated in 6 h. Hence, this typical sterilization efficiency of these membranes shows their applicability in various biomedical applications as the number of bacteria in the open environment is very less compared to the bacterial culture ( $\sim$ 115 cfu/ml).

As a biological response to the water-wettable surface is quite different from the biological response to poorly-water-wettable surfaces as the surface energy of material drives the biological response to a given material. Hence, the biocompatibility of material can be shown as a function of the wettability and surface energy of the material. Chemical nature, Surface structure, and surface roughness affect the wettability i.e. contact angle of the solid surface. Hence, the measurement of the contact angle has been performed by the determination of the water contact angle on the membranes. The result indicates that the contact angle is varied from 125° to 66° with the increasing percentage of TiO<sub>2</sub> NPs in PNC. This is important to note here that up to 0.5% incorporation of TiO<sub>2</sub> NPs, variation in contact angles was very small/ negligible; this may be due to a very low amount of NPs on the PNC surface. However, with the further increase of TiO<sub>2</sub> incorporation, the contact angle varies significantly showing that the wettability of the

 Table 3

 Water contact angle and surface energy of PNCM.

Sample	Contact Angle ( $\theta$ in degree)	Surface Energy (mJ/m <sup>2</sup> )
Pristine PMMA	125 ± 1	31.80 ± 0.52
0.1% TiO <sub>2</sub> + PMMA	125 ± 1	31.80 ± 0.52
0.5% TiO <sub>2</sub> + PMMA	121 ± 1	35.37 ± 0.58
1.0% TiO <sub>2</sub> + PMMA	103 ± 1	56.48 ± 0.65
2.0% TiO <sub>2</sub> + PMMA	85 + 1	79 19 ± 0.78
$3.5\% \text{ TiO}_2 + \text{PMMA}$	75 ± 1	91.68 ± 0.85
$5.0\% \text{ TiO}_2 + \text{PMMA}$	68 ± 1	100.11 ± 0.86
$8.0\% \text{ TiO}_2 + \text{PMMA}$	66 + 1	102 44 + 0.92
	0011	1021112 0102

PNC increases or the membranes becomes hydrophilic (Table 3). As the surface energy is inversely proportional to the contact angle, hence surface energy increase with the increase of the TiO<sub>2</sub> incorporation in PNC or the decrease in the contact angle. This makes the water drop more stable on the PNC surface for a longer duration. The Surface energy of the polymer films calculated is shown in Table 3. An important study performed on improving the wetting properties for the biocompatibility of the material used in medicine shows similar behaviour where p-TiO<sub>2</sub> increases the wettability of polymer [28].

# 4. Conclusion

Reinforcing the polymer with nanoparticles for the formation of PNC has started a new technology that is currently using for the fabrication of biomedical sensors, solar cells, biomaterials and implants (such as artificial bone, kidney, skin, skin diaphragm, valves of heart and catheter synthesis. The use of PNC depends on the type, property and amount of nanoparticles that have been used to modify the properties of the base polymer. The apt amount of nanomaterials can modify the surface and physiochemical properties in a controlled manner, so it becomes a crucial task to select the number of nanoparticles that have been loaded. In this particular study, we have quantifies the number of nanoparticles that are suitable for improvement in the properties of polymers. TiO<sub>2</sub> NPs (as advanced biomedical applications) and PMMA (used as a biomaterial for a long time) were selected for this investigation. Anatase phase TiO<sub>2</sub> NPs having a particle size between 5 and 10 nm has been synthesized by the wet-chemical method and used for this particular membrane. The PNC was synthesized in the form of polymers membranes by solution casting method and characterized using various techniques. Based on the results obtained, a comparison is made on the account of surface and physicochemical modifications. The UV-Vis, XRD, SEM and AFM results collectively show that below the 2% of TiO<sub>2</sub> incorporation, the surface content of the NP is very low, so that surface roughness for PNC material is very low, while more than 5% of TiO<sub>2</sub> incorporation in PMMA the particle starts agglomerating during the synthesis of PNC. On the other hand, 3% to 4% of TiO<sub>2</sub> incorporation in PMMA shows the apt amount of NPs on the PNC surface to modify its surface roughness, with maintaining the original particle size of TiO<sub>2</sub> NPs used (8.8 nm as determined by XRD). Further, the investigation was continued by I-V measurements, which shows 2% of TiO<sub>2</sub> incorporation is not sufficient for providing the conductivity to PMMA but as further TiO<sub>2</sub> mixing is increased, the PNC becomes more conductive as at higher percentage it obtains the percolation limit enhances the conductivity. The focused aim of this investigation was to show the use of this PNC for the synthesis of biomaterials with enhanced properties, hence investigation of wettability, surface energy and the bacterial response of the membranes becomes important. The result of this study, also illustrates that less than 2% of TiO<sub>2</sub> incorporation, there was not much increase in surface energy of the materials, hence the wettability of the material is poor but for higher TiO2 incorporation, the surface energy increases significantly, hence the wettability of the material and water contact angle of PNC is improved. The bacterial response of the PNC shows very interesting results because the 3.5% incorporation of TiO<sub>2</sub> NPs gives the best results of deactivation of bacteria, while higher and lower percentage TiO<sub>2</sub> incorporated PNC has shown poor efficiency to kill the bacteria comparatively, the result can be explained on the basis that the TiO<sub>2</sub> NPs below 15 nm is suitable for best deactivation of E. coli under UV illumination. Finally, the comparative study of various characterizations is sufficient to say that 3% to 4% TiO<sub>2</sub> incorporation of TiO<sub>2</sub> in PMMA is an

apt amount for significantly modifying the polymer properties for the fabrication of advanced class of materials.

# **CRediT authorship contribution statement**

**Narendra Kumar Agrawal:** Conceptualization, Investigation. : Methodology. **Ravi Agarwal:** Data curation, Writing - review & editing. **Priti Agarwal:** Supervision.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Acknowledgements

Authors are thankful to the Centre for Converging Technologies, University of Rajasthan for providing research facilities. Authors are also thankful to Council of Scientific and Industrial Research, New Delhi, India (09/149/0695/2016/EMR1) for financial support.

#### References

- M.P. Lutolf, J.A. Hubbell, Synthetic biomaterials as instructive extracellular microenvironments for morphogenesis in tissue engineering, Nat. Biotechnol. 23 (2005) 47–55.
- [2] C.E. Schmidt, J.M. Baier, Acellular vascular tissues: natural biomaterials for tissue repair and tissue engineering, Nat. Biotechnol. 23 (2005) 47–55.
- [3] M.P. Neupane, S. Park, T.S. Bae, H.K. Yi, M. Uo, F. Watari, M.H. Lee, Titania nanotubes supported gelatin stabilized gold nanoparticles for medical implants, J. Mater. Chem. 21 (2011) 12078–12082.
- [4] N.K. Agrawal, R. Agarwal, Y.K. Vijay, K.C. Swami, Characterization of N<sub>2</sub> plasma treated nano composites polymer membranes, J. Mater. Sci. Surf. Eng. 1 (1) (2013) 4–7.
- [5] N. Ehlert, P.P. Mueller, M. Stieve, T. Lenarzd, P. Behrens, Mesoporous silica films as a novel biomaterial: applications in the middle ear, Chem. Soc. Rev. 42 (2013) 3847–3861.
- [6] William R. Webb, Tina P. Dale, Alex J. Lomas, Guodong Zeng, Ian Wimpenny, Alicia J. El Haj, Nicholas R. Forsyth, Guo-Qiang Chen; The application of poly(3hydroxybutyrate-co-3-hydroxyhexanoate) scaffolds for tendon repair in the rat model, Biomaterials 34 (28) (2013) 6683–6694.
- [7] Xu Chen, Chuanyi Bai, Lin Xie, Yongyuan Zhang, Kunzheng Wang, Inflammatory response to orthopedic biomaterials after total hip replacement, J. Orthop. Sci. 17 (4) (July 2012) 407–412.
- [8] Amália Moreno, Marcelo C. Goiato, Daniela M. dos Santos, Marcela F. Haddad, Aldiéris A. Pesqueira, Lisiane C. Bannwart, Effect of different disinfectants on the microhardness and roughness of acrylic resins for ocular prosthesis, Gerodontology 30 (1) (March 2013) 32–39.
- [9] Oh Heung-II, Sang-Ho Ye, Carl A. Johnson Jr, Joshua R. Woolley, William J. Federspiel, William R. Wagner, Hemocompatibility assessment of carbonic anhydrase modified hollow fiber membranes for artificial lungs, Artificial Organs 34 (5) (May 2010) 439–442.
- [10] V.L.M. Rundell, R.T. Beck, C.E. Wang, K.A. Gutowski, M. Sisco, G. Fenner, M.A. Howard, Complication prevalence following use of tutoplast-derived human acellular dermal matrix in prosthetic breast reconstruction: a retrospective review of 203 patients Available online J. Plastic, Reconstr. Aesthetic Surg. (28 May 2014), https://doi.org/10.1016/j.bjps.2014.05.032.
- [11] N.K. Agrawal, K. Awasthi, Y.K. Vijay, K.C. Swami, Synthesis and characterization of plasma treated TiO<sub>2</sub> nano composites polymer membranes, Adv. Electrochem., J. Adv. Electrochem. 1 (2) (2013) 98–104.
- [12] T.G. Mackay, G.M. Bernacca, A.C. Fisher, C.S. Hindle, D.J. Wheatley, In vitro function and durability assessment of a novel polyurethane heart valve prosthesis, Artificial Organs 20 (9) (September 1996) 1017–1025.
- [13] Wesley N. Sivak, Jacqueline M. Bliley, Kacey G. Marra, Polymeric biomaterials for nerve regeneration: fabrication and implantation of a biodegradable nerve guide, Axon Growth Regeneration Methods Mol. Biol. 1162 (2014) 139–148.
- [14] Roger S. Smith, Zheng Zhang, Michael Bouchard, Jun Li, Heather S. Lapp, Gregory R. Brotske, David L. Lucchino, Douglas Weaver, Laurence A. Roth, Arthur Coury, John Biggerstaff, Sivaprasad Sukavaneshvar, Robert Langer, Christopher Loose, Vascular catheters with a nonleaching poly-sulfobetaine surface modification reduce thrombus formation and microbial attachment pp. 153ra132 Sci. Transl. Med. 4 (153) (26 September 2012), https://doi.org/ 10.1126/scitransImed.3004120.
- [15] M.K. Sarath Josh, S. Pradeep, S. Balachandran, R. Sudha Devi, K.S. Vijayalakshmi Amma, Sailas Benjamin, Temperature- and solvent-dependent migrations of di (2-ethylhexyl)phthalate, the hazardous plasticizer from commercial PVC blood storage bag, J. Polym. Res. 19 (June 2012).

- [16] Marie Baeck, Bénédicte Cawet, Dominique Tennstedt, An Goossens, Allergic contact dermatitis caused by latex (natural rubber)-free gloves in healthcare workers, Contact Dermatitis 68 (1) (January 2013) 54–55.
- [17] Y. Mizuno, N. Hayashi, K. Nakamura, Polarisation state optimization in observing Brillouin scattering signal in polymer optical fibers, Electron. Lett. 49 (1) (2013) 56–57.
- [18] Amirpasha Peyvandia, Saqib Ul Abideenb, Yue Huang, Ilsoon Leed, Parviz Soroushiana, Lu Jue, Surface treatment of polymer microfibrillar structures for improved surface wettability and adhesion, Appl. Surf. Sci. 289 (15) (January 2014) 586–591.
- [19] R. Agarwal, N.K. Agrawal, A. Bansal, A. Upadhyay, R. Singh, Neutron irradiation sensitivity of thermal conductivity for Al<sub>2</sub>O<sub>3</sub> nanofluids, Mater. Res. Express (2020).
- [20] R. Agarwal, N.K. Agrawal, R. Singh, Cicer arietinum leaf extract mediated synthesis of silver nanoparticles and screening of their antimicrobial activity, Adv. Sci. Eng. Med. 6 (2) (2014) 203–207.
- [21] N.K. Agrawal, R. Agarwal, Y.K. Vijay, K.C. Swami, Reactive polymer surfaces for cell colonization, J. Mater. Sci. Surf. Eng. 1 (2) (2014) 32–35.
- [22] N.K. Agrawal, M. Singh, Y.K. Vijay, K.C. Swami, Synthesis and characterization of colloidal TiO2 nanoparticles: through titanium chloride rich solutions, Adv. Sci. Eng. Med. 6 (5) (2014) 595–602.
- [23] N.K. Agrawal, R. Agarwal, Y.K. Vijay, K.C. Swami, Plasma etching technology for surface and chemical modifications of aluminium and poly methyl meth acrylate (PMMA) nanocomposites, Adv. Sci. Eng. Med. 6 (6) (2014) 698–703.
- [24] N.K. Agrawal, R. Agarwal, Y.K. Vijay, K.C. Swami, Enhancement of sterilization efficiency of polymer nanocomposite by argon plasma irradiation, J. Bionanosci. 8 (2014) 108–115.
- [25] Guido Kickelbick, Concepts for the incorporation of inorganic building blocks into organic polymers on a nanoscale, Prog. Polym. Sci. 28 (1) (2003) 83–114.
- [26] Ami Eitan, Kuiyang Jiang, Doug Dukes, Rodney Andrews, Linda S. Schadler, Surface modification of multiwalled carbon nanotubes: toward the tailoring of the interface in polymer composites, Chem. Mater. 15 (16) (2003) 3198–3201.
- [27] Naureen Shahida, Richard G. Villateb, Andrew R. Barron, Chemically functionalized alumina nanoparticle effect on carbon fiber/epoxy composites, Compos. Sci. Technol. 65 (14) (2005) 2250–2258.
- [28] Roya Dastjerdi, Majid Montazer, A review on the application of inorganic nano-structured materials in the modification of textiles: focus on antimicrobial properties, Colloids Surf., B 79 (1) (2010) 5–18.
- [29] R. Agarwal, N.K. Agrawal, R. Singh, Low-temperature annealing of cadmium sulphide thin films for improving surface-interface properties, Mater. Focus 3 (4) (2014) 267–271.

- [30] O. Carp, C.L. Huisman, A. Reller, Photoinduced reactivity of TiO<sub>2</sub>, Progr. Solid State Chem. 32 (2004) 133–177.
- [31] H. Tada, T. Ishida, A. Takao, S. Ito, Synthesis, properties, and applications of oxide nanomaterials, Langmuir 20 (2004) 78–98.
- [32] Y.Q. Wang, H.M. Zhang, R.H. Wang, Investigation of the interaction between colloidal TiO<sub>2</sub> and bovine hemoglobin using spectral methods, Colloids Surf., B 65 (2008) 190–196.
- [33] Yanzhong Zhanga, Jayarama Reddy Venugopal, Adel El-Turki, Seeram Ramakrishna, Su Bo, Chwee Teck Lim, Electrospun biomimetic nanocomposite nanofibers of hydroxyapatite/chitosan for bone tissue engineering, Biomaterials 29 (32) (2008) 4314–4322.
- [34] Hassna R.R. Ramay, M. Zhang, Biphasic calcium phosphate nanocomposite porous scaffolds for load-bearing bone tissue engineering, Biomaterials 25 (2004) 5171–5180.
- [35] Moncy V. Jose, Vinoy Thomas, Kalonda T. Johnson, Derrick R. Dean, Elijah Nyairo, Aligned PLGA/HA nanofibrous nanocomposite scaffolds for bone tissue engineering, Acta Biomater. 5 (2009) 305–315.
- [36] Xian Liu, Kun Zhao, Tao Gong, Jian Song, Chongyun Bao, En Luo, Jie Weng, Shaobing Zhou, Delivery of growth factors using a smart porous nanocomposite scaffold to repair a mandibular bone defect, Biomacromolecules 15 (3) (2014) 1019–1030.
- [37] A. Priti Agarwal, S. Kachhwaha Mehta, S.L. Kothari, Green synthesis of silver nanoparticles and their activity against mycobacterium tuberculosis, Adv. Sci. Eng. Med. 5 (2013) 1–6.
- [38] H. Baylay, L. Jayasinghe, Functional engineered channels and pores, Mol. Membr. 21 (4) (2004) 209–220.
- [39] Li Wei, Li Hong, Z. Yong-Ming, Preparation and investigation of PVDF/PMMA/ TiO2 composite film, J. Mater. Sci. 44 (2009) 2977–2984.
- [40] K. Verma, R. Agarwal, R.K. Duchaniya, R. Singh, Measurement and prediction of thermal conductivity of nanofluids containing TiO<sub>2</sub> nanoparticles, J. Nanosci. Nanotechnol. 17 (2017) 1068–1075.
- [41] R. Agarwal, K. Verma, N.K. Agrawal, R. Singh, Comparison of experimental measurements of thermal conductivity of Fe<sub>2</sub>O<sub>3</sub> nanofluids against standard theoretical models and artificial neural network approach, J. Mater. Eng. Perform. 28 (2019) 4602–4609.
- [42] R. Agarwal, K. Verma, N.K. Agrawal, R.K. Duchaniya, R. Singh, Synthesis, characterization, thermal conductivity and sensitivity of CuO nanofluids, Appl. Therm. Eng. 102 (2016) 1024–1036.