Highly Optimized PMMA-TiO_2Nanocomposite using Solution Casting

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***Abstract* - Titanium dioxide polymer nanocomposite are of significant interest due to their extraordinary properties such as high antimicrobial effect, high degree of branching, miscellaneous morphologies and architectures has intensified application in the field of chemical catalyst, antibacterial membranes, biomaterials from tissue engineering, cryogenic superconducting materials, optical -fibers, super lens, DNA screening, biosensors. But most of them work efficiently only for optimized loading/mixing of titanium dioxide nanoparticles in polymer matrix. Hence, we have made a detailed study for optimization of titanium dioxide NPs percentage in polymers. Nanocomposite were synthesized by solution casting method and TiO_2 nanoparticles were mixed in various percentages into these. These nanocomposite were characterized by X-ray diffraction, Scanning electron microscope and I-V measurement; results are discussed in this paper.**

Keywords:Nanocomposite, antibacterial activity, titanium dioxide nanoparticles, solution casting method.

1. INTRODUCTION

Poly(methyl methacrylate) PMMA gathering importance due to its less costs & promising properties such as optical [1], thermal resistance [2], medical applications [3] as in dentistry & implants. PMMA is also known as acrylic glass or plexiglass. PMMA formed with a combination of monomers with chemical reactions [4]. PMMA is cheaper to produce. Many properties which promised better use when applied but some of them needs to be enhanced in order to get the best outcome [5].

In order to overcome or say to get the better result, reinforcing of Nano fillers, nanorods& nanoparticles to the polymers were made, tested & characterized [6]. PMMA nanocomposites were prepared using different techniques such as solution mixing & in situ polymerization. The oxide nanoparticles majorly used in the preparation of the nanocomposites because of their low costing & easily availability [6]. To synthesize oxide nanoparticles, methods such as sol-gel, microemulsion used [7-8].

As there are three ways to prepare nanocomposites which can be given as Solution casting, melt blending & in-situ polymerization [9]. Out of these three stated above, solution casting method is mostly used which is very cheap to use & to obtain results very fast [10]. Therefore, we have used this method in which a polymer, a Solvent &a nanoreinforcement combined & mixed by use of ultrasonification& solvent is allowed to evaporate leaving the nanocomposite in form of a thin film [11].

Applications of the nanocomposites includes fields such as High Performance Fibre/Fabrics [12], Ballistic Protection [13], Microwave Absorbers [14], Microwave Absorbers [15], Solid Lubricants [16], Fire Retardation [17], Ultraviolet Irradiation Resistance [18], Porous Nanocomposites [19], Electrostatic Charge Dissipation in Space Environment [20], Corrosion Protection [21], Actuators [6], Sensors [20]. Recent developments in manufacturing technologies, fabrication, spectroscopic characterization, properties, structure-property relationships, rheology, crystallization behavior, degradability of biodegradable nanocomposites, processing are few commercial applications of polymer nanocomposites [5].

TiO_2 most used material due to its properties in fields include sensors, solar cells, coatings. Being used as to provide whiteness in paints, coatings, papers, inks, and sunscreen. TiO_2 extensively used for inhibiting the bacterial growth with cons as chemically inert, nontoxicity, low cost, biocompatibility. As TiO_2 is pretty much successful, which created interest for improvement of the TiO_2 activity for antibacterial application [20].

TiO_2used as size range upto 15nm which can be said as anatase type which cause photocatalysis& in turn smaller size increases the surface to volume ratio & their photocatalysis performance. Anatase is most stable at sizes less than 11 nm [3-5,13].Static Water contact angle of TiO_2 as 10 degrees indicating a hydrophilic surface. [8,11] Since PMMA is hydrophobic, the interaction between the TiO_2 nanoparticles and the surrounding PMMA is repulsive. [6-7]

2. MATERIALS AND METHODS

The Chemicals used as Titanium trichloride ($TiCl_3$), Ammonium hydroxide (NH_4OH), 2-Propanol ($(CH_3)_2CHOH$ and Double distil (D.D) Water. The $TiCl_3$solution about 20ml taken with 60ml 0.1M NH_4OH (solution) & stir them for 48hours on a magnetic stirrer. The clear indication of the NPs formation of TiO_2 can be judged by white colorless solution formation. The obtained solution was being centrifuged and the extract obtained as a result being washed by D.D water. To get the fine powder form of the NPs, we used iso-propanol to get NPs dried at room temperature.

PMMA granules were obtained as commercial grade from Loxim Polymers, Jaipur and used to prepare flat sheet membranes by solution cast method. PMMA granules are weighed and dissolved in dichloromethane (CH_2Cl_2) to prepare a 10% solution. The solution is stirred by magnetic stirrer to ensure the uniform dissolution and to enhance the rate of dissolution at room temperature for around 5 hours. 3.5% and 8% TiO_2 nanoparticles (PMMA) were dispersed in thesolvent dichloromethane using ultra-sonicator. Thisdispersed solution was added to the PMMA solution and stirred for around 30 minutes. The solution was put into flat-bottomed petri-dishes floating on mercury to ensure a uniform structure of membranes. Solvent was allowed to evaporate slowly over a period of 10-12 hours. The films so obtained were peeled off using forceps.

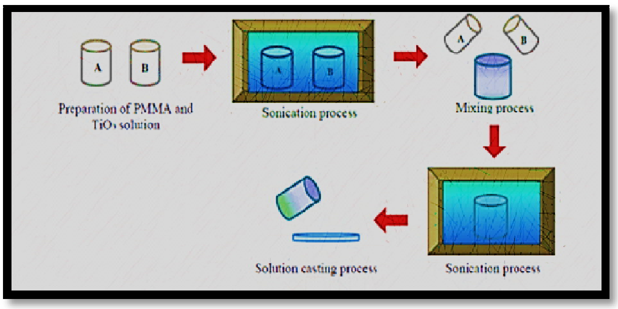

Figure 1. Process of Solution casting for preparation of PMMA membranes.

The particle size and morphology ofTiO_2NPs determined by SEM.SEM analysis was done using scanning electron microscope (Carl ZEISS EVOR -18) operated at 15kV.

The particle size and morphology of TiO_2NPs determined by transmission electron microscopy (TEM). The imaging isperformed using a Technika TEM instrument operating at 200 kV.

3. RESULTS AND DISCUSSION

The figures indicate the quality to determine the NPs size. This image best leads us to use this concentration for the reinforcing with the PMMA NCs whereas the particles seem to be in stable state as they can be seen as set of individual particles.

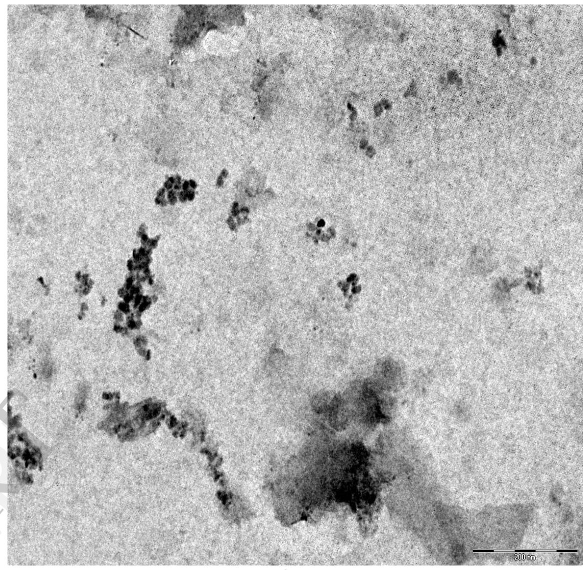

Figure 2. TEM Image of TiO_2 NPs at 100 nm scale.

The TEM image signifies the nanoparticles in the range of approximately 10 – 20nm sizes. The dark areas are the particles while the greyish regions are to be said as the grid of the sample holder in TEM tool.

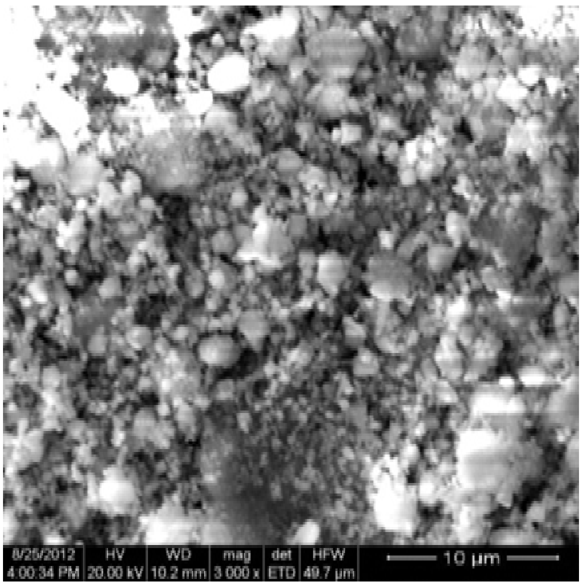

Figure 3. SEM Image of TiO_2 NPs at 10μm scale

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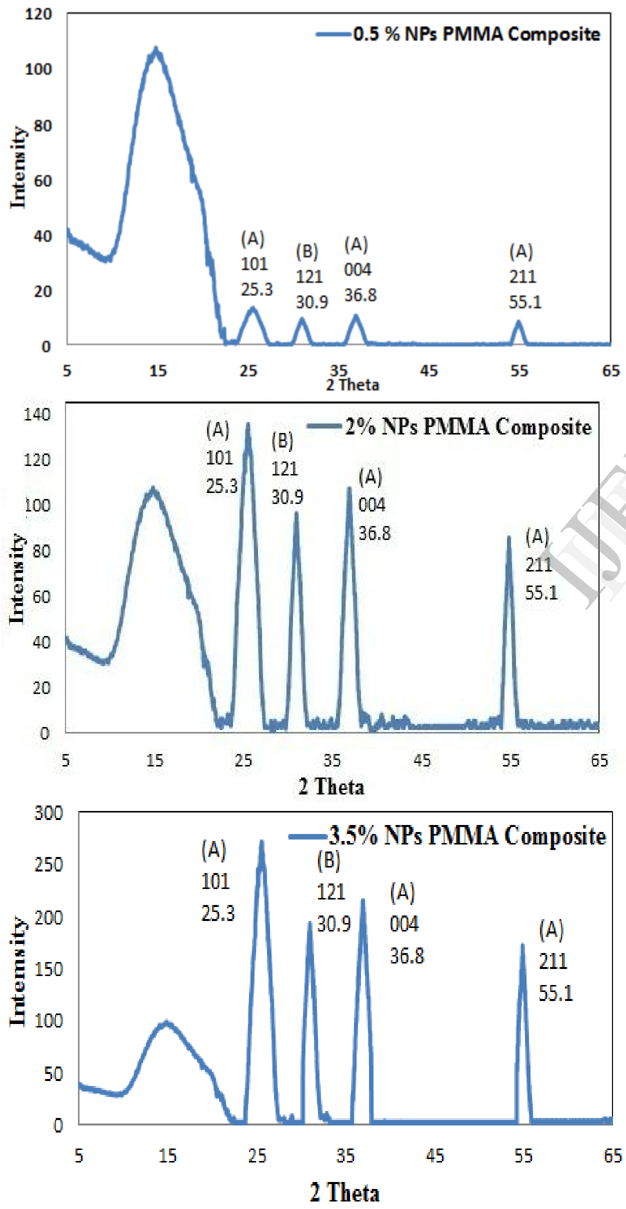
The SEM tool used to determine the structure and the size of the particles so prepared. In order to conclude as we have the nano-dimensions of the particles so synthesized. The spherical shaped nanoparticles were being observed ranging from 10-16nm. As for the determination of the size of NPs, we have used TEM. With using this, the agglomeration of the particles could be seen as with naked eye itself. The TEM tool also being used so as to have the close look at the nanoparticles in order to be in consideration that no agglomeration took place and the particles so formed are not in bulk form but nano-dimensions.



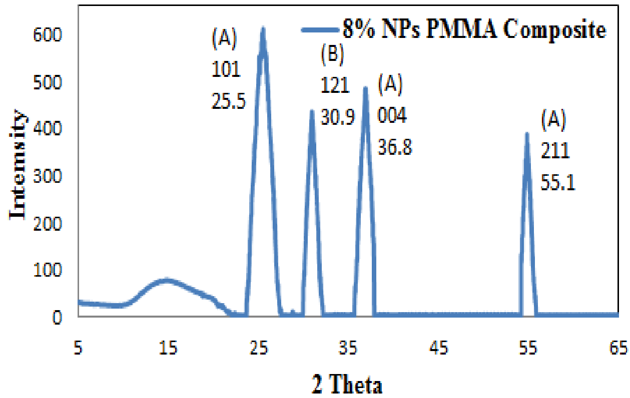
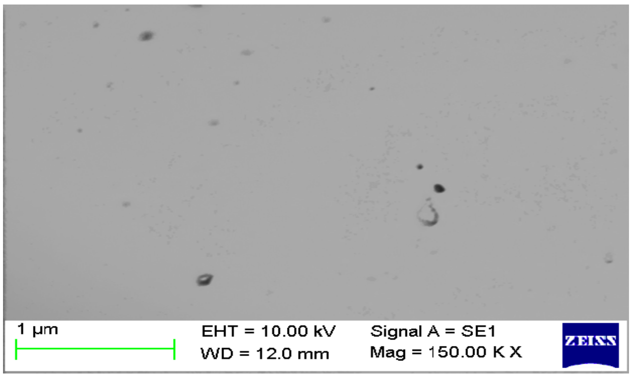
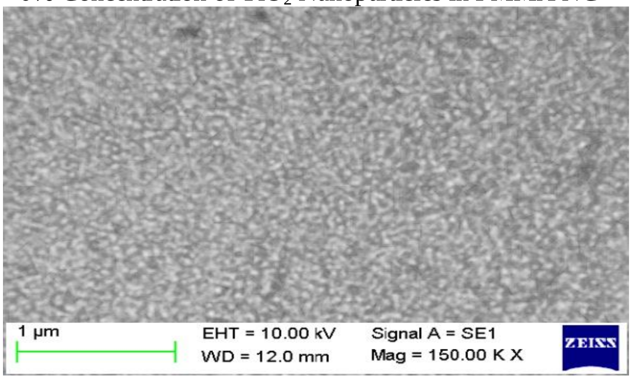


Figure 4.XRD graphs showing the comparison between the nanocomposite sheets having varied concentrations of TiO_2 nanoparticles in PMMA.

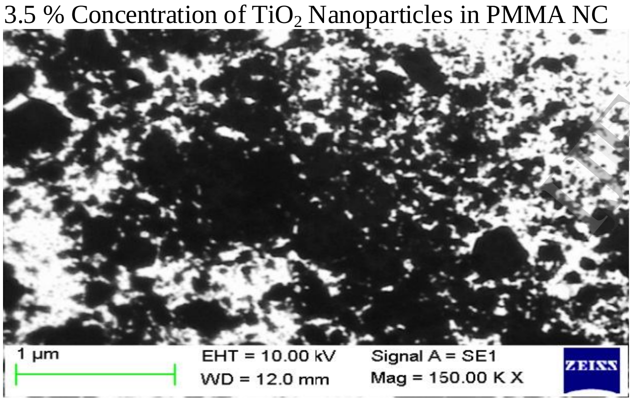
Figure 4 showing the comparision between 0.5% , 2% , 3.5% and 8% of TiO_2 NPs incorporated into PMMA sheets. The XRD images here signify the dimensions of formation of the nanoparticles reinforced into the polymer nanocomposites. We have here 4 samples examined as 0.5%, 2% , 3.5% & 8% as concentrations of NPs into the polymers. The FWHM (Full Width at half Maximum) is the difference between the two extreme values of the independent variable at which the dependent variable is equal to half of its maximum value.The varied NPs concentrations keeps on increasing as the concentration of the NPs increases from 0.5% to 8 wt. %. The angles at which we had recorded peaks are as 25.3°,30.9°, 36.8°and 55.1°with the parameters as A (101), B (121), A (004) & A (211). With respect to the Scherrer equation, crystallite size is reflected in the broadening of a particular peak in a diffraction pattern associated with a particular planar reflection from within the crystal unit cell. It is inversely related to the FWHM of an individual peak, the more narrow the peak, the larger the crystallitesize. If the individual crystallite domains are periodic and in phase, the diffraction of the X-Ray beam is reinforced (the waves are constructively added together), resulting in a tall narrow peak. If the crystals are defect free and periodically arranged, the X-ray beam is diffracted to the same angle even through multiple layers of the specimen. If the crystals are more randomly arranged or they have low degrees of periodicity, resultant is a broader peak.The intensity could be seen to be increasing with the NPs size increased i.e. the particles tend to loose its nanometer sized range and they turned to be in bulk particles. Crystallite sizes were determined using the Scherrer formula for peaks at 25.3°, 30.9° , 36.8° and 55.1° are 14.5, 15.2, 16.0 and 17.5 nm respectively.



0% Concentration of TiO_2 Nanoparticles in PMMA NC



3.5 % Concentration of TiO_2 Nanoparticles in PMMA NC



8 % Concentration of TiO_2 Nanoparticles in PMMA NC

Figure 5.SEM images of the TiO_2NPs reinforced in PMMA sheets.

The SEM images here present us when the agglomeration comes into play with the concentration of the NPs increased in the polymer nanocomposites. The 0% TiO_2 NPs showing very low particle concentrationinto the sheet. The 3.5% concentration of NPs into the Polymer, the spherical shaped NPs could be seen. As in the 8% NPs Polymer sheet, the agglomeration could be seen very clearly as thereis bulk formation.

Figure 6representsseries of the NPs in polymer nanocomposites to test the conductivity of the thin film so prepared. The IV characteristics reveal that the flow of the current is much higher than its counterparts at the 3.5% NPs into the polymer nanocomposites. It can be easily concluded that the loading of 3.5% TiO_2 NPs in the PMMA composite resulted in very conductive thin film rather than its other counterparts. As the concentration made above 3.5%, the NPs starts to get agglomerated which does not account for the best passage of electric current through it.

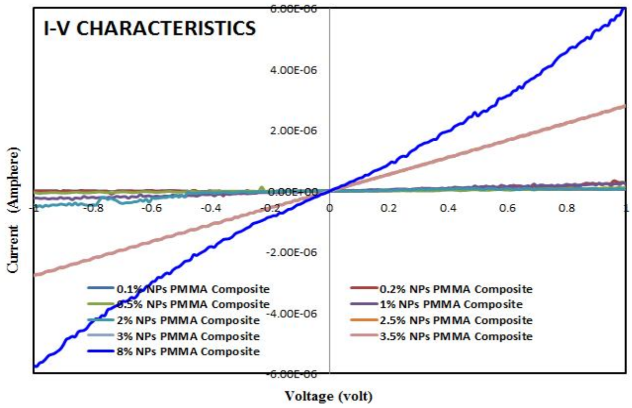


Figure 6. I-V Measurements of the nanocomposites

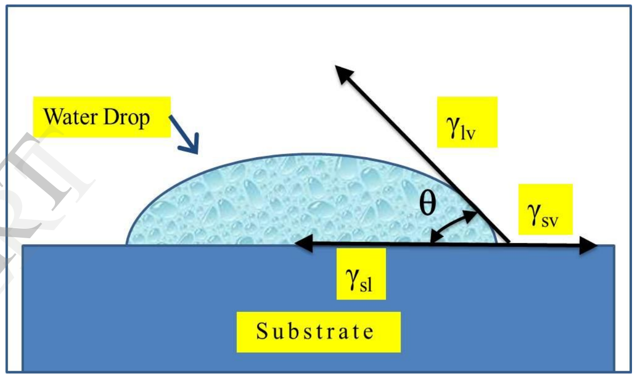


Figure 7. Schematic of contact angle measurement.

The theory of contact arises from the consideration of a thermodynamic equilibriumbetween the three phases: the vapor phase (V), liquid phase (L), the solid phase (S). If the solid–vaporinterfacial energy is denoted by γ_{sv}, the solid–liquid interfacial energy by γ_{sl}, and the liquid–vapor interfacial energy (i.e. the surface tension) by γ_{lv}, then the contact angle θ is determined using Young's Equation for Measurement of Contact Angle[8], figure 7.

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv}\cos\theta$$

Sample	Contact Angle	Surface Energy
0.1%	125	31.10
0.2%	125	31.10
0.5%	121	35.37
1.0%	103	56.48
2.0%	85	79.19
3.5%	75	91.68
5.0%	68	100.11
8.0%	66	102.44

Tabular figure indicates that with decreasing Contact Angle the Surface Energy increases as this can be seen from first angle having Surface energy as 31.10 with last angle having surface energy as 102.44. This shows us the wettability property of the drop over the surface to be more. The Surface energy of the polymer films were found out using the Young's Surface Energy formula.By having the wettability of the polymer highest, the surface would be able to repel the water drops and the surface to be said as to have the hydrophobic property at its highest level.

4. CONCLUSIONS

The primary indication that the particles of the Titanium dioxide being transformed into nanoparticles is the color change of the solution when preparing using the chemical route i.e. white colorless solution, which is further confirmed by analyzing these NPs by different characterization techniquesas TEM, SEM and XRD.Particle size of synthesized titanium dioxide nanoparticles were further confirmed by XRD, TEM and SEM measurements which comes around 10 - 18 nm.

PMMA membranes and TiO_2nanocomposite membrane were prepared by solution cast method. As nanocomposite membranes are prepared without help of any support, it can be concluded that the 3.5% concentration of the loading of the nanoparticles into PMMA is the best which is being studied by IV measurements, water contact angle measurement and surface energy analysis.

The thin films so obtained have the high wettability property so that it can be used as coatings over automobiles.

5. ACKNOWLEDGEMENTS

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