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Investigation of Antibacterial Behavior of Polymethyl Methacrylat Supported TiO_2 Nanophotocatalyst Film

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Abstract: Polymethylmethacrylat / TiO_2 nanophotocatalyst is synthesized by irradiating the solution of TiO_2 in methylmethacrylate monomer by γ-ray. In this method, polymerization of the methylmethacrylate monomer and the TiO_2 reduction occurred simultaneously. Optical properties of the polymethylmethacrylat / TiO_2 solutions are investigated using UV-Vis spectroscopy. The structural characterizations of the polymethylmethacrylat / TiO_2 nanophotocatalyst are determined by FTIR spectroscopy and SEM measurements. The SEM image shows that the TiO_2 nanoparticles disperse in the polymethylmethacrylat matrix with a relatively uniform distribution. The antibacterial studies show that the polymethylmethacrylat / TiO_2 nanophotocatalyst is antibacterial against E.coli, as a model for gram-negative bacteria.

Keywords: TiO_2, PMMA, Film, Antibacterial activity

1. Introduction

Titanium dioxide (TiO_2) as a photocatalytic antibacterial material has considerable beneficial properties such as incompatibility, high potential for self-cleaning and high antibacterial activity and is now the basis for a number of commercial antibacterial products [1,2]. Not surprisingly, there is an increasing interest in combining photocatalytic activity of TiO_2 and hydrophobic polymer for preparation of polymer supported TiO_2 [3-5]. So, polymeric materials are a good candidate to use in the health care industry and environment materials [6,7]. Mills et al. produced low density polyethylene (LDPE)–TiO_2 films by an extrusion method and tested photocatalytic antibacterial activity, via the destruction of Klebsiella. Polymeric material such as Poly Methyl Methacrylate (PMMA) due to hydrophobic nature and low surface energy leads to low bacterial adhesion [2].

The photocatalysis and ultraviolet or visible absorption properties of TiO_2 nanoparticles (NPs) that can also be utilized in antibacterial finishing and anti-ultraviolet finishing of textiles to meet the demand of multi-functional finishing of textiles [8-10]. The aim of this examination is using of polymethylmethacrylat/TiO_2 (hereafter PMMA/TiO_2) NPs that was prepared by ionic liquid based microemulsion in continuation of our research works on microemulsion systems as soft template for nanomaterial's synthesis [11,12]. In previous report, at the first time they are prepared and characterized the PMMA/TiO_2/IL as highly efficient visible light photocatalyst and as an application in waste water treatment field the photodegradation of methylene blue dye was investigated [13]. Having this in mind, in current work, as a new application the antibacterial effect of PMMA/TiO_2 nancomposite based on the destruction of clinical strain of Gram-negative Klebsiella spp. (MTCC 7407*)* with, various loading of TiO_2 was tested in harvest of visible light. With the above in mind, we hope to offer practical approach with our suggested work for a direct industries application because TiO_2 conveniently available in market and the fabrication method is easy.

2. Methodology

2.1. Materials

Hydrophilic ionic liquid, ([BMIM][BF4]) and the nonionic surfactant Triton X-100 were purchased from Sigma- Aldrich. The TiO_2 NPs used in this study was Degussa P25 (ca. 80% anatase, 20% rutile, with a BET

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surface area of 50 m^2/g and particle size of less than 15 nm). Methyl methacrylate (MMA) monomer (AR grade), benzoyl peroxide (BPO) and 1-butanol was received from Merck. All aqueous solutions were prepared with deionized water.

2.2. Preparation of the modified PMMA/TiO_2

In making the PMMA/TiO_2 NPs microemulsion consisting of hydrophilic ionic liquid [BMIM][BF4] (3 wt.%), MMA (88.94 wt.%), TX-100 (5 wt.%) and 1-buthnol (2.24 wt.%) with different loading of TiO_2 NPs was prepared at 60 °C. Benzoyl peroxide (BPO) as an initiator (0.2 wt.%) based on the weight of MMA was added to a range of variety formulated of TiO_2-microemulsion for starting polymerization process. Finally some photocatalyst-embedded PMMA films were prepared and for labeling purposes, the resultant transparent nanohybrid thin films of TiO_2 in PMMA were termed as S1, S2, S3, and S4 refering to the amount (wt.%) of TiO_2 corresponding to 0.008 wt.% PMMA/TiO_2, 0.01 wt.% PMMA/TiO_2, 0.012 wt.% PMMA/TiO_2 and 0.014 wt.% PMMA/TiO_2 respectively. No apparent visible phase separation was observed during polymerization process for all samples. Pure PMMA was also prepared under otherwise the same condition and identically formulated microemulsion without TiO_2 loading. All the films produced were of the uniform thickness with an average central thickness as measured using a micrometer, was 100 μm. All the films were optical transparent, as illustrated by the photograph of example applied PMMA/TiO_2 in Figure .1, indicating transparency and flexibility of films.

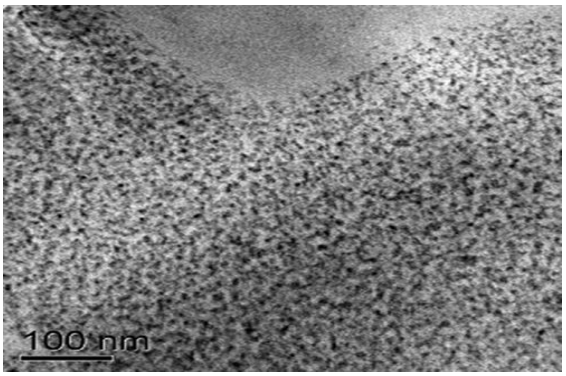

Fig1. The photograph of PMMA/TiO_2 transparent thin film.

2.3. Pilot study

A pilot study was performed to assess the antimicrobial activity of 3 wt.% and 5 wt.% of TiO_2 in PMMA in three forms, using methodology described below. Since comparable antimicrobial activity against S. aurous was seen in both concentrations, 3 w% of NPs was considered, for economic reasons to the end user and less effect on the mechanical properties of denture base resins.

2.4. Preparation of samples with TiO_2

Sample preparation of TiO_2-PMMA composite was done by 3 methods. Mould spaces for specimens were prepared using wax pieces (5 mm™ 5 mm™ 2 mm thickness) in a dental flask. 3 wt.% and 5 wt.% TiO_2 by weight of polymer i.e. 0.3 g and 0.5 g of NPs were weighed and mixed with 1.7 ml of methyl methacrylate monomer and then 8.55 g of polymer (DPI Heat Cure, India) was added to the same. It was thoroughly mixed and on reaching the dough stage was heat cured

3. Results

3.1. Antibacterial activity results

The zone of inhibition toward clinical isolate Klebsiella spp. with pure PMMA and PMMA/TiO_2 NPs with different loading of TiO_2 was evaluated under visible light. The data shows that PMMA/TiO_2 NPs exhibited the antibacterial activity against Klebsiella spp. bacteria than pure PMMA. With increasing TiO_2 dosage, firstly antibacterial activity increases and with further loading, the antibacterial activity decreases. The maximum antibacterial efficiency was belonging to sample S2 of PMMA/TiO_2 NPs and has broad spectrum.

The determined zones of inhibition with pure PMMA as a control sample, S1, S2, S3 and S4 samples were 0, 8 ± 0.50, 20 ± 0.72, 19 ± 0.51 and 12 ± 0.28, respectively. Figure .6, presents the zone of inhibition against toward Klebsiella spp. as an example of Kirby-bauer method. As expected, the antibacterial activity was found to increase with the increasing dosage of TiO_2 and loss of antibacterial activity can be observed at high loading of TiO_2 due to aggregation of NPs in polymer matrix which causing a decrease in the number of surface active site. The main killing mechanism for the antimicrobial effect of TiO_2 photocatalysis is attributed to the hydroxyl radicals and oxygen reactive species as part of the photocatalytic mechanism. The creation of electron–hole pairs during visible light irradiation, which, in turn, can lead to the photocatalytic process. The hydroxylradicals and oxygen reactive species in which the bacterial cell membrane is the primary oxygen reactive species attack site, leading to lipid peroxidation cell membrane. Youssef et al. reported the killing mechanism of the microorganisms originally may be explained as follows: the degradation of the cell wall and cytoplasmic membrane by hydroxyl radicals and hydrogen peroxide that initially leads to leakage of cellular contents. Finally cell lysis followed by complete mineralization of the organism. As can be seen from Figure .2, no zone of inhibition was observed for PMMA in contrast of the conductive polymer such as polypyrrole. Key factors such as electrostatic adsorption between conductive polymer and bacteria, higher molecular weight, surface hydrophilicity and

direct contact between polymer and bacteria cell lead to existence of antibacterial activity of pure conductive polymer.

4. Conclusion

The possible physicochemical interaction Between the TiO_2 nanophotocatalyst and PMMA was tested by FT-IR. It is known that the shift of the peaks toward the lower wave numbers in the FT-IR spectrum is an indicator of the chemical bonding of surfactant onto the nanoparticle surface. The spectra of the neat PMMA and the PMMA/TiO_2composite are shown in Figure .1. As can be seen all the characteristic absorption peaks of standard PMMA including: the sharp absorption at 1728cm-1 (C=O groups), the peaks at 1147 and 1193 cm^{-1} (C–H deformations), and 1244 and 1272cm-1 peaks (C–C–O stretch coupled with C–O stretch), are observed in neat and PMMA stabilized Ag nanoparticles indicating the occurrence of MMA polymerization by γ-ray.

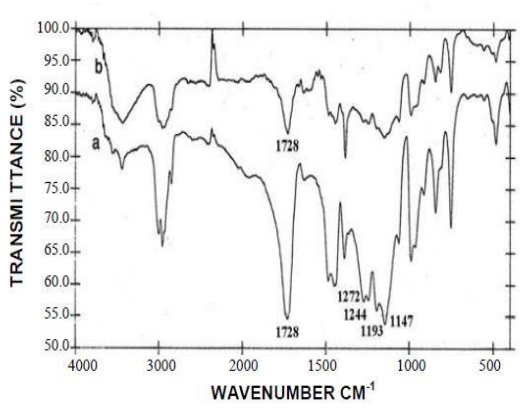

Fig2. FT-IR spectrum of the a) neat PMMA b) PMMA/TiO_2 nanophotocatalyst.

UV-Vis absorption spectra are quite ensitive to the formation of Ag NPs because the position of the surface plasmon absorption peak depends on their particle diameters and shapes. Therefore UV-Vis absorption spectra of the neat PMMA and PMMA/Tio2were obtained (Figure .3). In comparison to neat PMMA, the PMMA/TiO2composite shows an absorption band at about 428nm, which is consistent with the established absorbance wavelength of TiO_2 nanophotocatalyst to determine the size and distribution of the TiO2 nanophotocatalyst, scanning electron microscopy was performed. The SEM micrograph of PMMA/TiO2 composite indicates that Ag particles with mean size of 90±14.4nm disperse in the PMMA matrix with a relatively uniform distribution. This confirms that when reduction of silver ions and the polymerization of monomer take place simultaneously during irradiation, the TiO_2 nanophotocatalyst are homogeneously dispersed in the polymer matrix.

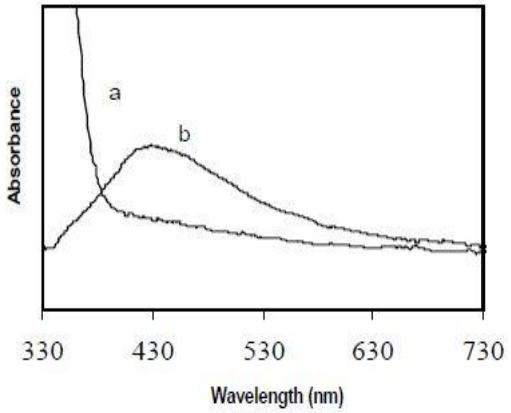

Fig3. UV-Vis absorption spectra of neat PMMA and PMMA/TiO_2 nanocomposite.

Literature reveals many investigations wherein antifungal & antiseptic agents were incorporated /coated on denture base resins or soft liners. However their effect was not persistent, as these agents were rapidly released. Hence, the main objective of this study was to develop and evaluate antibacterial activity of a denture base resin with minimum percentage of visible light photocatalytic additive. Various techniques of preparing visible light activated TiO_2 have been proposed including sol-gel technique, N doped, C doped, Co ion doped – TiO_2 photocatalyst. The disadvantages of doped materials were low surface energy because of using high temperature, requirement of expensive chemicals and synthesis methods and an increase in carrier recontamination. Randron et al. recommended the use of TiN as an alternate precursor in perdioxide based route because of its air and moisture stability, organic and chloride ion free route, simplicity and low cost. In concurrence with the above study, authors would like to state here that TiO_2 NPs were synthesised by a simple and organic free precipitate technique using TiN as a precursor. patterns of the as-prepared & anatase phase confirmed the respective phases of TiO_2. The particle size of TiO_2 as calculated by Debye-Scherer equation was 31 nm. The obtained phase transformation from yellow amorphous to anatase at 800 °C and particle size were consistent with the previous work. Since the anatase form of TiO_2 showed photocatalytic phase which was the required form in our work, we continued the use of anatase form in our work.

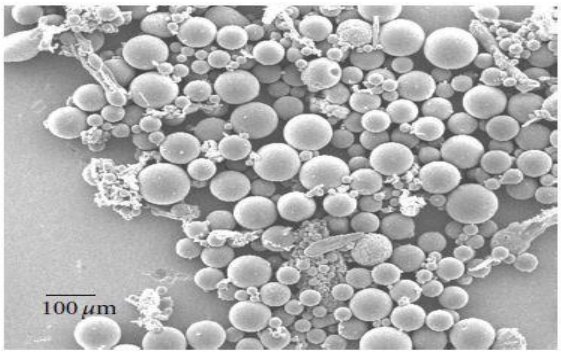

Fig4. Representative SEM photomicrograph of surface of poly methyl methacrylate incorporated with TiO_2 NPs.

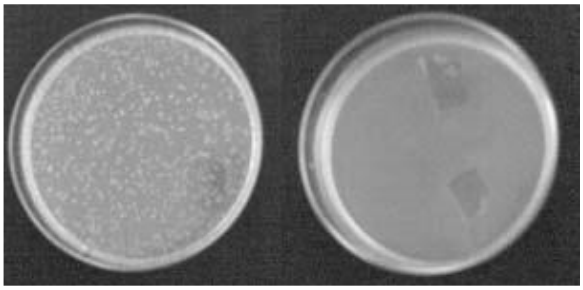

Fig5. Number of E. coli colonies grown on control plates without PMMA/TiO_2

5. References

1) V.K. Sharma, R.A. Yngard, Y. Lin, TiO2 nanophotocatalyst : green synthesis and their antimicrobial activities, Advances in Colloid and Interface Science 145 (2009) 83–96.
2) Q. Li, S. Mahendra, D.Y. Lyon, L. Brunet, M.V. Liga, D. Li, P.J.J. Alvarez, Antimicrobial nanomaterials for water disinfection and microbial control: potential applications and implications, Water Research 42 (2008) 4591–4602.
3) M. Rai, A. Yadav, A. Gade, TiO2 nanophotocatalyst as a new generation of antibacterials, Biotechnology Advances 27 (2009) 76–83.
4) X. Zhang, H. Niu, J. Yan, Y. Cai, Immobilizing TiO2 nanophotocatalyst onto the surface of magnetic silica composite to prepare magnetic disinfectant with enhanced stability and antibacterial activity, Colloids and Surfaces A: Physicochemical and Engineering Aspects 375 (2011) 186–192.
5) M. Zada, Z. Lei, C. Jong-geun, P. Chong-yeon, O. Won-chun .Rare earth oxide-treated fullerene and titania composites with enhanced photocatalytic activity for the degradation of methylene blue, chinese Journal of Catalysis 32 (2011) 1457–1464.
6) M. Sökmen, I. Tatlıdil, C. Breen, F. Clegg, C.K. Buruk, T. Sivlim, Ş. Akkan, A new nano-TiO2 immobilized biodegradable polymer with self-cleaning properties, Journal of Hazardous Materials 187(2011) 199–205.
7) D. Campoccia, L. Montanaro, C.R. Arciola, A review of the biomaterials technologies for infection-resistant surfaces, Biomaterials 34 (2013) 8533–8554
8) T. Harifi, M. Montazer, A review on textile sonoprocessing: A special focus on sonosynthesis of nanomaterials on textile substrates, Ultrasonics Sonochemistry 23 (2015) 1–10.
9) R. Almas, A. Zeeshan, K. Muhammad, H. Memon, I.S. Kim, Antibacterial property and characterization of cotton fabric treated with chitosan/AgCl–TiO2 colloid, Carbohydrate Polymers 96 (2013) 326–331.
10) S. Doakhan, M. Montazer, A. Rashidi, R. Moniri, M.B. Moghadam, Influence of sericin/TiO2 Nanoparticle on cotton fabric: Part 1.Enhanced antibacterial effect, Carbohydrate Polymers 94 (2013) 737–748.
11) A. Salabat, H. Saydi, Microemulsion route to fabrication of silver and platinum-polymer Nanoparticles, Polymer Composites 35 (2014) 2023-2028.
12) S. Soleimani, A. Salabat, R.F. Tabor, Effect of surfactant type on platinum nanoparticle size of composite Pt/α Al2O3 catalysts synthesized by a microemulsion method, Journal of Colloid and Interface Science 426 (2014) 287- 292.
13) F. Mirhoseini, A. Salabat, Ionic liquid based microemulsion method for fabrication of poly(methyl methacrylate)–TiO2 Nanoparticle as highly efficient visible light photocatalyst, RSC Advances (DOI: 10.1039/C4RA14612C).