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Silver on PEG-PU-TiO_2 Polymer Nanocomposite Films: An Excellent System for Antibacterial Applications

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Silver impregnated on polymer-titania nanocomposite films exhibit excellent antibacterial properties with the added advantage of repeated use. The polyethylene glycol-polyurethane-titania designated as PEG-PU-TiO_2 polymer nanocomposite films were synthesized by simple solution casting technique. Silver has been incorporated into these films by photochemical reduction of silver nitrate solution. The TiO_2 facilitated the UV photoreduction of $AgNO_3$ to Ag, which is active as an antibacterial agent. Fourier Transformed Infrared Spectroscopy (FT-IR) confirms the formation of the polymer, polyurethane. X-ray Diffraction (XRD) determined the structure and scanning electron microscopy (SEM), the morphology of the films. XPS confirms the Ag to be in zero oxidation state and the amount of silver impregnated in the films as estimated by scanning electron microscopy−energy-dispersive X-ray analysis (SEM-EDAX), and atomic absorption spectroscopy (AAS) is about 2−4 at %. The antibacterial properties of these films were studied on *Escherichia coli* and *Bacillus subtilis* by the disk-diffusion method and this has been correlated with the percentage of Ag in the films. One very encouraging observation is that the antibacterial activity of the Ag in polymer-titania nanocomposite films showed reasonable activity even when tested in the microbial broth.

Introduction

Nanometer-sized inorganic particles and composites display very interesting physical and chemical properties and thus herald a new class of materials for the development of novel devices, which have a wide range of applications.[1] In particular, composites of inorganic particles in polymer matrices have been proven to be advantageous because of the properties exhibited by the inorganic nanoparticles and the flexibility offered by the polymer host.[2,3] In this context, metal nanoparticles like Ag, Au, etc., and oxides like SnO_2, TiO_2, etc., in different polymer matrices have been tried. The biological activity of silver makes it a suitable candidate for applications in industry and hospitals as an antimicrobial. Silver is also known for its water and air purifying ability. In spite of these findings, research is going on to develop still more convenient methods to exploit the beneficial properties of silver in newer applications. In this context, the study of interaction of nanoparticles with biological systems including living cells has become one of the challenging areas of collaborative research in materials science and biology.

Certain metal ions exhibit antimicrobial activity by a number of methods, such as binding themselves to a variety of organic ligands causing denaturation of proteins, including enzymes; disrupting cell membranes; and decomposing essential metabolites.[4] Silver is probably the most powerful antimicrobial that exhibits a strong cytotoxicity toward a broad range of microorganisms, and simultaneously a remarkably low human toxicity compared to other heavy metal ions. It has an oligodynamic effect, that is, silver ions are capable of causing a bacteriostatic (growth inhibition), or even a bactericidal (antibacterial) impact. In recent years it has been used in a variety of medical applications ranging from wound dressings to urinary catheters.[5–8] It even finds application in biomedical materials, such as bone cement, and artificial skin, and in the prevention of nosocomial infections related to the use of medical devices.[9,10] Polymer with its characteristic morphology serves as a convenient substrate, or matrix, and is one of the ideal choices for use in devices. Incorporation of silver into polymer matrix would lead to development of materials that could conveniently be used for the above explicit application.

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Within an expanding polymer market, attention can be drawn to polyurethanes, which have found applications in furniture, automobiles, construction materials, coatings, adhesives, medical applications, etc.[11] The high mechanical and chemical resistance, and high rubber like elasticity, ductility has made thermoplastic polyurethanes (TPUs) suitable for a number of medical applications like catheters, etc. In this scenario the synthesis, and application of polymer-inorganic hybrid films for biomedical applications is of great importance. Silver-polymer composites have been utilized for many other applications because of their electrical conductivity, antimicrobial effects, optical properties, and oxidative catalysis. Some results on silver-reinforced polymer composites have been reported in various polymer matrices.[12–17] However, in order to make use of silver economical, there is a need to find cheaper ways of using silver in potential applications without sacrificing its specific functionalities, and one of the present-day challenges is to develop a material, that provides high, and long-lasting antimicrobial effects, while maintaining low human toxicity.

Our earlier work demonstrated the antibacterial activity of silver doped titania nanoparticles.[18] The present study is an effort toward the synthesis of silver in polymer-TiO_2 nanocomposites to obtain an easy and convenient system with good antibacterial activity, with the capability for reuse. The PEG-PU networks were synthesized with TiO_2 nanoparticles and silver was incorporated into this system by invoking the photocatalytic activity of TiO_2, which facilitates the photoreduction of $AgNO_3$ to obtain Ag in the polymer matrix. In this system, the role of the polymer film is that of a support material for easy, and convenient handling, and reuseability.The films have been well characterized by XRD, FT-IR, EDAX, AAS, etc. The presence of silver has been confirmed by XRD and its oxidation state by XPS. SEM images showed that metallic silver gets deposited both on the exterior and in the interior part of the polymer films. The antibacterial activity of these films was studied by the disk diffusion method.

Experimental Section

Materials. Castor oil (CO) (BSS grade), diphenylmethane diisocyanate (MDI) (Merck), poly (ethylene glycol) (PEG) ($M_w \approx$ 4000) (s.d. fine-chem Ltd.), titanium tetrachloride ($TiCl_4$) (Spectrochem. Ltd.), hydrochloric acid (HCl) (RANKEM), hydrazine hydrate (s.d. fine-chem Ltd.), tetrahydrofuran (THF) (RANKEM), benzyl alcohol (Aldrich), 4-*tert*-butylcatechol (S.D. Fine-Chem Ltd.), dichloro methane (s. d. fine-chem Ltd.), N,N-dimethyl aniline (DMA) (s. d. fine-chem Ltd.), silver nitrate (LOBA CHEMIE), titanium isopropoxide (Lancaster), isoproponol (Merck), and commercial anatase titania (referred to as CT) (Aldrich). The solvent THF was dried over molecular sieves prior to use. All other chemicals were used as received without further purification.

Synthesis. *(a) Synthesis of Titania Nanoparticles.* Twenty-five milliliters of 50% (v/v) HCl solution of $TiCl_4$ was first diluted in 4 L of deionized water. Then 1:1(v/v) solution of hydrazine hydrate in deionized water was added dropwise under stirring to adjust the pH of the solution to 8. The reaction mixture was left under vigorous stirring for 4 h and the precipitate was allowed to settle down. Precipitate was washed several times with distilled water to remove chloride ions and then dried at 70 °C in an oven. The titania nanoparticles were characterized for their size and morphology by transmission electron microscopy.

(b) Synthesis of 4-tert-Butylcatechol-Coated Titania Nanoparticles. 4-*tert*-Butylcatechol coated titania has been synthesized by following the procedure reported earlier.[19] In brief, 0.5 g of (3.0 mmol) 4-*tert*-butylcatechol was dispersed in 60 mL benzyl alcohol inside a hood. Three milliliters of (27.2 mmol) $TiCl_4$ was slowly added to the above solution under vigorous stirring at room temperature. The dark red reaction mixture was aged at room temperature for about 2 h and then heated to 70 °C and then aged for 5 days. The resulting brown suspension was centrifuged and the precipitate was thoroughly washed with methylene chloride twice. After each washing step the solvent was removed by centrifugation. The collected material was left for drying at room temperature and subsequently at 60 °C and this is designated as catechol coated titania (CCT).

(c) Synthesis of Carbon-Doped Titania. The carbon doped titania nanoparticles have been synthesized by controlled hydrothermal method using titanium isopropoxide (TIP) as the titanium source. In a typical reaction, 4.5 mL of TIP was diluted with 50 mL of isopropyl alcohol (IPA) in cold condition. This solution was added to 100 mL of distilled water and after this addition the transparent solution became white turbid. Then required amount of distilled water was added dropwise under cooling and stirred for another 15 min in cold and for further 15 min at room temperature. The solution was then transferred to an autoclave and subjected to hydrothermal treatment for 0.5 h at 175 °C. After completion of the reaction, the whole system was allowed to cool to room temperature. The product was washed with distilled water, dried, and ground to a fine powder. This has been designated as CaT.

(d) Preparation of PEG-PU Polymer Network Films. CO and MDI were taken in THF. The reaction mixture was then degassed and stirred under nitrogen atmosphere at room temperature for 1 h. A solution of PEG in THF was added along with DMA (catalyst) and continued stirring for another one hour. The resulting yellow colored solution was cast on a glass petri dish and allowed to dry at room temperature for 24 h and at 80 °C for another 24 h. For the synthesis of PEG-PU network, the OH/NCO ratio of 1:1.1 was maintained. These PEG-PU polymer films designated as (P) were stored in a desiccator till further use.

(e) Preparation of PEG-PU-TiO_2 Polymer Nanocomposite Films. Titania nanoparticles have been used to prepare uniform PEG-PU-TiO_2 films.During the process of synthesizing PEG-PU network as described above, 1 h after the addition of PEG, a solution (in the case of CCT) or dispersion (in the cases of ST, CT or CaT) of 2 wt % titania in THF was added and stirred continuously for about 20 h at room temperature. The resulting mixture was then

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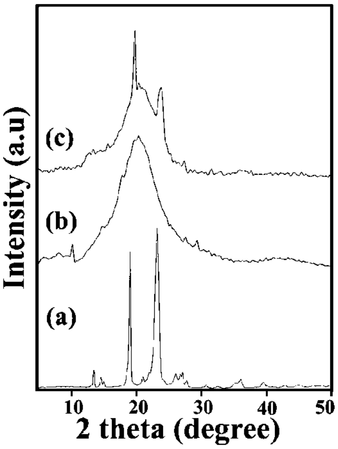

Figure 1. Typical X-ray diffractogram of (a) PEG, (b) PU, and (c) PEG-PU polymer network.

cast on a glass petridish and the further processing is the same as described earlier.

(f) Deposition of Silver on the PEG-PU-TiO$_2$ Films. PEG-PU-TiO$_2$ films were taken in the form of small discs of about 11 mm in diameter and 0.3 mm thickness. The discs were dipped into a solution containing 40 mL of 1.25% AgNO$_3$ (w/w) and 10 mL THF and exposed to 400 W, UV light of wavelength 365 nm. The photochemical reaction was carried out for an hour under stirring condition with external cooling to avoid heating effects. The discs were dried at room temperature and stored in a desiccator. Silver has been deposited using both visible and UV light on the polymer films containing carbon doped titania and referred to as AgPCaT (vis) AgPCaT (UV) respectively.

Characterization. The synthesized materials were characterized by XRD, SEM-EDAX for their structure, morphology and composition, FT-IR for the confirmation of the polymer network formation and UV-DRS, XPS and AAS for the nature and concentration of the silver in the films.

X-ray powder diffraction (XRD) patterns were taken in reflection mode (Cu Kα radiation) in the 2θ range from 2 to 80° on a Siemens (Cheshire, UK) D5000 X-ray diffractometer by continuous scanning with a step size of 0.01°. Scanning electron microscopic (SEM) images were obtained on a Hitachi S520 scanning electron microscope. EDAX was taken in an Oxford link ISIS-300 instrument. FT-IR spectra were recorded at room temperature in the range of 4000 to 400 cm^{-1} using a Perkin-Elmer Spectrometer GX model with a wavenumber resolution of 4 cm^{-1}. XPS spectra were recorded on a Kratos X-ray photoelectron spectrometer and AAS data were collected in a Flame AAS Perkin-Elmer Analyst 300. UV–visible diffuse reflectance spectra UV–DRS) were recorded on a GBC UV–visible Cintra 10/20/40 spectrometer on dry-pressed disk solid-samples using KBr as dilutor and pure KBr as the reference.

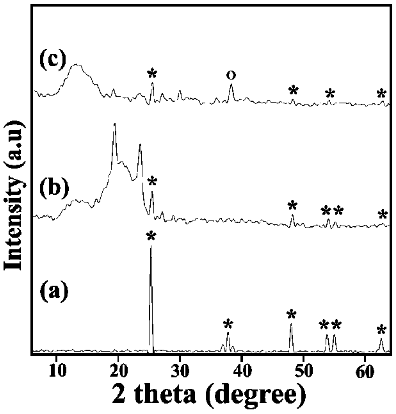

Figure 2. Representative XRD patterns of (a) CT, (b) PEG-PU-TiO$_2$, and (c) Ag-PEO-PU-TiO$_2$ polymer nanocomposite. ∗ indicates peak for anatase TiO$_2$. whereas o corresponds to metallic silver.

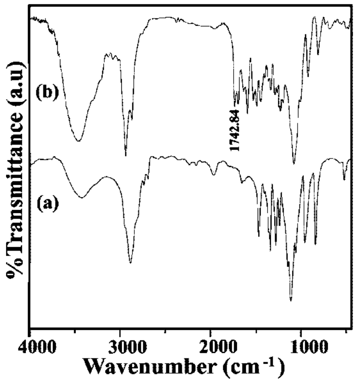

Figure 3. FT-IR spectra of (a) PEG and (b) PEG-PU polymer network.

Results and Discussion

XRD. X-ray diffraction patterns of PEG, PU and PEG-PU films are shown in Figure 1a−c. The diffractogram of PEG (Figure 1a) shows the presence of a crystalline phase with the characteristic diffraction peaks in the 2θ range from 10° to 30° particularly located at 2θ =19° and 23.5°.[20] Such a crystalline nature of PEG originates from the ordering of the polyether chains. These peaks become less intense in the PEG-PU networks (shown in Figure 1c), which implies PEG becomes less crystalline in the polymer due to the formation of network. Figure 1(b) shows the weak diffraction peak near $2\theta = 20°$,[21] which is due to the hard segment of PU, its intensity being associated with the hard segment content. The XRD patterns after incorporation of titania in the polymer matrix and the deposition of silver are shown in Figure 2(a-c). Figure 2a exhibits the peaks at $2\theta = 25$, 48, and 54°, characteristic of anatase titania. Figure 2(b) is the diffraction pattern of PEG-PU-TiO$_2$ nanocomposite. In this diffractogram TiO$_2$ peaks are observed, but with reduced intensity. As seen in Figure 2c, the Ag-PEG-PU-TiO$_2$ displays a new peak at $2\theta = 38.2°$ which is the characteristic (111) plane of face-centered cubic crystalline silver.[22] This confirms the formation of crystalline silver in PEG-PU-TiO$_2$ polymer nanocomposite matrix by the reduction of silver nitrate under UV-light.

FT-IR. Figure 3 shows the FT-IR spectra of PEG and PEG-PU network in the region 4000–400 cm^{-1}. The band of the C−O−C stretching vibrations at 1111.60 cm^{-1} as shown in Figure 3a is evidence for the presence of crystalline phase of PEG and this is clearly observed in the IR spectrum of PEG. Characteristic absorption peak at 1742.84 cm^{-1},

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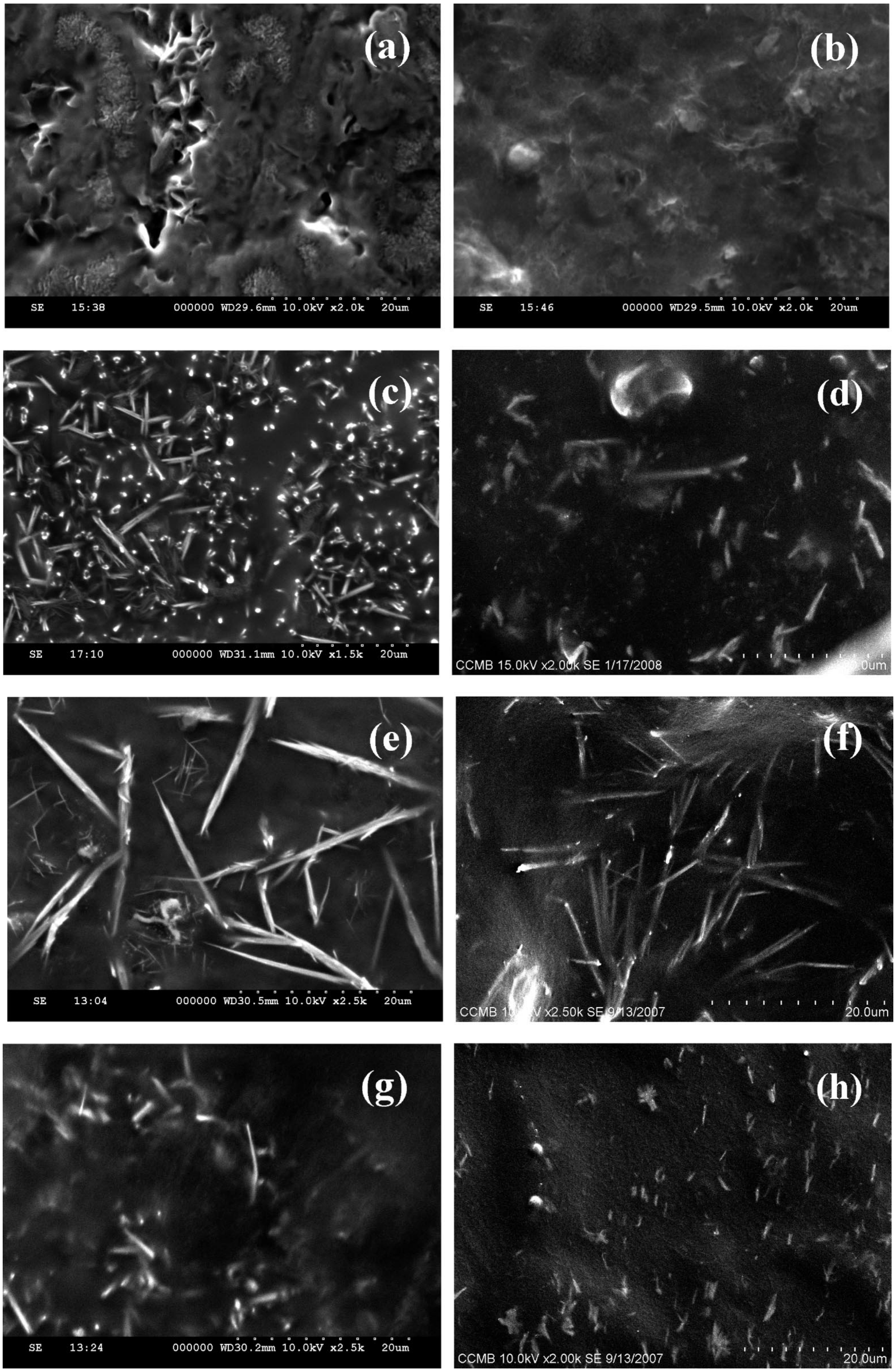

Figure 4. SEM micrographs of exterior surfaces of (a) PEG-PU, (b) PEG-PU-TiO_2(c) AgPCT, (e) AgPST and (g) AgPCCT, and the fractured surfaces of (d) AgPCT, (f) AgPST, and (h) AgPCCT.

shown in Figure 3b, is associated with the carbonyl group stretching frequency of urethane linkage of polyurethane, which has been formed by the reaction of OH groups of CO and PEG with NCO groups of MDI. The broadband around 3440 cm^{-1} is for free N−H stretching frequency of urethane linkage. The band appearing at 1520 cm^{-1} is assigned to the bending vibration of the N−H group[23,24] in PU. Peaks at 2926 and 2858 cm^{-1} correspond to methylene C−H and methyl C−H stretching frequency respectively. No change in FT-IR spectrum is observed after TiO_2 incorporation and even after Ag deposition.

SEM. Images a and b in Figure 4 represent typical SEM micrographs of PEG-PU and PEG-PU-TiO_2 films, respec-

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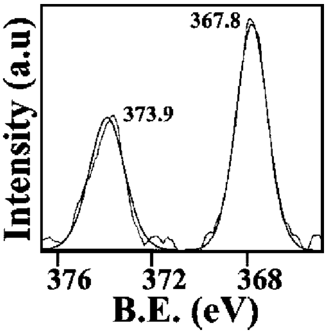

Figure 5. Ag (3d) XPS spectrum of Ag-PEG-PU-TiO$_2$ film.

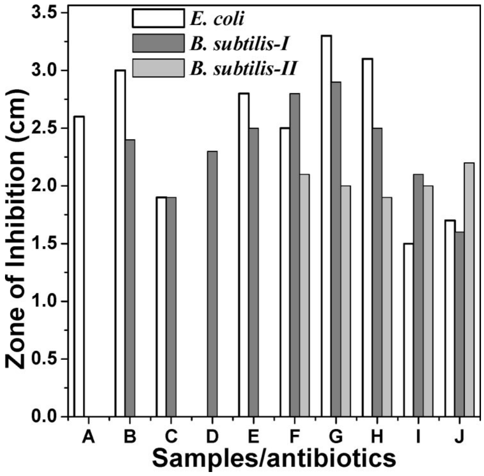

Figure 6. Comparison of antibacterial activity in terms of the zone of inhibition of the discs with standard antibiotics where A−E are antibiotics penicillin, tetracycline, ampicillin, kanamycin, and streptomycin respectively, and F−J are prepared samples, respectively, AgPST, AgPCT, AgPCCT, AgPCaT (UV), and AgPCaT (vis).

tively. The micrographs of PEG-PU and PEG-PU-TiO$_2$ show similar morphology, which implies that titania nanoparticles are embedded inside the polymer matrix uniformly and their presence does not change the network structure. Only difference in these two micrographs is that the presence of titania decreases the roughness on the polymer surface. For comparison, we have used micron sized titania particles to make the composite. The particles tend to settle down and we do not get a uniform distribution of particles inside the polymer matrix.

SEM micrographs of Ag-PEG-PU-TiO$_2$using different titania sources are shown in Figure 4(c−h). Images c, e, and g in Figure 4 show the unfractured faces of AgPCT, AgPST, and AgPCCT nanocomposites, respectively, and images d, f, and h in Figure 4 show the interior face of these films obtained by fracturing in liquid nitrogen. SEM micrographs of Ag-PEG-PU-TiO$_2$ show silver microrods of width of about 400 nm scattered in the polymer matrix. During the process of silver incorporation the films were soaked in the silver nitrate solution and when exposed to UV light the silver ions got reduced to metallic silver. As a result silver is incorporated both inside and on the polymer matrix as seen in the micrographs.

XPS. The Ag 3d$_{5/2}$ regions of the XPS spectra for silver nanocomposite films are very sensitive to the chemical environment surrounding the silver and can provide important information to distinguish between silver ions and metallic silver.[25–28] Figure 5 shows the Ag 3d$_{3/2}$ and 3d$_{5/2}$ XPS spectrum of Ag-PEG-PU-TiO$_2$ polymer nanocomposite films. The Ag 3d spectrum shows single peaks at 367.8 and 373.9 eV assigned to Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$ peaks, respectively, matching with binding energy value of silver in zero oxidation state as reported by Shah et al.[29] This XPS peak position of the Ag 3d$_{5/2}$ is somewhat lower than the values reported by Kobayashi et al.[27] and Gole et al.[28] This difference could be because the silver binding energy is very much dependent on the environment and in this case the polymer network is responsible for the observed shift. Probably the silver is interacting with electronegative oxygen and nitrogen present in the polymer network, resulting in a small distortion of electron density from the silver atoms toward these electronegative atoms, leading to the small shift in the silver binding energy toward lower values. Support for this conclusion of the metallic state of Ag comes from XRD, which shows a peak for the Ag (111) at $2\theta = 38.2°$ and the characteristic plasmon peak of metallic silver at about 430 nm in the UV-DRS.

Antibacterial Properties of the Films by the Disc Diffusion Method. The antibacterial tests of the Ag-PEG-PU-TiO$_2$ films were carried out by the standard disk diffusion assay according to the procedure of Conner and Beuchat,[30] and Elgayyar et al.,[31] on LB agar medium. In these tests *E. coli* and *B. subtilis* were used as model bacteria. It is well-known that titania in the anatase form shows enhanced photocatalytic and antimicrobial activity only under UV illumination. To exclude the effect of titania, the antibacterial tests on these coatings were conducted without any special illumination in order to see the antibacterial effect of silver only. All bactericidal activity tests were performed in daylight and in these tests discs of 11 mm diameter and 0.3 mm thickness were used. The discs of PEG-PU-TiO$_2$ impregnated with silver were very efficient as antibacterial agents. The discs of PEG-PU and PEG-PU-TiO$_2$ (for all types of titania) without the silver were not able to create a zone of inhibition in the bacterial growth lawn, which implies that these discs have no antibacterial activity. The silver containing discs were effective both against Gram-negative and Gram-positive bacteria and showed better antibacterial activity compared to standard antibiotics and they could be used repeatedly. Figure 6 shows the bar-graph comparison of antibacterial efficiency of the prepared discs with standard antibiotics. Two of the samples AgPCT and AgPCCT even showed better activity than the standard antibiotics. AAS studies showed that in these two systems the amount of silver is

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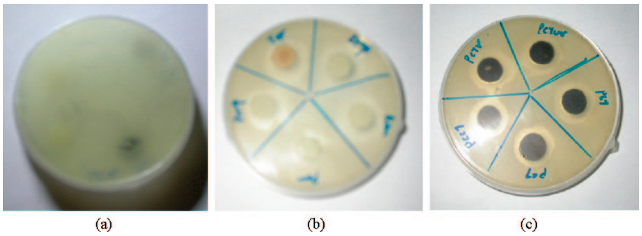

Figure 7. Visual images of zone of inhibition of (a) control, (b) with antibiotics, and (c) with synthesized Ag-PEG-PU-TiO_2 films.

nearly same (∼4 at %). It is seen that the other samples (AgPST, AgPCaT (UV), AgPCaT (vis)) showed a comparatively lesser activity and this could be attributed to the lower content of silver in these samples (∼2–3 at %) as revealed by AAS analysis. The discs showed reasonable activity even after being used second time (*B. subtilis*-II).

The antibacterial activity of the discs was also assessed in suspension culture. About 5 mL of LB media broth were taken in sterile bottles and incubated with *E. coli*. The discs were left in the media. After 48 h, the optical density of the samples was measured to assess the growth of bacteria. There was significant decline in the bacterial growth in presence of these discs in broth cultures revealing their effectiveness in broth also.

Figure 7 displays the zone of inhibition for the antibiotics and prepared samples. It is clearly showing that the synthesized samples are more effective in creating a sharp zone of inhibition compared to the antibiotics.

A plausible reason for this excellent antibacterial activity exhibited by the films could be understood from earlier studies. It is well-known that Ag^+ hinders DNA replication and inhibits expression of ribosomal proteins and enzymes for ATP hydrolysis.[32,33] But the exact role of silver nanoparticles is not very clear. Most likely Ag nanoparticles display the same mechanism as Ag^+ and create redox imbalance causing extensive bacterial death and the large surface area of the nanoparticles makes this action more effective. It has been shown that release of silver is controlled by an oxidation mechanism at the surface of the nanoparticles and this diffusion of the Ag^+ ions determines the extent or zone of activity as seen as the zone of inhibition.[34] One unpublished study tracked tagged silver ions, indicating an absence of silver from within bacterial cells; only surface −S−H groups were affected (Davies and Etris 1997). This could explain why only bacteria and viruses are affected by silver ions, as opposed to mammalian cells that do not have exterior sulfhydryl groups. Silver ions may not be capable of permeating through cell membranes to react with the interior −S−H groups, rendering silver relatively nontoxic to humans and animals. This also explains the huge zones of inhibition produced by the film discs in the present study.

Conclusions

In summary: (1) Polyethylene glycol-polyurethane (PEG-PU)-TiO_2 nanocomposite films were synthesized by simple solution casting technique and silver has been deposited on these films by photochemical-reduction of silver nitrate solution under UV light.

(2) XRD, XPS and UV-DRS confirm the presence of metallic silver. The amount of silver incorporated in the films was determined by EDAX and AAS and is estimated to be between 2 and 4 at %.

(3) The silver incorporated polymer-titania nanocomposite films showed excellent antibacterial activity, even better than standard antibiotics with the added advantage of repeated use. The antibacterial activity of these films was studied on *E. coli* and *B. subtilis*by the disk diffusion method. Further these films were active even when tested in the microbial broth.

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