



## Antimicrobial applications of TiO<sub>2</sub> coated modified polyethylene (HDPE) films

N. Saraschandra<sup>a</sup>, M. Pavithra<sup>b</sup> and A. Sivakumar<sup>a\*</sup>

<sup>a</sup>Environmental & Analytical Chemistry Division, School of Advanced Sciences, VIT University, Vellore, India

<sup>b</sup>Medical Biotechnology Division, School of Biosciences & Technology, VIT University, Vellore, India

### ABSTRACT

*This work describes titanium dioxide (TiO<sub>2</sub>) nanoparticle coating on surface modified High density polyethylene films (HDPE) films and verifying the antimicrobial activity of the coated films against Escherichia coli (E. coli) and Staphylococcus aureus (S. aureus). Ultrasonication method was employed for coating the TiO<sub>2</sub> nanoparticles on polymeric film and presence of TiO<sub>2</sub> nanoparticles on the coated films was confirmed by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) And EDAX. Zone inhibition method was used to verify the antimicrobial activity of the coated films. This developed coating process is observed to render the HDPE film, a reasonable level of antimicrobial activity against the said microorganisms.*

**Key words** TiO<sub>2</sub>, HDPE, SEM, X-ray diffraction, Antibacterial.

### INTRODUCTION

Researchers have been focusing on development of new materials as well as new coating processes on materials suitable for food packaging for quite some time but there has been no ideal material which is available to protect the food stuff from microbial attack. With the advent of nanotechnology, it is expected that it can provide not only innovative solutions to increase the performance of the polymers but can also provide safety, economical and environmental advantages [1-3]. The packaging films with nanoparticle coating have shown great potential to control growth of food borne pathogens. Hydroxypropyl methylcellulose (HPMC) is a biopolymer used as a binder has the ability to help in formation of good and uniform films from thermally induced gelatinous coatings [4], allowing their use as materials to retard oil absorption in deep frying food products [5]. These coated films on coming in contact with food stuff, act upon food-born microorganisms and inhibit their growth. These agents belong to a wide spectrum of organic/inorganic compounds, essential oils, bacteria originated antibacterial proteins (bacteriocins), enzymes, fruit extracts etc. These antibacterial films have shown great potential in inhibiting microbial growth in food stuff. However, the development of new resistant strains of bacteria to current antibiotics has led to the search for new bactericides that can effectively reduce the harmful effects of microorganisms.

With the emergence of nanotechnology, the search for effective biocidal agents has focused on the development of nano-sized particles of materials such as silver [6], copper, zinc oxide [7] and gold [8]. Out of these, silver and gold are prohibitively expensive to be used on industrial scale. Therefore, current research work focuses metal oxides like TiO<sub>2</sub> as effective antibacterial agents for coating on the high density polyethylene (HDPE) films. TiO<sub>2</sub> has been chosen for the nanoparticle coating on HDPE films since the antimicrobial activity of TiO<sub>2</sub> nanoparticles is well established [9-13].

Although biodegradable polymers like cellulose based polymeric films have been in existence as the best materials for preparation of packaging films [14, 15] their hydrophilic nature has put several restrictions on its usage. On the other hand, polyethylene based films show excellent mechanical strength, hydrophobic nature and moisture barrier

properties which are some essential features for a good packaging film. It should also be noted here that these polymeric materials cannot be functionalized, which restricts its usage.

In the present work we have reported in situ Coating of TiO<sub>2</sub> nanoparticles onto surface modified; HPMC coated HDPE films and verified their antimicrobial activity against *E. coli* and *S. aureus*.

## MATERIALS AND METHODS

### Materials

Analytical grade titanium tetrachloride, ammonium hydroxide were obtained from SD Fine Chemicals and hydroxypropylmethyl cellulose (HPMC) was procured from Aldrich Chemicals. Muller Hinton Agar was obtained from HiMedia. Polyethylene sheets (10 µm) used were procured from local market. Millipore water was used in all the experiments.

### Synthesis and coating of TiO<sub>2</sub> nanoparticles onto modified PE sheets

TiO<sub>2</sub> nanopowder was prepared by simple sol-gel method, firstly TiCl<sub>4</sub> was added drop wise and under stirring to 100 ml of water at about 0°C for 1h and 3 ml of Tween 20 was added as a surfactant to prevent the agglomeration of particles then aqueous ammonia was added drop wise while stirring for 30 min, after stirring the resultant solution was sonicated for 90 min at 80 Hz of amplitude and the output was 22 volts. Filter the solution and dry the sample at 80°C for 2 h and calcinated at 450°C for 3 h. The surface modification of HDPE was carried out as per method available in the literature [16]. The coating of TiO<sub>2</sub> nanoparticles onto surface modified HDPE sheets was carried out at room temperature and the modified films were cut into pieces of size 4cm x 4cm. These cut sheets were then placed into a aqueous solution containing 0.2 % (w/v) HPMC powder and stirred for 2 h then the films were dried in dust free oven at 37°C for 90 min. Ultrasonic assisted coating process was adopted to coating of TiO<sub>2</sub> nanoparticles onto treated HPMC films. Different concentrations of TiO<sub>2</sub> suspension were prepared ranging from 0.1 % - 0.8 % (w/v) of TiO<sub>2</sub> and the films were dip-coated in the suspension using a sonicator bath for 30 sec. The coated films were dried in dust free oven at 50°C for 30 min before testing.

### Antibacterial activity

Antimicrobial activity of TiO<sub>2</sub> nanoparticle coated HDPE film was investigated by zone inhibition method against two bacterial strains, *E. coli* and *S. aureus*. In the zone inhibition method, sterilized Muller Hinton agar was poured in petriplates, after solidification the inoculum was spread on the plate using L-rod. TiO<sub>2</sub> coated films were cut into pieces and placed on the bacterial lawns. The plates were incubated for 24 h at 37°C in aerobic incubation chamber. The plates were visually examined for zones of inhibition around the film disc and the size of the zone was measured at two cross-sectional points and the average was taken as the diameter of inhibition zone. For estimating the Minimum inhibitory concentration (MIC), each film was cut into squares (1cm x 1cm). These sample squares were immersed in 5 mL nutrient broth. The medium was inoculated with 100 µL of culture and then transferred to an orbital shaker at room temperature. The MIC was noted as 0.6% (w/v) where the maximum inhibition was noticed. All the experiments were conducted in triplicate and average of the three reading has been taken and incorporated in the data tables.

## RESULTS AND DISCUSSION

### Characterization of TiO<sub>2</sub> coated polyethylene films

Fig.1 shows XRD pattern of polymer material with TiO<sub>2</sub> coating on HDPE films. The peaks obtained for reflection at different crystal planes of TiO<sub>2</sub> nanoparticles were very close to the reported data (JCPDS #053-0619\*). The 2θ values 20.9, 23.3 and 35.7 for reflections at (0 2 1), (1 2 0) and (1 1 0) planes

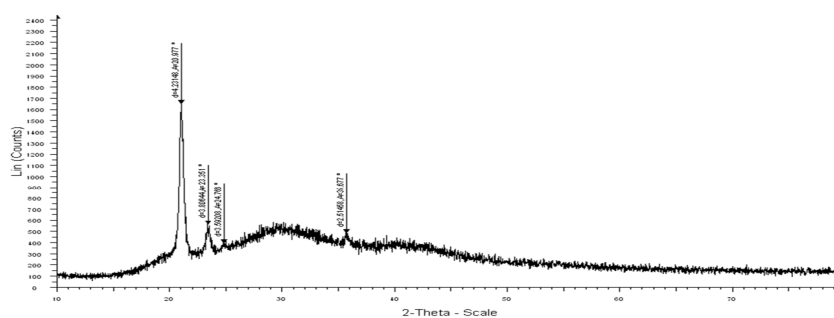


Fig. 1 XRD pattern of nano TiO<sub>2</sub> coated HDPE film

The coating of TiO<sub>2</sub> nanoparticles on HDPE and their dispersion on the film have been studied using scanning electron microscopy (SEM). Fig.2 (a) shows the SEM micrographs of uncoated HDPE film and Fig.2 (b) and (c) shows morphology of polyethylene coated with TiO<sub>2</sub> nanoparticles.

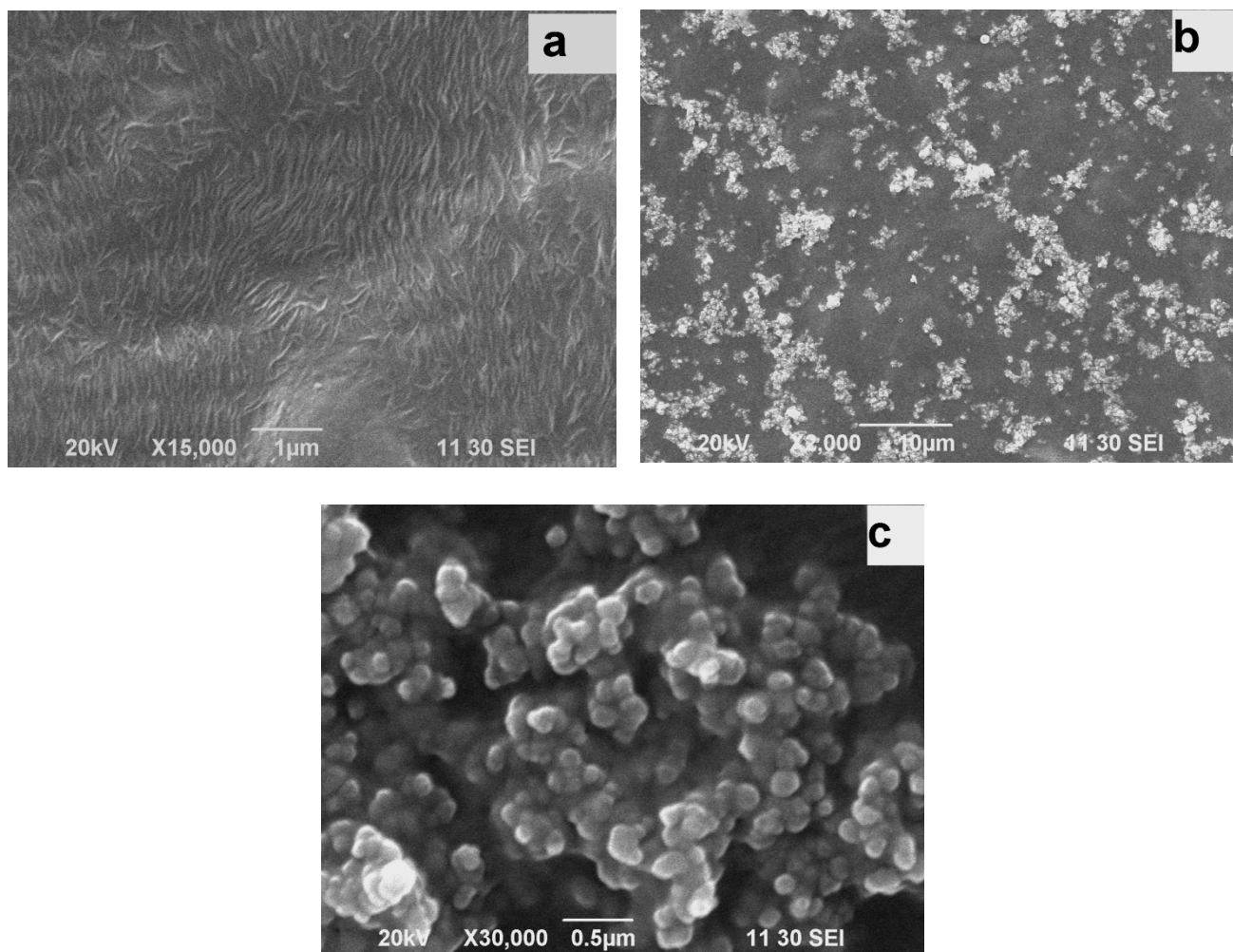


Fig. 2 The Scanning Electron Microscopic (SEM) images of (a) plain HDPE film and (b) & (c) TiO<sub>2</sub> nanoparticle coated films

Figure 3 shows EDAX pattern of coated films indicating the presence of TiO<sub>2</sub> nanoparticles on the film. The surface morphology of plain HDPE and TiO<sub>2</sub> coated HDPE films were checked by AFM measurements. From SEM data, it can be seen that the TiO<sub>2</sub> particles have formed clusters on HDPE film but interestingly the nano dimension of the particles is maintained.

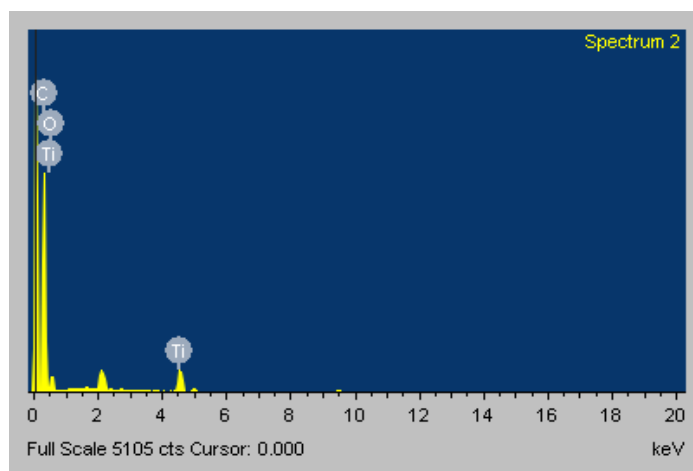


Fig. 3 EDAX pattern of TiO<sub>2</sub> coated HDPE film

#### Antimicrobial activity

The antimicrobial activity of TiO<sub>2</sub> coated polyethylene film was investigated against *E.coli* and *S.aureus* bacteria by zone inhibition method. Figure 4 Explains assessment of the antibacterial activity of TiO<sub>2</sub> coated HDPE films with the concentration of TiO<sub>2</sub>. The results of zone inhibition method has been described from the figure 5 (a) & (b) , it clearly shows that TiO<sub>2</sub> coated polyethylene films shows good inhibition zone around the films. Figure 5 (a) shows the activity against *E.Coli* and Fig 5 (b) shows against *S.aureus*. From Table 1 it illustrates the zone of inhibition will increase with increase of TiO<sub>2</sub> concentration and Table 2 illustrates Assessment of the antibacterial activity of TiO<sub>2</sub> coated HDPE films at different time intervals.

Table 1. Assessment of the antibacterial activity of TiO<sub>2</sub> coated HDPE films

Conc. of TiO <sub>2</sub> % (w/v )	Zone of inhibition (in mm)	
	<i>S.aureus</i>	<i>E.coli</i>
0.1	10	12
0.2	12	12
0.3	12	16
0.4	18	19
0.5	24	26
0.6	27	29
0.7	29	29
0.8	34	36

Table 2. Assessment of the antibacterial activity of TiO<sub>2</sub> coated HDPE films at different time intervals

Conc. of TiO <sub>2</sub> % (w/v)	Zone of Inhibition (in mm)					
	<i>S.aureus</i>			<i>E.coli</i>		
	24hrs	48hrs	72hrs	24hrs	48hrs	72hrs
0.1	09	10	10	09	12	12
0.2	10	12	12	09	12	12
0.3	11	12	12	12	16	16
0.4	15	18	18	16	19	19
0.5	20	21	22	20	26	26
0.6	22	23	23	26	29	29
0.7	23	23	23	29	31	31
0.8	24	24	25	30	36	36

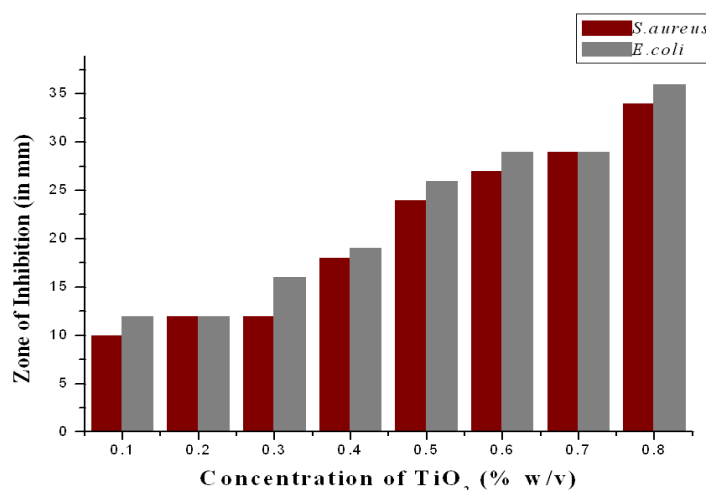


Fig.4 Assessment of the antibacterial activity of TiO<sub>2</sub> coated HDPE films

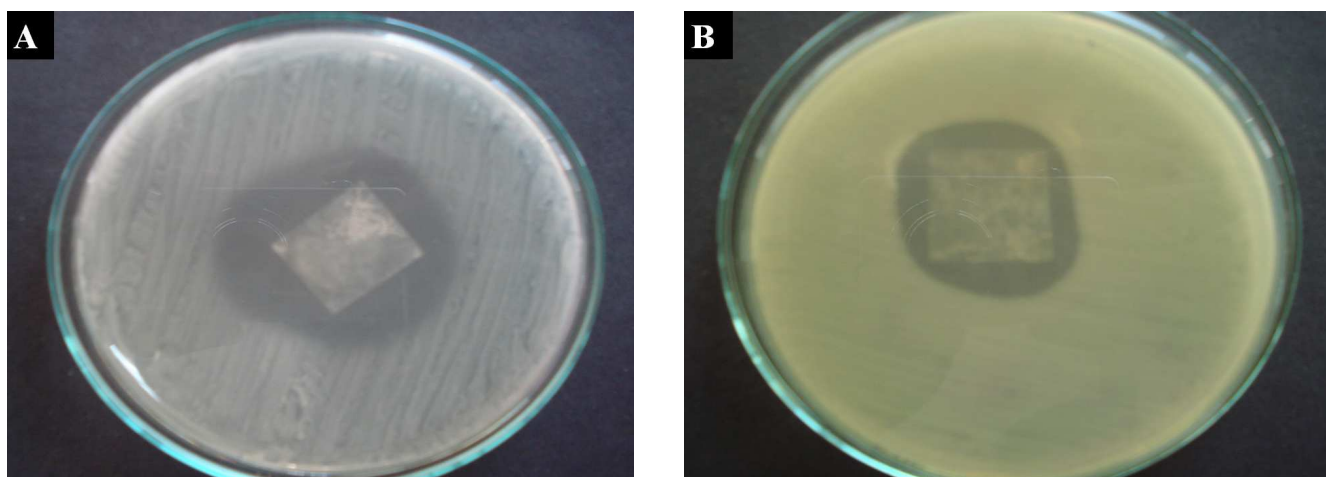


Fig.5 Evolution of antimicrobial action for TiO<sub>2</sub> coated HDPE films by zone inhibition method

### CONCLUSION

Surface modified and HPMC treated TiO<sub>2</sub> nanoparticle coated films were prepared by simple method using ultrasonication technique. These films exhibited good antibacterial activity against *E. coli* as well as *S. aureus*. From this study, it could be clearly brought out that the well known antimicrobial activity can be exploited on polymeric films in the form of thin coating. This is expected to show direction in developing a coated polymeric film that could be used in packing and packaging of food.

### REFERENCES

- [1] Silvestre, C.; Duraccio, D.; Cimmino, S. *Prog Polym Sci.* **2011**, 36, 1766.
- [2] Jeffrey, J.; Karl, I. J.; Rina, T.; Mohammed, A. S.; Iwona, J. *Mat Sci Eng A-Struct.* **2005**, 393, 1.
- [3] Li, J. X.; Wu, J.; Chan, C.M. *Polymer.* **2000**, 41, 6935.
- [4] Maffione, G.; Iamartino, P.; Guglielmini, G.; Gazzaniga, A. *Drug Dev Ind Pharm.* **1993**, 16, 2043.
- [5] Balasubramaniam, V.M.; Chinnan, M. S.; Mallikarjunan, P.; Phillips, R. D. *J. Food Process Eng.* **1997**, 20, 17.
- [6] Chen, X.; Schluesener, H. J. *Toxicol Lett.* **2008**, 176, 1.

- 
- [7] Ahmed, A. T.; El-tras, W. F.; Shaaban, M. J. Food Safety, **2011**, 31, 211.
- [8] Granmayeh Rad, A.; Abbasi, H.; Hossein Afzali, M. *Gold Nanoparticles: Synthesising, Characterizing and Reviewing Novel Application in Recent Years*, International Conference on Physics Science and Technology, Physics Procedia, **2011**, pp. 203 – 208.
- [9] Wist, J.; Sanabria, J.; Dierolf, C.; Torres, W.; Pulgarin, C. *J. Photoch Photobio-A*, **2002**, 147, 241.
- [10] Kim, B.; Kim, D.; Cho, D.; Cho, S. *Chemosphere*, **2003**, 52, 277.
- [11] Cho, M.; Chung, H.; Choi, W.; Yoon, J. *Water Res*, **2004**, 38, 1069.
- [12] Maneerat, C.; Hayata, Y.; *Int J. Food Microbiol*, **2006**, 107, 99.
- [13] Arora, A.; Padua, G. W. *J. Food Sci.* **2010**, 75, R43.
- [14] Catia, B. *Polym Degrad Stabil.* **1998**, 59, 263.
- [15] Holton, E.E.; Asp, E.H.; Zottola, E.A. *Cereal Foods World*, **1994**, 39, 273.
- [16] Fa´varo, S.L.; Rubira, A.F.; Muniz, E.C.; Radovanovic, E. *Polym Degrad Stabil*, **2007**, 92, 1219.