

Trade Science Inc.

# Nano Science and Nano Technology

*An Indian Journal*

*Full Paper*

NSNTAJ, 7(2), 2013 [60-65]

## Macrostructure and optical study of PMMA/TiO<sub>2</sub> nanoparticles composites

Osiris W.Guirguis<sup>1\*</sup>, Mohamed S.Melegy<sup>1</sup>, Nabawia A.El-Zaher<sup>2</sup>

<sup>1</sup>Biophysics Department, Faculty of Science, Cairo University, Giza, (EGYPT)

<sup>2</sup>Textile Metrology Lab, National Institute for Standards, Giza, (EGYPT)

E-mail: osiris\_wgr@yahoo.com

Received: 8<sup>th</sup> May, 2012 ; Accepted: 10<sup>th</sup> September, 2012

### ABSTRACT

Polymer nanocomposites have elicited extensive research efforts due to their potential to exhibit spectacular properties. In the present work, mixtures of four different concentrations (2.5, 5, 7.5, and 10 wt%) of titanium oxide (TiO<sub>2</sub>) nanoparticles with poly (methyl methacrylate) (PMMA) were prepared. Fourier transform infrared spectroscopy (FTIR) and optical analysis were employed to characterize and reveal the miscibility map and the relationship of the structure properties. From the obtained results, it is clear that the TiO<sub>2</sub> nanoparticles have a great effect on improving the performance properties of PMMA greatly depends on the concentration of nanoparticles. Moreover, the organic parts are attached with the inorganic parts in the PMMA/TiO<sub>2</sub> nanoparticles composites.

© 2013 Trade Science Inc. - INDIA

### KEYWORDS

Poly (methyl methacrylate);  
Titanium oxide  
nanoparticles;  
FTIR;  
Tristimulus values;  
Color parameters.

### INTRODUCTION

Polymer nanocomposites have elicited extensive research efforts due to their potential to exhibit spectacular properties. They have immense potential and are befitting materials to serve as an ideal and futuristic alternative for varied applications. Polymer–inorganic oxide nanoparticle composites have attracted considerable attention in the field of material science because they exhibit enhanced material properties as compared to pure polymers. The presence of inorganic oxide nanoparticle fillers in polymers can alter the thermomechanical, optical, electrical, and magnetic properties of the polymers<sup>[1]</sup>. Nanoparticles (NPs) have an enabling role in various branches of nanotechnology

due to their capability of being a bridge between bulk materials and atomic or molecular structures. Recently, composite materials made of polymers and NPs, such as inorganic, metal, semiconductor, carbon black, and magnetic nanomaterials have attracted great attention because of the stabilizing effects of the polymer matrix on the NPs and relative easiness and flexibility of engineering this class of materials with advanced functionalities<sup>[2-6]</sup>.

Poly (methyl methacrylate) (PMMA) is one of the best organic optical materials which is very suitable for numerous imaging and non imaging microelectronic applications, including as a photoresistance for direct-write e-beams, X-rays and deep UV microlithographic process and has been widely used to make a variety of

optical devices, such as optical lenses either in the pure or doped state<sup>[7-9]</sup>. PMMA has been used in skeletal surgery for more than 40 years as a means of securing prosthetic implants and more recently is used as a delivery agent for local high-dose antibiotics to treat soft tissue and osseous infections<sup>[10]</sup>. Moreover, since PMMA is a nondegradable biopolymer, it has been extremely utilized for antibiotic delivery system purposes for the treatment of osteomyelitis<sup>[11]</sup>. Also, PMMA is a widely used support medium for the embedding of intact, undecalcified bone<sup>[12]</sup>. Its hardness makes it ideal for calcified tissue sectioning and subsequent histological examination<sup>[13]</sup>.

Titanium oxide (TiO<sub>2</sub>) nanoparticle (that is, species composed of titanium and oxygen) represents an important material that is used widely in photocatalysis, sensor technology, optical coatings, adsorbents, production of paper, plastics, cosmetics, paints and pigments. It has been used in purification of polluted air and wastewaters<sup>[14]</sup>. Nano-TiO<sub>2</sub> is not inert and is a UV light attenuator; therefore, it finds applications as a catalyst and as a UV light attenuator as opposed to a visible light attenuator<sup>[15]</sup>. Nano-TiO<sub>2</sub> is used as a UV stabilizer or blocker in products other than sunscreens, such as plastic products and textiles. Nano-TiO<sub>2</sub> protects both the matrix and the material behind the matrix from degradation due to UV light<sup>[16]</sup>. Chen et al.<sup>[17]</sup> reported in their study the synthesis and characterization of trialkoxysilane-capped poly (methyl methacrylate)-titania hybrid optical thin films. The effect of shape and surface chemistry of TiO<sub>2</sub> colloidal nanocrystals on the organic vapor absorption capacity of TiO<sub>2</sub>/PMMA composite is studied by Convertino et al.<sup>[18]</sup>.

In the present work, PMMA is mixed with different concentrations (2.5, 5, 7.5, and 10 wt%) of TiO<sub>2</sub> nanoparticles. Fourier Transform infrared spectroscopy (FTIR) and optical analyses are employed to characterize and to reveal the relationship of the structure properties of PMMA.

## EXPERIMENTAL

### Materials and sample preparation

Poly (methyl methacrylate) powder of chemical formula [CH<sub>2</sub>C(CH<sub>3</sub>)(CO<sub>2</sub>CH<sub>3</sub>)]<sub>n</sub> with average molecular

weight of 320,000 and melting point > 150 °C was supplied from Alfa Aesar, GmbH & Co., UK. Titanium (IV) oxide, mixture of rutile and anatase, nanopowder, < 100 nm (BET), 99.5% trace metals Basis was supplied from Sigma-Aldrich, China.

The PMMA powder is mixed with TiO<sub>2</sub> nanoparticles powder for four different concentrations (2.5, 5, 7.5 and 10 wt%). The starting materials were grounded using a Phillips PW 4018/00 MiniMill for 15 minutes with a rotating speed of 3400 rpm to form a homogenous mixture.

### Fourier transform infrared (FTIR)

The FTIR transmittance spectra of the prepared mixtures over the range 4000-500 cm<sup>-1</sup> was obtained using potassium bromide pellet technique<sup>[19]</sup>. The pellets were prepared by mixing 1 mg of powdered sample with 100 mg of dried potassium bromide powder. Mixing was carried out using a pestle and agate mortar. The mixture was then pressed in a special die at a pressure of 10,000 pounds per square inch to yield a pellet. The FTIR spectra of the prepared pellets were then recorded at room temperature by using Perkin-Elmer FTIR Spectrophotometer Model 1650 TX in the wavenumber range from 4000 to 500 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>.

### Visible spectroscopic measurements

The measurements in the visible region from 400 to 700 nm for PMMA/TiO<sub>2</sub> were carried out using a Shimadzu (VIS) Double Beam Spectrophotometer with standard illuminant C (1174.83) Model V-530 and band width 2.0 nm covers the range 200–2500 nm with accuracy ±0.05%. The color properties were analyzed using the CIE Colorimetric System, CIE 1931 2-degree Standard Observer<sup>[20,21]</sup>. The tristimulus reflectance values (x<sub>r</sub>, y<sub>r</sub> and z<sub>r</sub>), the relative brightness (L), the color constants 'a' and 'b', the whiteness index (W), the color difference (ΔE), the chroma (C) and the hue (H) are calculated using the CIE relations previously reported<sup>[22]</sup>.

## RESULTS AND DISCUSSION

### Fourier transform infrared (FTIR) spectral analyses

FTIR spectroscopy has long been recognized as a powerful tool for elucidation of structural information.

## Full Paper

The position, intensity, and shape of vibrational bands are useful in clarifying conformational and environmental changes of polymers at the molecular level<sup>[23]</sup>.

The FTIR transmission spectra of PMMA, TiO<sub>2</sub> nanoparticles and their mixtures in the frequency range 4000-500 cm<sup>-1</sup> are shown in Figure 1. The chemical assignments for PMMA, TiO<sub>2</sub> and their composites are considered and are also illustrated in TABLE 1. The FTIR spectrum of PMMA indicates the details of functional groups present in the synthesized PMMA and is comparable to that of earlier reports<sup>[24-26]</sup>.

From the figure and the TABLE, it is noticed that,

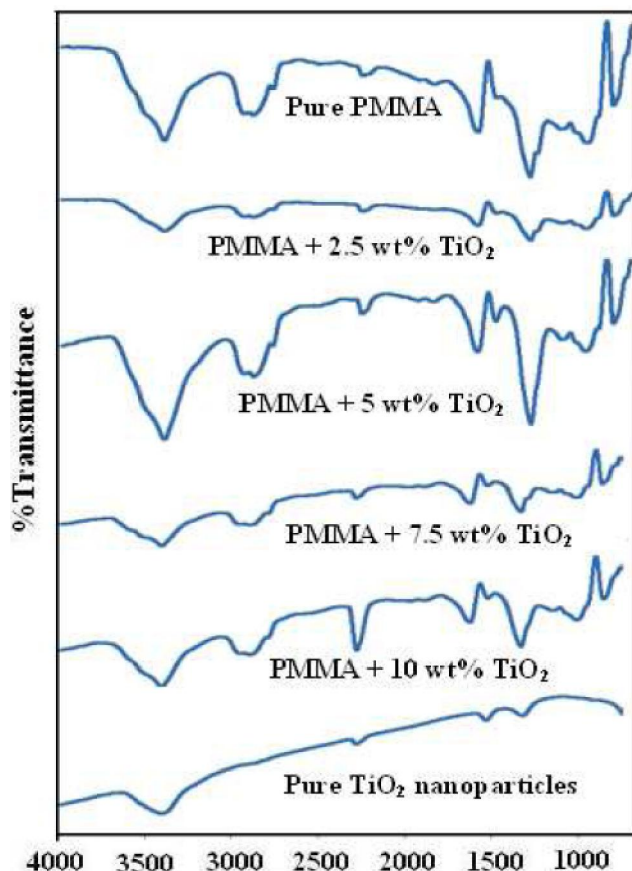


Figure 1 : Variations in FTIR spectra of PMMA/TiO<sub>2</sub> nanoparticles composites

the PMMA spectrum exhibits broad band near 3445 cm<sup>-1</sup> due to the OH-stretching vibrations of free and hydrogen-bonded hydroxyl groups (most probably due to the humidity absorbed by the KBr during the preparation of the pellets). Also, the band in the region 1632 cm<sup>-1</sup> is most probably due to the humidity absorbed by the KBr during the preparation of the pellets (i.e., O-H group). Absorption that arises from C-H stretching of

the methyl groups occurs in the region of 3020-2840 cm<sup>-1</sup>, which contain two distinct peaks at 3012 and 2964 cm<sup>-1</sup> resulting from asymmetrical and symmetrical stretching modes of C-H bonding in the methyl group, respectively. Also, the distinct band appeared at 2855 cm<sup>-1</sup> arises from the C-H bond vibration of the methyl group. The peak in the region 1750-1730 cm<sup>-1</sup> represents C=O double bond stretching vibration of the aliphatic esters, was used to characterize the existence of PMMA in the blend. The band at 1632 cm<sup>-1</sup> corresponds to the C=O stretching ester group, also, it may appear from deformative water molecules which is probably due to water absorption during the compaction of the powder specimens with KBr. The asymmetrical bending vibration ( $\delta_{as} CH_3$ ) of methyl group is identified near 1450 cm<sup>-1</sup>. The bands at 1286 cm<sup>-1</sup> is associated with C-O stretching vibration. The band at 755 cm<sup>-1</sup> corresponds to out-of-plane C-H bending. The band at 1147 cm<sup>-1</sup> is attributed to asymmetric vibration of C-C groups. The band at 991 cm<sup>-1</sup> arises from the aliphatic-CH<sub>2</sub> group. The bands at 847 cm<sup>-1</sup> is assigned to -CH<sub>2</sub> rocking vibration group.

Also from Figure 1, it is shown that the FTIR spectra of PMMA/TiO<sub>2</sub> nanoparticles composites indicate the details of functional groups present in correlation with the pure PMMA spectrum. The heights of the peaks of the assigned groups at their wavenumbers shown in the spectra were taken to represent the variation in the group band intensities for different TiO<sub>2</sub> concentrations. A clear deviation was observed in the transmittance bands of the PMMA/TiO<sub>2</sub> composites when compared with that detected for pure PMMA. The increase and/or decrease in the intensity mean that there is a change in the molecular configuration of the polymer network.

As shown by the FTIR results, an increase in the concentration of TiO<sub>2</sub> nanoparticles changed the chemical bonds and hence changed the molecular configuration of PMMA which is shown by the pronounced variation in the intensity of transmittance bands and shifts in band positions. The change in intensity of some spectral bands associated with infrared active groups of PMMA and TiO<sub>2</sub> may be attributed to the fact that in the materials that contain two or more components, the resulting spectrum is approximately the sum of their components. In addition, the change in the spectral position of some bands of PMMA after the additions of differ-

ent TiO<sub>2</sub> nanoparticles concentrations may be attributed to some of the monomer units of PMMA are sensitive to their environment. Furthermore, the hydroxyl and carbonyl stretching vibration bands are affected by hydrogen bonding interactions and are most amenable to quantitative analysis.

### Visible spectroscopic analysis

From the values of reflectance (figure is not shown for simplicity data), the tristimulus reflectance values ( $y_r$ ) are calculated and plotted as a function of wavelength

(400-700 nm) and shown in Figure 2 for PMMA/TiO<sub>2</sub> nanoparticles composites. It is observed from the figure that, the behaviors of  $y_r$  for the composites are similar and no change in peak position (550 nm) is detected. It is also observed that  $y_r$  value increases at TiO<sub>2</sub> nanoparticles concentration increases up to 10 wt% towards the value of the pure TiO<sub>2</sub> nanoparticles. Figures 3 and 4 show the variations of the tristimulus reflectance values ( $x_r$  and  $z_r$ , respectively) with wavelength in the range 400-700 nm for PMMA/TiO<sub>2</sub> nanoparticles composites. It is clear that the behaviors of the samples

TABLE 1 : Positions and assignments of the most bands of PMMA/TiO<sub>2</sub> nanoparticles composites

Wavenumber (cm <sup>-1</sup> )						Assignments
PMMA/TiO <sub>2</sub> composites (wt/wt%)						
100/0	97.5/2.5	95/5	92.5/7.5	90/10	0/100	
3445	3456	3450	3452	3455	3460	Hydrogen bonded and hydroxyl O-H group
3012	3019	3014	3021	3021	-	Asymmetrical stretching modes of C-H bonding in the methyl group
2964	2969	2965	2958	2967	-	Symmetrical stretching modes of C-H bonding in the methyl group
2855	2858	2868	2862	2862	-	C-H bond vibration of the methyl group
1740	1744	1741	1743	1741	-	C=O double bond stretching vibration of the aliphatic esters
1632	1638	1635	1639	1636	1651	C=O stretching ester group
1450	1455	1446	1456	1455	1456	O-CH <sub>3</sub> deformation
1286	1288	1289	1284	1294	-	associated with C-O stretching vibration
1147	1156	1156	1150	1152	-	Asymmetric stretching vibration of C-C groups
991	994	993	993	989	-	aliphatic-CH <sub>2</sub> group
847	848	847	849	842	-	-CH <sub>2</sub> rocking vibration group
755	757	754	756	750	-	Out-of-plane C-H bending

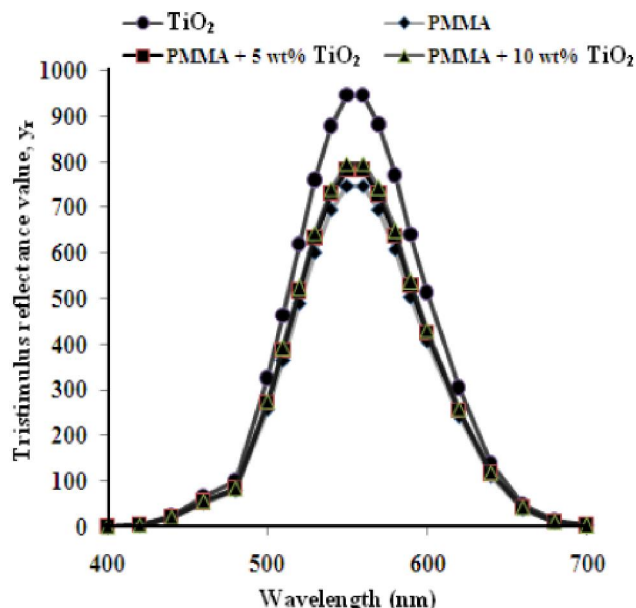


Figure 2 : Variation of the tristimulus reflectance value ( $y_r$ ) with wavelength for PMMA/TiO<sub>2</sub> nanoparticles Composites

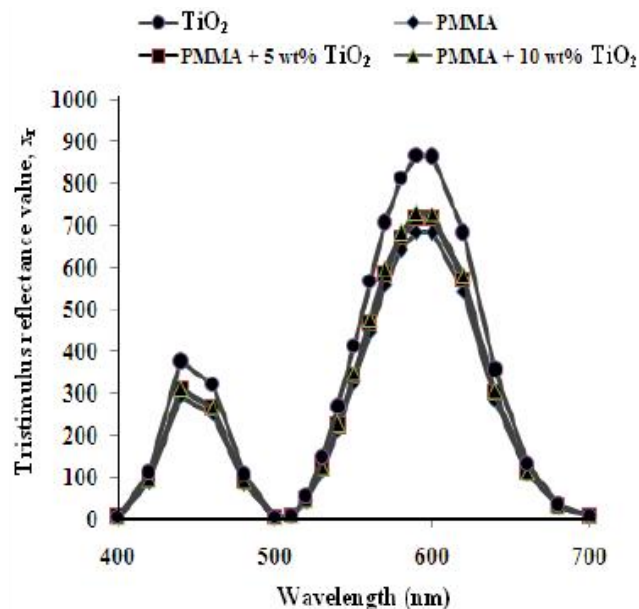


Figure 3 : Variation of the tristimulus reflectance value ( $x_r$ ) with wavelength for PMMA/TiO<sub>2</sub> nanoparticles composites

## Full Paper

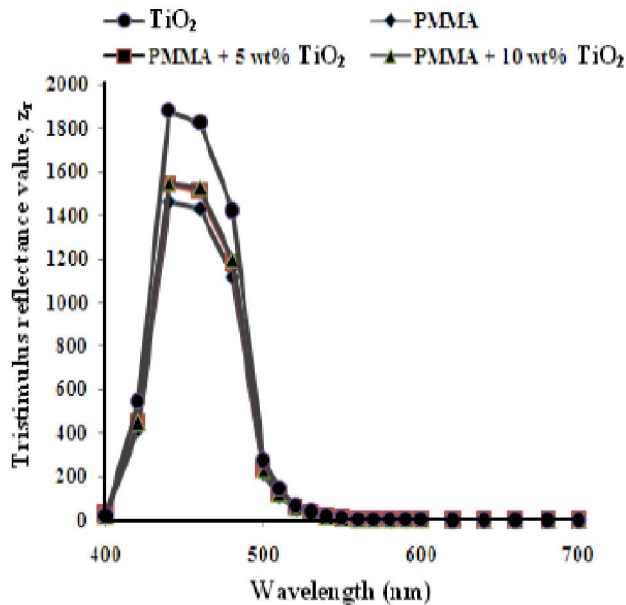


Figure 4 : Variation of the tristimulus reflectance value ( $z_r$ ) with wavelength for PMMA/TiO<sub>2</sub> nanoparticles composites

TABLE 2 : The  $x_r$ ,  $y_r$  and  $z_r$  tristimulus reflectance values of PMMA/TiO<sub>2</sub> nanoparticles composites

PMMA/TiO <sub>2</sub> nanocomposites (wt/wt%)	$x_r$		$y_r$	$z_r$
	$\lambda =$ 440 nm	$\lambda =$ 590 nm	$\lambda =$ 550 nm	$\lambda = 440$ nm
100/0	291.53	683.95	748.12	1462.25
97.5/2/5	294.03	694.55	758.74	1474.81
95/5	308.14	716.02	782.82	1545.59
92.5/7.5	308.35	721.68	787.74	1546.62
90/10	309.81	728.78	796.29	1553.97
0/100	375.76	866.15	946.23	1884.74

TABLE 3 : The color parameters for PMMA/TiO<sub>2</sub> nanocomposites and their percentage changes

Color parameters	PMMA/TiO <sub>2</sub> nanocomposites (wt/wt %)					
	100/0	97.5/2.5	95/5	92.5/2.5	90/10	0/100
L	89.82	90.34	91.54	91.68	92.10	98.41
$\Delta L\%$	-	0.58	1.91	2.07	2.54	-
a	-0.47	-0.39	-0.25	-0.48	-0.53	-0.31
$\Delta a\%$	-	17.02	46.81	-2.13	-12.77	-
b	2.20	2.23	1.37	2.34	2.23	1.56
$\Delta b\%$	-	1.36	-37.73	6.36	1.36	-
W	65.4	66.5	73.3	69.0	70.5	89.1
$\Delta W\%$	-	1.68	12.08	5.50	7.80	-
$\Delta E$	-	1.48	1.01	1.92	1.06	-
$\Delta C$	-	2.3	1.4	2.2	2.3	-
$\Delta H$	-	99.9	103.3	102.1	99.9	-

are similar and show the same peak positions. TABLE 2 illustrates the values of  $x_r$ ,  $y_r$  and  $z_r$  at the peak positions for PMMA/TiO<sub>2</sub> nanoparticles composites.

TABLE 3 represents the variations of color parameters calculated from the reflectance data and their percentage changes for PMMA/TiO<sub>2</sub> nanoparticles composites. From the table it is observed that: The relative brightness (L) shows an increase with increasing the concentration of TiO<sub>2</sub> nanoparticles. The value of the color constant (a) increase by increasing the TiO<sub>2</sub> nanoparticles concentration up to 5 wt% which indicates that, there is an increase in red component instead of green one. The values of the color constant (b) decrease by increasing TiO<sub>2</sub> nanoparticles concentration up to 5 wt% which indicates that there is an increase in blue component instead of yellow one and then return to the value of pure PMMA at 10 wt% TiO<sub>2</sub> nanoparticles. The whiteness index (W) shows same behavior as the color constants (a and b). The obtained results indicate that variations in color difference between samples are occurred by the presence of TiO<sub>2</sub> nanoparticles by different concentrations with PMMA.

The observed changes in the color parameters calculated from the reflectance curves with the increase in the concentration of TiO<sub>2</sub> nanoparticles may be due to the change in the physical bonds and then changes in the molecular configuration of PMMA as mentioned before which may lead to formation of new dopant centers of the polymeric material. In addition, the obtained results of the color parameters are of great importance for the improvement of the optical properties of the PMMA.

## REFERENCES

- [1] E.Ozkaroglu, I.Tunc, S.Suzer; Polymer, **50**, 462 (2009).
- [2] B.Choudhary, S.Chawla, K.Jayanthi, K.N.Sood, S.Singh; Curr.Appl.Phys., **10**, 807 (2010).
- [3] P.K.Khanna, N.Singh, S.Charan; Mater.Lett., **61**, 4725 (2007).
- [4] A.Singh, U.K.Kulkarni, C.Khan-Malek; Microelectron.Eng., **88**, 939 (2011).
- [5] K.Matsuyama, K.Mishima; J.Supercrit.Fluid, **49**, 256 (2009).
- [6] J.C.K.Lai, M.B.Lai, S.Jandhyam, V.V.Dukhande, A.Bhushan, et al.; Int.J.Nanomed., **3**, 533 (2008).
- [7] M.Wenzhong, Z.Jun, W.Xiaolin, W.Shengmin; Appl.Surf.Sci., **253**, 8377 (2007).

- [8] C.Wochnowski, S.Metev, G.Sepold; *Appl.Surf.Sci.*, **154-155**, 706 (2000).
- [9] T.Kardinahl, H.Franke; *Appl.Phys.A*, **61**, 23 (1995).
- [10] V.L.Schade, T.S.Roukis; *J.Foot Ankle Surg.*, **49**, 55 (2010).
- [11] S.P.Mohanty, M.N.Kumar, N.S.Murthy; *J.Orthop. Surg.*, **11**, 73 (2003).
- [12] N.L.Pleshko, A.L.Boskey, R.Mendelsohn; *J.Histochem.Cytochem.*, **40**, 143 (1992).
- [13] A.Stevens, J.Germain; 'Resin embedding media', J.D.Bancroft, A.Stevens, (Eds); *The theory and practice of histological techniques*, 3rd Edition, New York, Churchill Livingstone, (1990).
- [14] A.Fujishima, T.N.Rao, D.A.Tryk; *J.Photoch. and Photobio. C*, **1**, 1 (2000).
- [15] X.Chen, S.S.Mao; *Chem.Rev.*, **107**, 2891 (2007).
- [16] S.M.Khaled, R.Sui, P.A.Charpentier, A.S.Rizkalla; *Langmuir*, **23**, 3988 (2007).
- [17] W.C.Chen, S.J.Lee, L.H.Lee, J.L.Lin; *J.Mater. Chem.*, **9**, 2999 (1999).
- [18] A.Convertino, G.Leo, M.Striccoli, G.Di Marco, M.L.Curri; *Polymer*, **49**, 5526 (2008).
- [19] V.Sankar, T.Suresh Kumar, K.Panduranga Rao; *Trends Biomater.Artif.Organs*, **17**, 24 (2004).
- [20] CIE Recommendation on Colorimetry; CIE Publ.No. 15.2. Central Bureau of the CIE, Vienna, (1986).
- [21] CIE Recommendation on Uniform Color Spaces; Color Difference Equations, Psychometric Color Terms, Suppl.No.2 of CIE Publ.No.15 (E-1.3.1), Paris (1971/1978).
- [22] W.G.Osiris, M.T.H.Moselhey; *J.Mater.Sci.*, **46**, 5775 (2011).
- [23] C.S.Ha, W.K.Lee, W.J.Cho; *Macromolecular Symposia*, **84**, 279 (1994).
- [24] M.Prusty, B.J.Keestra, J.G.P.Goossens, P.D.Anderson; *Chem.Eng.Sci.*, **62**, 1825 (1925).
- [25] Ismayil, V.Ravindrachary, Ismayil, R.F.Bhajantri, S.D.Praveena, B.Poojary, D.Dutta, P.K.Pujari; *Polym.Degrad.Stabil.*, **95**, 1083 (2010).
- [26] M.Wenzhong, Z.Jun, W.Xiaolin, W.Shengmin; *Appl.Surf.Sci.*, **253**, 8377 (2007).