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Preparation of polymer composite by using hydrothermally synthesized titanium oxide fillers and its characterization

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ABSTRACT

Metal-oxide nanoparticles can be used to optimize UV absorption and to enhance the stiffness, toughness, and probably the service life of polymeric materials. In the present study TiO_2 nanoparticles were synthesized under mild hydrothermal conditions (Temperature > 200 ^{O}C and Experimental duration >24 h) and as prepared TiO_2 nanoparticles are inserted into polyurethane (PU) matrix. Polymer-TiO_2 composites have been prepared using castor oil based polyurethane as a host and TiO_2 as particulate filler. The prepared PU/TiO_2 composites have been characterized for mechanical properties such as tensile strength and tensile modulus. These PU composites exhibited an improved mechanical performance compared to the unfilled PU. PU/TiO_2 composites were prepared by varying amounts of TiO_2 fillers (2.5%, 5%, and 10%) in PU matrix. As obtained PU/TiO_2 composites were characterized by analytical techniques like XRD, FTIR, SEM to study the nanostructure and dispersion of TiO_2 nanoparticles in PU matrix and structure-property relationships. Microstructure, chemical elucidation, TiO_2 particles dispersed and other characterizations of PU/TiO_2 composites obtained are discussed. The photocatalytic activity and weight loss under the aqueous medium was investigated and mechanistic aspects of the liquid-phase photocatalytic activity, and photodecomposition, their implication for developing photo decomposable polymer composites were discussed.

KEYWORDS

Nanoparticle;
Hydrothermal conditions;
Polyurethane;
Castrol oil;
Mechanical properties;
Tensile strength.

INTRODUCTION

Nowadays the enormous use of polymer materials is attributed to their extraordinary combination of properties, low weight and ease of processing. However for improvement of some properties such as thermal and mechanical stability, large numbers of additives were added to polymeric matrix and formed polymer matrix composite[1,2]. To improve the properties of composite materials investigate composites with lower and lower fillers size, leading to the development of microcomposites and the recent trend in composite research is nanocomposites. Nanocomposites refer to composites in which one phase has nanoscale morphology such as nanoparticles, nanotubes or lamellar nanostructure[1-4]. The improvement of the properties

by the addition of particles can be achieved when adequately good interaction between the nanoparticles and the matrix and good dispersion of particles within the matrix. In nanocomposites, covalent bonds, ionic bonds, Vander Waals forces, hydrogen bonding could exist between the matrix and filler components[3]. The use of renewable resources has attracted the attention of many researchers due to their application potential as substitutes for petrochemical derivatives. Much attention has been focused on the innovation and development of newer materials from renewable resources, i.e., forest products that could be grown again and again. One of the most naturally and abundantly occurring vegetable oil is castor oil. Castor oil possesses both unsaturated and conjugated hydroxyl functional groups. Castor oil reacts with different diisocyanates, which is also polyfunctional to form polyurethane (PU)[5-7]. Chain extended PU elastomers have a wide range of industrial applications and they are well known for their mechanical properties. These polymers typically exhibit a two-phase morphology because of the incompatibility of hard and soft segments. The excellent mechanical properties of polyurethane such as high tensile strength and toughness are primarily a result of the two-phase microstructure from this phase separation[8,9]. Metal-oxide particles such as TiO_2 and ZnO, serve many functions in the various polymeric materials. Traditionally, they have been used as pigments to enhance the appearance and improve the durability of polymeric products, and usually they have been considered to be inert. As nanosized particles, these materials exhibit broad band UV absorption, a benefit that currently has been exploited only in sunscreen applications. Also, the addition of nanoparticles would likely enhance the stiffness, toughness, and service life of polymeric materials, for example, in applications in which mar resistance is important. Optimizing the material properties of metal-oxide nanoparticle/polymer composites, the microstructure and dispersion (sizes and spatial distribution) of nanoparticles must be characterized as a function of different process conditions. Composite materials have a wonderful and different range of applications. Important advantages of composites over many metal compounds are high specific stiffness and specific strength, high toughness, corrosion resistance, low density and thermal insulation[1,2]. It is interesting to note that the solid-phase photocatalytic degradation of polymer–TiO_2 composites has been known and studied for quite a long time in relation to the *chalking* phenomenon in the pigmented paint/polymer systems[10]. Several studies on photodegradation of TiO_2-blended polymer in air such as polyethylene[11] and PVC[12,13] have been carried out. However, their main interests focused on inhibiting the photocatalytic activity of TiO_2 in relation to weathering of the polymer composites. The present study tried to take advantage of such effects on the contrary. Unlike their liquid - or gas-phase counterpart, the solid -phase photocatalytic reactions have been far less studied and little is known for their mechanistic pathways. It needs to be understood how they initiate and propagate within the solid matrix for the development of efficient photodegradable polymer composites. Whereas the number of metal oxides is small and limited, that of organic and biological molecules is vast and virtually unlimited. Naturally, hybridization of these two parent families can enrich the property library and widen the application scope offered by each of them individually. Recently, this principle has been behind a series of studies[14-19] that introduced a new family of materials, designated as organic compound-doped by metal oxides. The unique properties of titanium oxide (TiO_2) make them one of the most useful inorganic materials in the world. Polymers constitute very important host materials for a variety of filler materials leading to the formation of composites with technological potential. In recent years, there is a growing tendency to search for new properties for materials like TiO_2, $AlPO_4$ and ZnO filled polymer composites, optically active molecules such as non-linear optical materials, luminescent materials, catalytic materials, etc. Hence, we have selected PU as the matrix with TiO_2 as the particulate filler in order to establish structure–property relationship. The present work deals with the influence of TiO_2 particulate filler on the performance of the PU composites.

MATERIALS AND METHODOLOGY

Castor oil was obtained from the local market and it was dried over night at 90 °C before use. Its average molecular weight (Mn) is 930, and hydroxyl group per molecule is 2.24. Toluene diisocyanate (TDI), dibutyl tin dilaurate (DBTL) (catalyst) and tartaric acid (TA)

supplied by Fluka were used without dilution and distillation. Methyl ethyl ketone (MEK) of AR grade was used after distillation. Other chemicals such as TiO_2, orthophosphoric acid and di-propylamine of AR grade were procured from Aldrich, USA.

Preparation of TiO_2 filler

TiO_2 nanoparticles were synthesized under mild hydrothermal conditions (T=150°C, P= autogeneous). 1M of pure TiO_2 was taken as starting material and a known amount of 1M HCl was added as mineralizer to the precursors. The mixture was stirred vigorously for a few minutes. The final compound was then transferred to the Teflon liner (Vfill =10 mL), which was later placed inside a General-Purpose autoclave. Then the assembled autoclave was kept in an oven with a temperature programmer-controller for 24 h. The temperature was kept at 150°C. After the experimental run, the autoclave was cooled to the room temperature. The product in Teflon liner was then transferred to a clean beaker, washed with double-distilled water, and later allowed the product to settle down. The surplus solution was removed using a syringe and the remnants were centrifuged for 20 minutes at 1500 rpm. The product was recovered and dried in a hot air oven at 40–50°C for a few hours. As obtained TiO_2 nanoparticles were fabricated and stored in desiccators. Further this material was used as filler in polyurethane matrix.

Preparation of PU/TiO_2 polymer composite

Castor oil (0.001 M) was initially dissolved in 50 ml of MEK and placed in three-necked round bottomed flask. Toluene diisocyanate (0.002 M) was added followed by two to three drops of DBTL as catalyst and the contents of the flask were stirred continuously for about 1 h under oxygen free nitrogen gas purge at 60–70 °C, to prepare the isocyanate-terminated pre PU polymer. Calculated amount of tartaric acid (0.001 M) weighed accurately, was completely dissolved in 10 ml MEK and added to the pre PU and stirred for 1 h, under nitrogen gas purge at 65–70 °C. The calculated amount of TiO_2 filler was added at this stage and stirred for 10 to 20 min or until the uniform mixture was obtained. The solution was degassed under vacuum, and poured into cleaned glass mould and allowed for 12 h at room temperature. The mould was kept in preheated circulating hot air oven at 70 °C for 8–10 h. The toughened PU composite sheet thus formed was cooled slowly and removed from the mould. The above procedure was repeated for different TiO_2 filler contents, viz. 2.5, 5 and 10 by weight percent. A flow chart of preparation of PU/TiO_2 composite is shown in Figure 1.

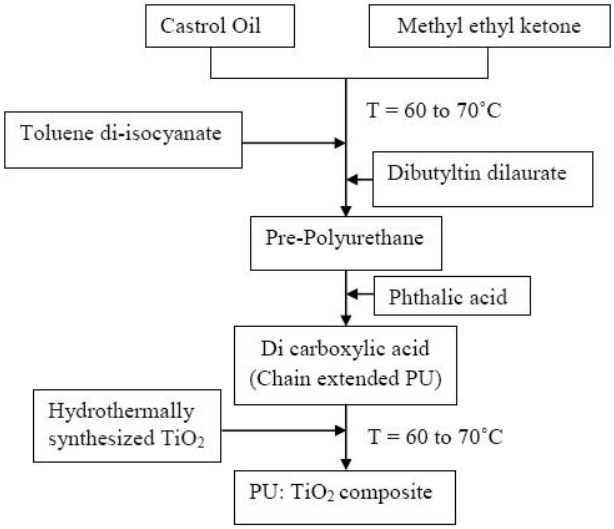

Figure 1 : Flow chart showing the preparation of PU/TiO_2 composite

Characterization methods

The prepared tartaric acid chain extended PU and its composites were characterized for surface hardness according to ASTM D 785 method. Mechanical properties such as tensile strength and tensile modulus have been performed as per ASTM D 638 method using 4302 model Hounsfield universal testing machine (UTM), UK. Minimum six samples were tested at room temperature for each formulation and the average values are reported. The XRD studies were also carried out using the *RIGAKU, Ultima III* Series, TSX System, Japan at a scanning speed of 2°/min, and 2θ ranging from 70 to 10 degrees with Cu target emitting the Cu Kα radiations with the operating current and voltage of 15 mA and 30 kV respectively. The identification of the crystalline phases was carried out by comparison with Joint Committee on Powder Diffraction Standards (JCPDS) database using PCPDF Win version 2.01[20,21]. The structural and quantitative elucidation of PU/TiO_2 composites were characterized by the Fourier Transform Infrared Spectroscopy (JASCO-460 PLUS, Japan) in the range of 400-4000 cm^{-1} at resolution of 4 cm^{-1}. The sample holder of the instru-

ment has a provision for the measurement of blank KBr as well as for the sample. The sample is prepared by mixing thoroughly with KBr and compound whose FTIR to be recorded in the ratio of 100:3. The background measurements were recorded for blank KBr before measuring the sample. The programme of the instrument has provision for automatic correction for background in the sample measurements. The spectrum obtained has been analyzed using JASCO Spectra analysis programme and JASCO file find programme. The surface morphology of PU composites was studied using a scanning electron micrograph (model HITACHI S- 4200). The micrographs of the composites were taken on SX-50 with probe microanalysis Sl. 320 after gold (100Å) coating. The magnification is displayed on the respective microphotographs of the samples. Photocatalytic activity of PU/ TiO_2 composites was carried out under UV light in aqueous medium by following standard method[22-25]. Each sample was weighed before and after irradiation to monitor the weight loss as a result of photodecomposition under different conditions.

RESULTS AND DISCUSSION

Well crystalline TiO_2 nanoparticle were synthesized under mild hydrothermal conditions and used as filler for the preparation of polyurethane composite. Physical and chemical properties of as prepared composite were studied systematically. The mechanical properties are very important in selecting a polymer material for suitable applications. The PU/TiO_2 composites were obtained as tough films with golden yellow color. The measured mechanical properties such as surface hardness, tensile strength and modulus, % elongation at break and density of the PU/ TiO_2 composites are given in TABLE 1. Surface hardness data reflects the resistance to local deformation, which is a complex property, related to cross-link density, modulus, strength, elasticity, plasticity and porosity of the polymer matrix. A slight increase in surface hardness values with increase in filler content was found and which falls in the range 25 to 44 Shore D. The increase in surface hardness with increase in TiO_2 is due to the reinforcing behavior of filler and good physical interaction between PU and TiO_2 nanoparticles. The incorporation of TiO_2 filler in the PU matrix seems to increase the dimensional stability with increase in filler content. A considerable improvement in both tensile strength and tensile modulus of composites with increase in filler content in PU matrix was noticed. Tensile strength and tensile modulus fall in the range 3.21–6.88 MPa and 2.96–5.71 MPa respectively (TABLE 1). The improvement in the tensile strength and tensile modulus with increase in filler content is due to good interaction and interfacial adhesion between PU and TiO_2 filler. Percent elongation at break and overall density of PU/TiO_2 composite also increased with increased wt % TiO_2 filler in PU matrix. A considerable increase in dimensional stability, tensile strength and drastic improvement in tensile modulus clearly supports the reinforcing behavior of TiO_2 fillers in PU matrix. Figure 2 showed the stress and strain curve of PU/ TiO_2 composites and it clearly indicating that considerable increased rate of stress and strain with respect to increased Wt % of TiO_2 filler in PU matrix. Mechanical properties are higher for TiO_2 filler reinforced PU composites compared to unreinforced PU indicating the good reinforcement by TiO_2 filler.

TABLE 1 : Mechanical properties of PU/ TiO_2 composites

PU/TiO_2 Composites (in Wt %)	Tensile Strength (MPa)	% Elongation at Break	Tensile Modulus (MPa)	Surface hardness (Shore D)	Density (g/cm^3)
Blank PU	3.21	218	2.96	25	1.02
PU+2.5% PU	3.55	250	3.4	29	1.35
PU+5% PU	4.67	281	3.95	36	1.85
PU+10% PU	6.88	393	5.71	41	2.13
TiO_2 Particles					4.23

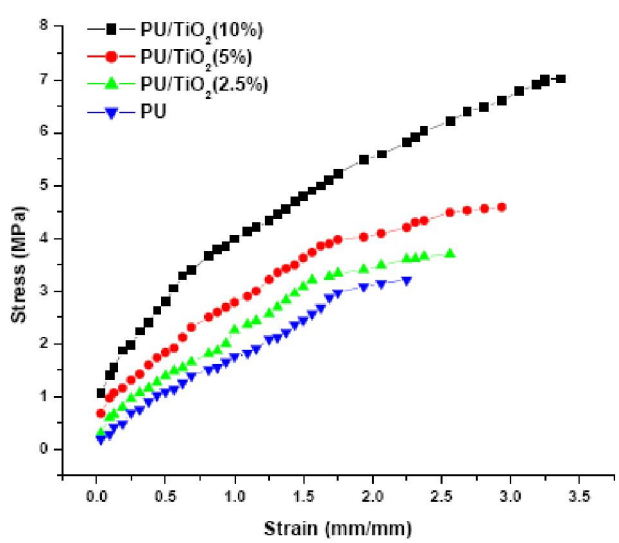

Figure 2 : Stress and strain curve of PU/ TiO_2 composites

The X-ray patterns of hydrothermally synthesized TiO_2, pure PU and PU/TiO_2 composites are shown in Figure 3. The hydrothermally synthesized TiO_2 shows stronger peaks at 25.4° (Figure 3a). The crystalline phase of TiO_2 identified matches well with PCPDF-841285 and it confirmed as anatase phase of TiO_2 obtained under hydrothermal conditions. The unfilled PU matrix showed single broad peaks at 2θ of 20.0°. The X-ray pattern of TiO_2 filler shows multiple sharp peaks. This is due to highly crystalline nature of TiO_2 filler than that of chain extended PU. After incorporation of TiO_2 filler into PU matrix, the peaks shape, size and position are changed. The PU/TiO_2 composite showed one sharp peaks at 20.0° and 25.4°. Also the peak position and intensity changed with composition of composites. This is due to change in microcrystalline behavior of composites with increase in filler content. The calculated crystalline cell parameters including the cell volumes of PU/TiO_2 composites are given in TABLE 2. The cell parameters were calculated using the Check cell software. The cell volume is lowest for TiO_2 (136.251.3Å^3) and highest for PU (1000.710 Å^3). For composites, cell volume increases significantly with increase in filler content and it lies in the range of 1110.7-1806.5 Å^3. This result clearly indicates physical interaction between PU and TiO_2. The data obtained from X-ray diffraction patterns showed the physical interaction or interfacial adhesion between the PU and well crystalline TiO_2 filler.

Figure 4 showed the FTIR spectra of TiO_2, PU and PU/TiO_2 composite. PU/TiO_2 composite and PU presented the same spectra in the wave number range of 400–4000 cm^{-1} while the weak peak located at 500–700 cm^{-1} is attributed to the stretching of Ti–O bond. FTIR spectra of PU and polymer composites show a narrow peaks attributed to the urethane carbonyl (C=O) stretching at 1710 cm^{-1} and stretching of the different C-H groups at 3084, 2985 and 2933 cm^{-1} are probably due to C-H aromatic, C- H asymmetric and symmetric vibrations. The amine groups such as C-N stretching and H-N stretching bands are found at the range 1320 cm^{-1} and 1650 cm^{-1} respectively. The broad and strong vibration stretching band of H-O group found at the range of 2500 to 3500 cm^{-1}. The TiO_2 stretching band in the FTIR spectra of PU/TiO_2 composite is observed at the range in between the 800 to 500 cm^{-1}.

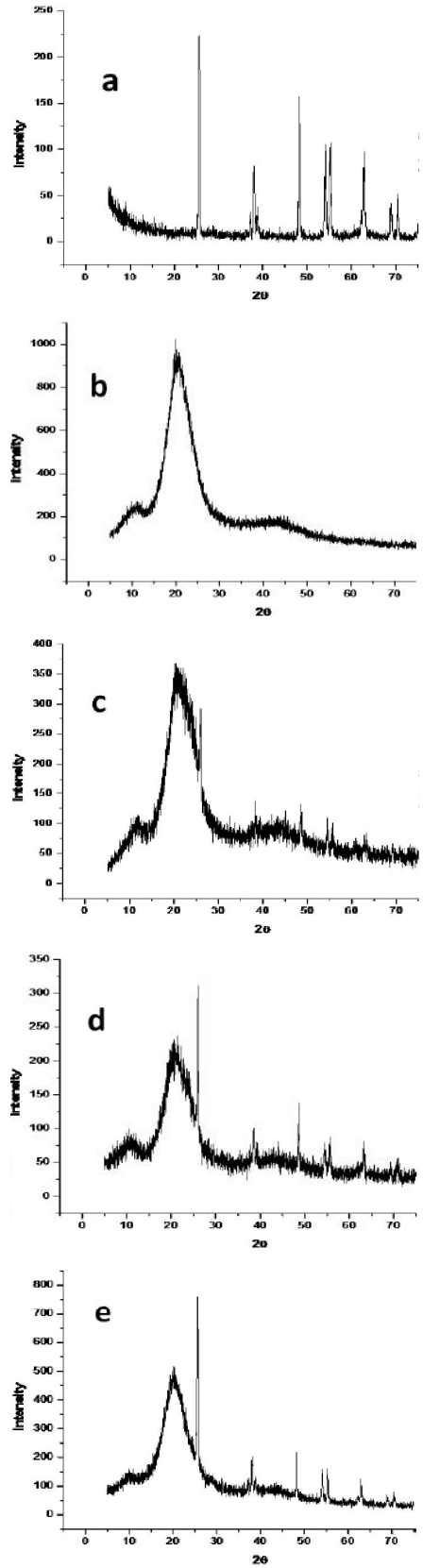

Figure 3 : X-ray patterns of (a) hydrothermally synthesized TiO_2; (b) pure PU; (c) PU/TiO_2 (2.5 wt %); (d) PU/TiO_2 (5 wt %); (e) PU/TiO_2 (10 wt %)

TABLE 2 : Cell parameters obtained for PU/TiO_2 filler composite

PU/TiO_2 composite (in Wt %)	Cell parameters						
	a (Å)	b (Å)	c (Å)	Alpha	Beta	Gamma	Volume (Å^3)
TiO_2	3.7842	3.7842	9.5146	90	90	90	136.251
Blank PU	5.9043	7.6116	25.960	95.96	115.34	71.74	1000.710
PU+2.5% PU	8.9853	10.727	12.525	90.28	109.56	78.11	1110.635
PU+5% PU	9.9104	12.017	14.213	90.07	109.79	79.91	1565.146
PU+10% PU	9.4526	12.469	16.522	90.13	109.35	80.03	1806.517

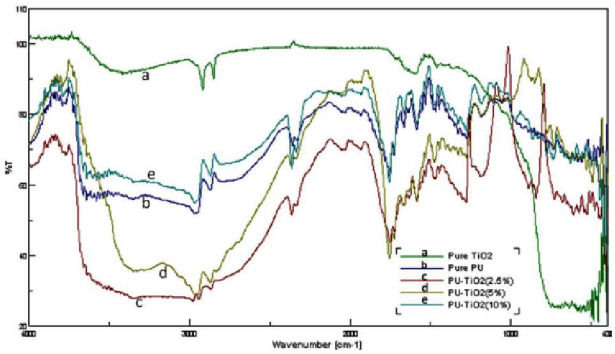

Figure 4 : FTIR spectra of PU/ TiO_2 composites

This result led to the conclusion that there were no major chemical structure changes in PU owing the presence of small amount of TiO_2 filler.

The surface morphology of chain-extended PU composites was studied by SEM. The electron photo micrographs of the surface of the composites are shown in Figure 5. From SEM photographs, two-phase morphology for PU was noticed. This is because chain extended PUs consists of both hard and soft segments. The SEM microphotographs also reveal that distribution of TiO_2 filler in PU matrix as a continuous phase. The TiO_2 filler is embedded in the PU matrix, which may be due to physical interaction between PU and filler. As the TiO_2 filler content increases, the domain size of second dispersed phase also increased, which may be due to the small agglomeration of TiO_2 filler. In the present investigation, in all the PU/ TiO_2 composites uniform distribution of second phase was noticed.

Photocatalytic activity of PU/TiO_2 composite was studied by using standard experimental procedures[22-25].

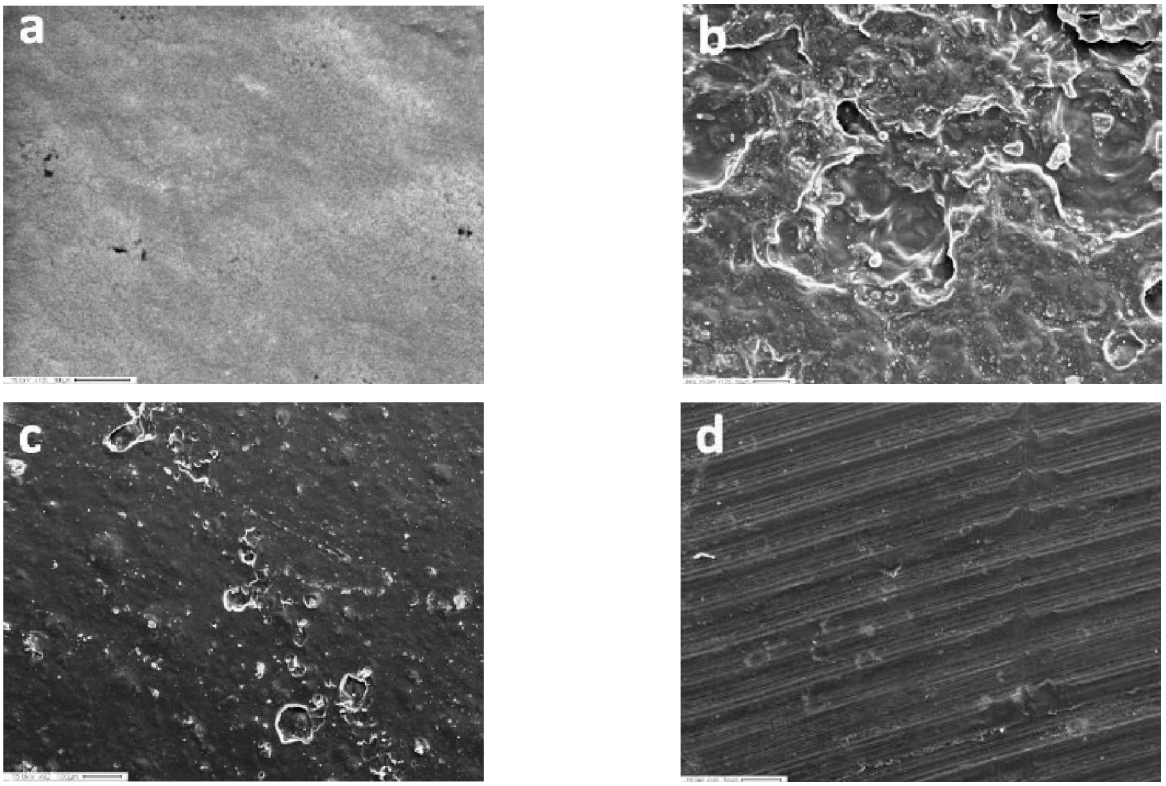

Figure 5 : SEM images of (a) pure PU; (b) PU/TiO_2 (2.5 wt %); (c) PU/TiO_2 (5 wt %); (d) PU/TiO_2 (10 wt %)

Photocatalytic experiments were carried out under UV light using 0.0001M Indigo Carmine dye solution of *pH* 6.8. Figure 6 showed the photocatalytic activity of pure TiO_2 and PU/TiO_2 composites. The surface hydroxyl groups on TiO_2 react with valence band (VB) holes to generate hydroxyl radicals, which are responsible for most of the oxidizing power of TiO_2 photocatalysts. In aqueous suspensions or in contact

with water vapors in the gas-phase, the surface OH group density remains unchanged during irradiation since the depleting OH groups are continuously replenished. The results obtained showed that PU/TiO_2 composites performed very less photocatalytic activity when compared to pure TiO_2 particles. On the other hand, in the present case TiO_2 particles were buried in the polymer matrix. The short length propagation of light in the polyurethane matrix will reduces the enough photon energy receive for activation of buried TiO_2 under UV light. Less transmission of light through the PU matrix limits the photons to reach TiO_2 surface and it significantly decreases the photocatalytic activity of PU/TiO_2 composites.

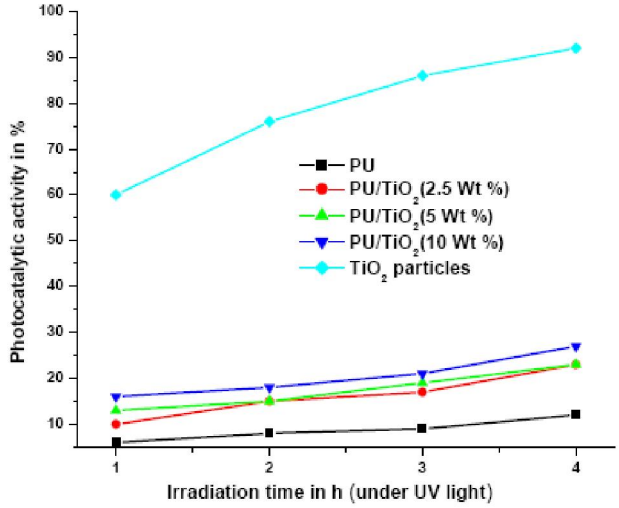

Figure 6 : Photocatalytic activities of pure TiO_2 and PU/ TiO_2 composites

Photocatalytic decomposition weigh loss of PU and PU/ TiO_2 composites were studied under UV light in aqueous medium. Figure 7 showed the photoinduced weight loss of the PU films under aqueous medium. The weight loss rates were much higher for the PU/TiO_2 composites than the pure PU film. The weight loss of the PU/TiO_2 composites films steadily decreased with irradiation under aqueous medium and led to the total 30% (PU/TiO_2 10 Wt % fill) reduction in 250 h while the PU film showed only 8 % weight loss under the identical experimental condition. The presence of O_2 was essential for the efficient photolytic degradation of PU. The photocatalytic decomposition of the PU matrix in the solid-phase seems to be initiated by active oxygen species (e.g. O^{2-}, $HO^{2\bullet}$ and $HO^{\bullet}$) that are generated from O_2 reacting with conduction band (CB) electrons like many other liquid- or gas-phase photocatalytic reactions[26-28]. On the other hand, in the present case where TiO_2 particles were buried in the polymer matrix, the surface OH groups were gradually depleted with irradiation. Although the surface OH groups were almost completely depleted after 48 h irradiation, the photocatalytic degradation of PU matrix steadily continued up to 250 h as shown in Figure 7. The C–H bands cleaved in the PU/TiO_2 composite film under irradiation in solid-phase due to higher photocatalytic activity of TiO_2 particles buried in the polymer matrix but remained intact in the pure PU film under irradiation. However, the initiation in the photocatalytic decomposition of PU is quite different. The photodecomposition initiates indirectly through oxidative radicals generated on TiO_2. The degradation process spatially extends into the PU matrix through the diffusion of the active oxygen species. Once the carbon-centered radicals are introduced in the PU chain, their successive reactions lead to the chain cleavage with the oxygen incorporation and CO_2 evolution.

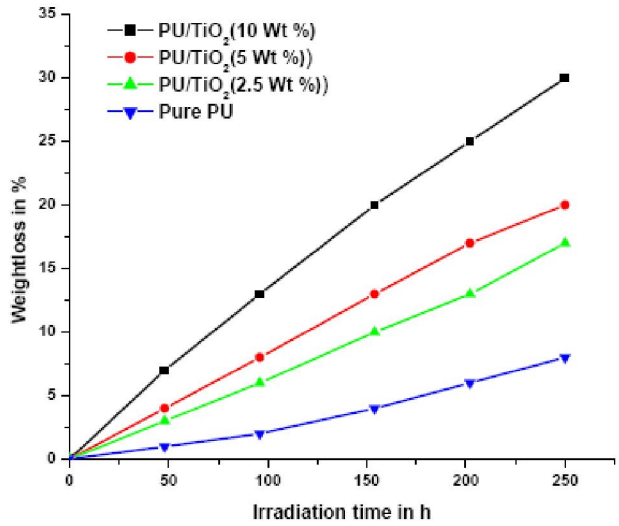

Figure 7 : Weight losses of the pure PU and PU/ TiO_2 composites films during UV light irradiation under aqueous medium

CONCLUSIONS

The improvement in tensile strength, tensile modulus and dimensional stability, density and % elongation at break of PU/TiO_2 composites was noticed with an increase in the TiO_2 filler content. This can be attributed to the fact that TiO_2 is acting as reinforcing filler in PU matrix. The data obtained from X-ray and FTIR showed

the physical interaction or interfacial adhesion between the PU and TiO_2 filler. The FTIR and X-ray data supports the improvement in the mechanical performance of the PU/TiO_2 composites. SEM photomicrographs revealed that uniform distribution of TiO_2 filler in PU and the domain size of the second phase depend on the filler content. The merit of using TiO_2 as filler lies in the fact that there is a good physical interaction between the PU and TiO_2 which seems to exhibit good photocatalytic behavior. This study reveals that the photocatalytic decomposition is distinguished from the direct photolytic decomposition of PU in several aspects. Firstly, the photocatalytic decomposition localized on the TiO_2–PU interface and grew cavities around particles while the direct photolytic centers were uniformly distributed in the PU matrix. Secondly, although both the photocatalytic and photolytic decompositon induced the chain cleavage and the oxygen functionality incorporation, the photocatalytic decomposition was much faster in the weight loss rate. This study demonstrates that the PU/TiO_2 composite has a potential viability to be used as a photodegradable product. On the other hand, the uniform dispersion of TiO_2 particles in the polymer matrix needs to be achieved for commercial applications. This study is successful in this respect and hydrothermally synthesized TiO_2 particles were incorporated into the PU matrix without agglomerates. Using renewable resources like Castrol oil for the preparation of polymer composites is the major scope of the present work.

REFERENCES

[1] A.P.Mouritz, A.G.Gibson; 'Fire Properties of Polymer Composite Materials', Springer, **(2006)**.

[2] T.R.Hull, B.K.Kandola; 'Fire Retardancy of Polymers New Strategies and Mechanisms', RSC, **(2009)**.

[3] D.Ratna; Epoxy Composites: Impact Resistance and Flame Retardancy Rapra Review Reports, **16(5)**, **(2005)**.

[4] K.Friedrich, S.Fakirov, Z.Zhang; 'Polymer Composite from Nano- to Macro-Scale', Springer, **(2005)**.

[5] G.M.Estes, S.L.Cooper, A.V.Tobolsky; J.Macromol. Sci.Rev.Macromol.Chem., **4**, 313 **(1970)**.

[6] J.W.C.Van Bogart, P.E.Gibson, S.L.Cooper; J.Polym.Sci.Polym.Phys.Ed., **21**, 65 **(1983)**.

[7] J.Ophir, G.L.Wilkes; J.Polym.Sci.Polym.Phys., **18**, 1969 **(1980)**.

[8] Z.Wirpsza; In: T.J.Kemp, (Ed); Polyurethanes: Chemistry, Technology and Applications. Ellis Horwood, New York, **(1993)**.

[9] J.Blackwell, M.R.Nagarajan, T.B.Hoitnik; Polym., **23**, 950 **(1982)**.

[10] S.P.Pappas, F.H.Winslow; 'Photodegradation and Photostabilization in Coatings', ACS Symposium Series 151, American Chemical Society, Washington, DC, **(1981)**.

[11] B.Ohtani, S.Adzuma, S.Nishimoto, T.Kagiya; Polym.Degrad.Stab., **35**, 53 **(1992)**.

[12] C.A.Prinet, G.Mur, M.Gay, L.Audouin, J.Verdu; Polym.Degrad.Stab., **61**, 211 **(1998)**.

[13] U.Gesenhues; Polym.Degrad.Stab., **68**, 185 **(2000)**.

[14] H.Behar-Levy, D.Avnir; Adv.Funct.Mater., **15**, 1141 **(2005)**.

[15] H.Behar-Levy, O.Neumann, R.Naaman, D.Avnir; Adv.Funct.Mater., **19**, 1207 **(2007)**.

[16] H.Behar-Levy, D.Avnirl; Chem.Mater., **14**, 1736 **(2002)**.

[17] H.Behar-Levy, G.E.Shter, G.S.Grader, D.Avnir; Chem.Mater., **16**, 3197 **(2004)**.

[18] G.E.Shter, H.Behar-Levy, V.Gelman, G.G.Srader, D.Avnir; Adv.Funct.Mater., **7**, 913 **(2007)**.

[19] I.Yosef, D.Avnir; Chem.Mater., **18**, 5890 **(2006)**.

[20] R.E.Dinnebier, S.J.L.Billinge; 'Powder Diffraction Theory and Practice', the Royal Society of Chemistry, Cambridge, UK, **(2008)**.

[21] Pecharsky, Vitalij, Zavalij, Peter; 'Fundamentals of Powder Diffraction and Structural Characterization of Materials', 2nd Edition, Springer, **(2008)**.

[22] H.P.Shivaraju; In.J.Environ.Sci., **1(5)**, 911 **(2011)**.

[23] H.P.Shivaraju, C.P.Sajan, T.Rungnapa, V.Kumar, C.Ranganathaiah, K.Byrappa; Mater.Res.Innov., **14(1)**, 80 **(2010)**.

[24] H.P.Shivaraju, K.Byrappa, S.Ananda; In.J.Chem. Eng.Res., **2(2)**, 219 **(2010)**.

[25] C.P.Sajan, B.Shahmoradi, H.P.Shivaraju, K.M.Lokanatha Rai, S.Ananda, M.B.Shayan, T.Thonthai, G.V.Narasimha Rao, K.Byrappa; Mater.Res.Innov., **1(14)**, 89 **(2010)**.

[26] D.F.Ollis, H.Al-Ekabi, (Eds); 'Photocatalytic Purification and Treatment of Water and Air', Elsevier, Amsterdam, **(1993)**.

[27] M.R.Hoffmann, S.T.Martin, W.Choi, D.W.Bahnemann; Chem.Rev., **95**, 69 **(1995)**.

[28] A.Mills, S.L.Hunte; J.Photochem.Photobiol.A: Chem., **108**, 1 **(1997)**.