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Preparation and Characterization of Polymer TiO_2 Hybrid Nanocomposites Via In-situ Polymerization

Feng Lin, Leonardo C. Simon

Institute for Polymer Research, Department of Chemical Engineering
University of Waterloo, 200 University Av. W., Waterloo, ON, Canada, N2L 3G1
lsimon@uwaterloo.ca; http://lsimon.uwaterloo.ca/

Abstract

Polymer nanocomposites have important applications in automotive and aerospace, electronics and electrical engineering, household products and appliance components, packaging, and defense systems. Among many nanocomposite precursors, TiO_2 nanopowder is being increasingly investigated due to its specific properties. This poster will discuss the preparation characterization of hybrid polymer-TiO_2 nanocomposites. When dispersed at the nanoscale level, TiO_2 nanopowders can act as visually transparent UV filters and high mechanical performance materials. Unfortunately, the dispersion of nanoscale TiO_2 in hydrophobic polymers, like polyolefins, is difficulty to obtain because most of the TiO_2 available from commercial sources has agglomeration of primary nanoscale particles forming secondary particles in the micrometer range. The objective of this research is to prepare hybrid nanocomposites using *in-situ* polymerization. The synthesis strategy involved two steps. Firstly, TiO_2 was modified with 3-(trimethoxysilyl)propylmethacrylate. The grafting density and efficiency were quantified and the particle size distribution and dispersibility characteristics in suspension were measured. Secondly, styrene was polymerized using free radical mechanism to attempt copolymerization with groups on the surface of the modified TiO_2 resulting in the formation of nanocomposites with polymer chains chemically bonded to the surface of TiO_2 nanopowders. The final polymer nanocomposites structure and properties have been and are being investigated.

Introduction

TiO_2 Surface Characteristics

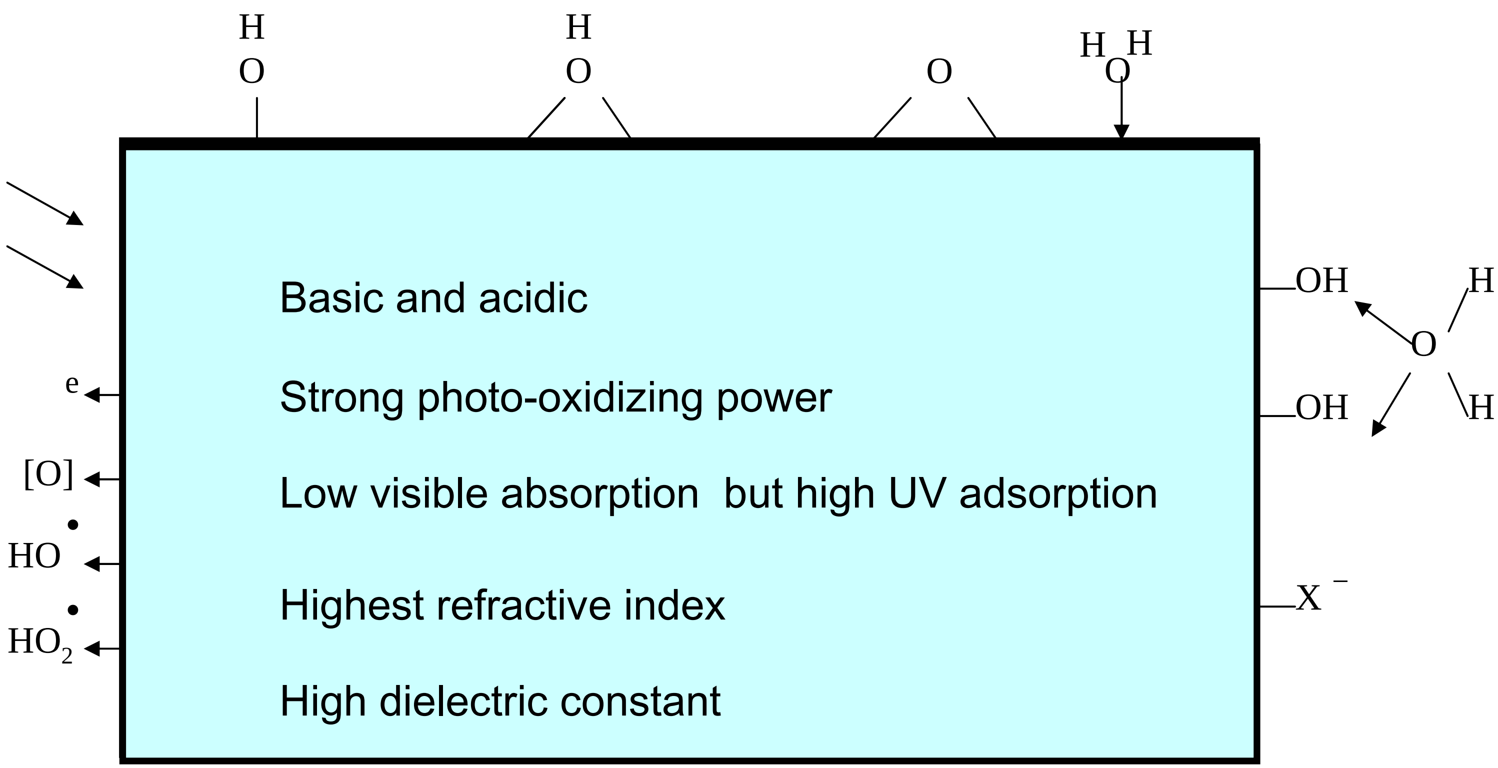

Figure 1 The principal surface features of a TiO_2 particle

Size Dependent Phenomena of Nanoparticles

- High surface to volume (S/V) ratio
- High activity
- Discrete electronic structure

Size induced conductive-nonconductive transition phenomena

Do not scatter light significantly

Magnetic moment per atom increases with the decreasing size of a particle

- No large stress build-up

Synthesis methods of Polymer TiO_2 Nanocomposites

- Direct mixing
- Sol gel process
- *In-situ* polymerization

Properties of Polymer TiO_2 Nanocomposites

- Increase in elastic modulus polyimide nanocomposites was around 30% at 9% nano-TiO_2 loading over its microcomposites (Chiang, Thin Solid Film, 2004,147, p359)
- 3-7% of nano TiO_2 was effective to increase the degradation temperature of polybenzoxazine-based nancomposites by 80-100°C and the effect of titania on flame resistance was also remarkable (Agag, Polymer, 2004, 45, p7903)
- Transparency but strong UV adsorption was observed for polyvinyl alcohol nanocomposites up to 35% TiO_2 loading (Nussbaumer, Macromol. Mater. Eng., 2003, 288, p44)
- Refractive index of PVL nanocomposites rose linearly from 1.521 for neat PVL to 1.609 at 35% TiO_2 (Nussbaumer, Macromol. Mater. Eng., 2003, 288, p44)
- Electrical breakdown strength of nanoTiO_2-filled LDPE nanocomposites was 50% higher than that for micro-filled (Ma, J Mater. Res.,2004,19,857)
- Dielectric constant of nanoTiO_2-dispersed polyimide hybrids increased with the increasing titania content (Chiang, Thin Solid Film, 2004,147, p359)

Objective

- Synthesize polymer-TiO_2 nanocomposites acting as visually transparent UV filters and improved mechanical performance materials

- Overcome three challenges

  i) Strong tendency of particle agglomeration
  ii) Hydrophilic TiO_2 is incompatible with hydrophobic polymers
  iii) Photoactivity of TiO_2 make polymer degrades

- Use two-step strategy

  Step 1 Preparation and characterization of modified TiO_2

  Step 2 Synthesis and characterization of TiO_2 nanocomposites by *in-situ* polymerization

Experimental

Modification of TiO_2 by MPS

- Premixed TiO_2 with ethanol under ultrasonic
- Added NH_4OH, H_2O, MPS, hydrolysis at R.T. ; condense at evaluated temp.
- Purified and dried after reaction

Polymerization of PS-TiO_2 Nanocomposites

- Dispersed the modified TiO_2 in styrene under ultrasonic
- Well sealed and purged with N_2 after adding initiator AIBN
- Free radical polymerization carried out at 60^{o}C by using a shaker
- Ethanol precipitated the polymer
- Centrifuge fractionated the nancomposite gel from the homo-PS

Methodology for Modified TiO_2 and Polymer Nanocomposites Characterization and Testing

- FTIR--------------- Chemical composition of modified TiO_2 and nanocomposites
- ^{1}H-NMR----------- Quantification of grafting by MPS in modified TiO_2
- BI-DCP sizer----- Particle size distribution of modified TiO_2 in ethanol
- Vis------------------ Dispersibility of modified TiO_2 in toluene
- TGA---------------- Quantitative polymer grafting on TiO_2 in nanocomposites
- DMTA--------------Thermal and Mechanical properties of nanocomposties
- UV-vis------------- Optical properties of nanocomposites
- SEM--------------- Morphology of modified TiO_2 and nanocomposites

Results and Discussions

Reaction Mechanism

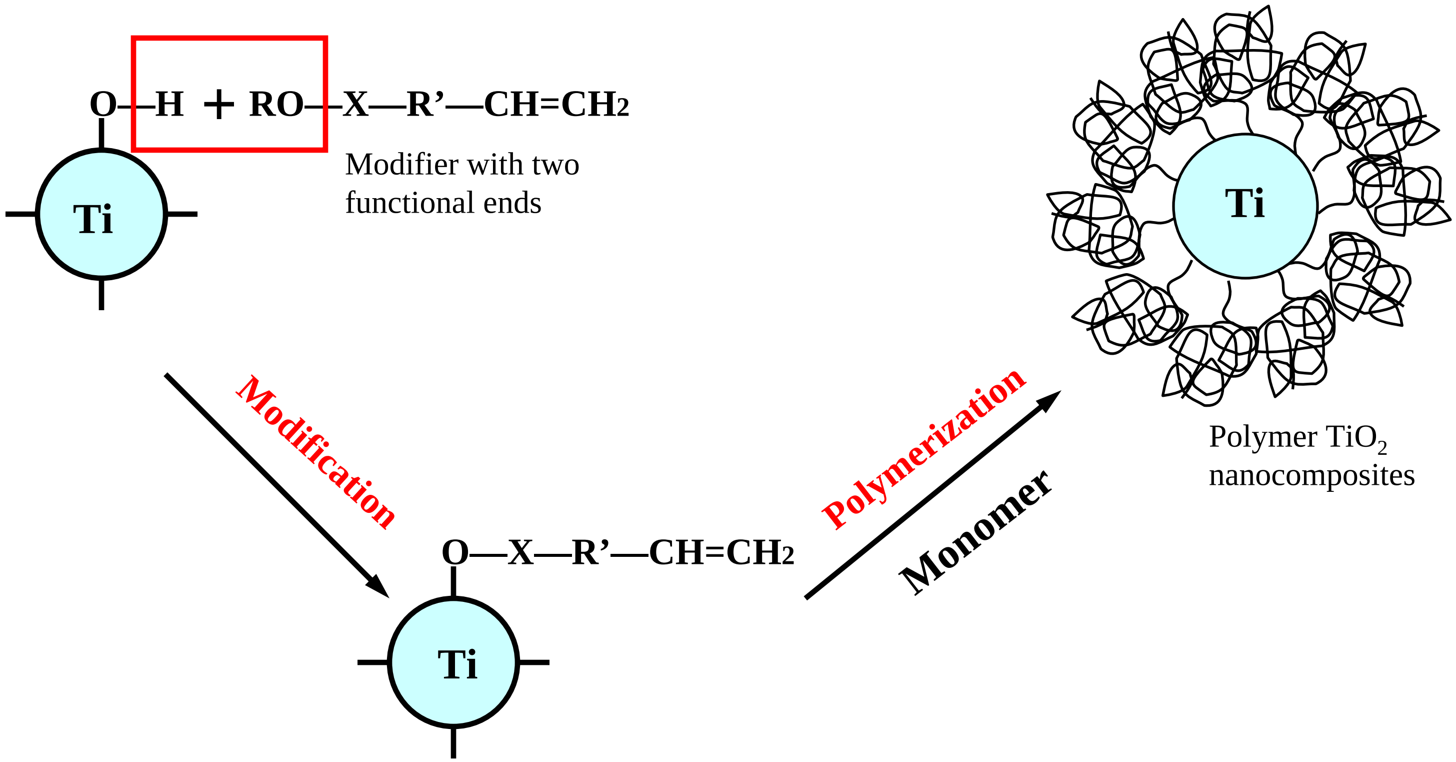

Figure 2 Reaction mechanism scheme for the deposition of modifier on TiO_2 surface and the formation of polymer TiO_2 nanocompoistes

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FTIR Spectra of modified TiO_2

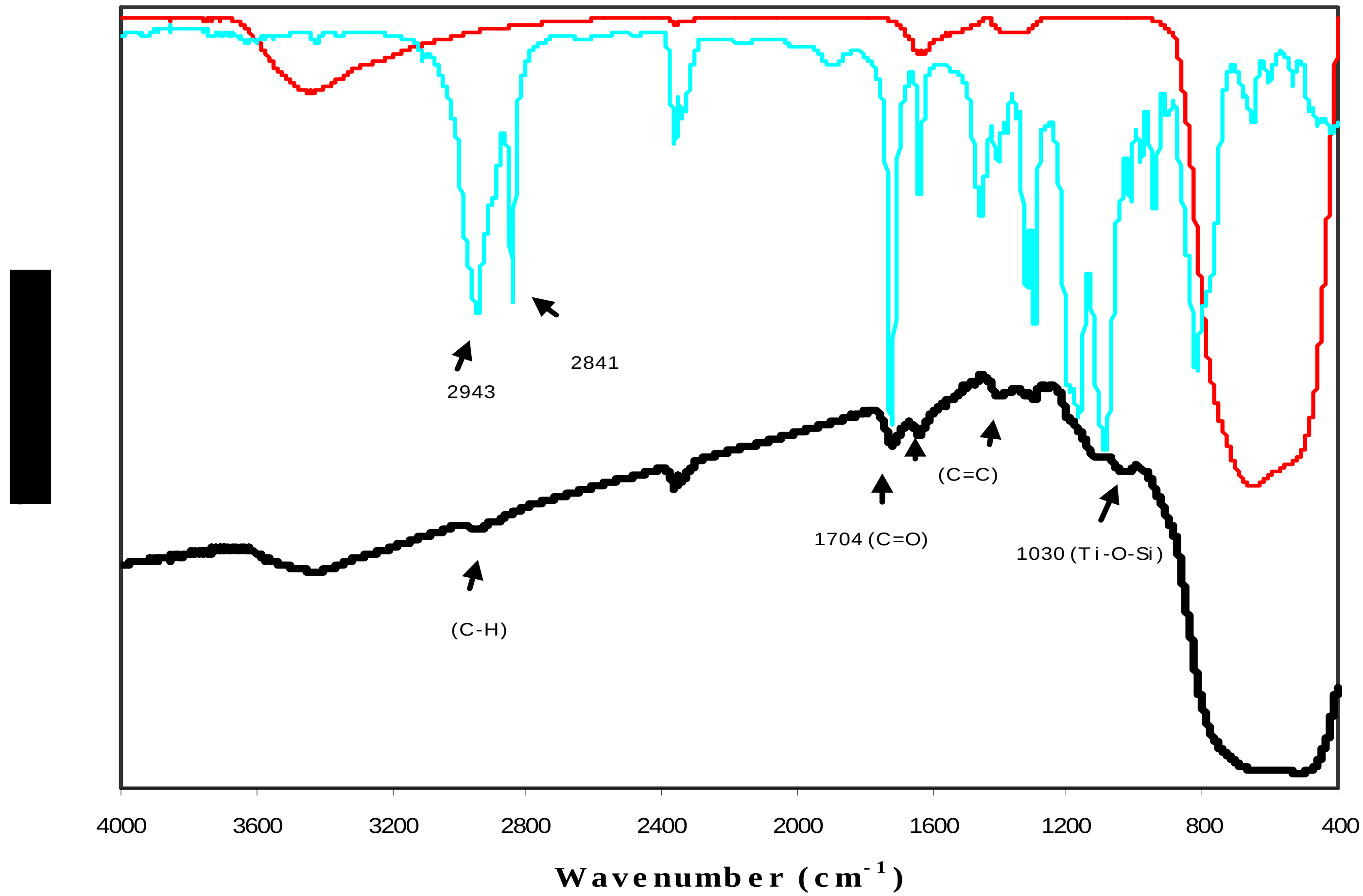


Figure 3 FTIR spectra of (red)pure TiO_2; (green)pure MPS; and (black) MPS-modified TiO_2

Quantification of Grafting by MPS

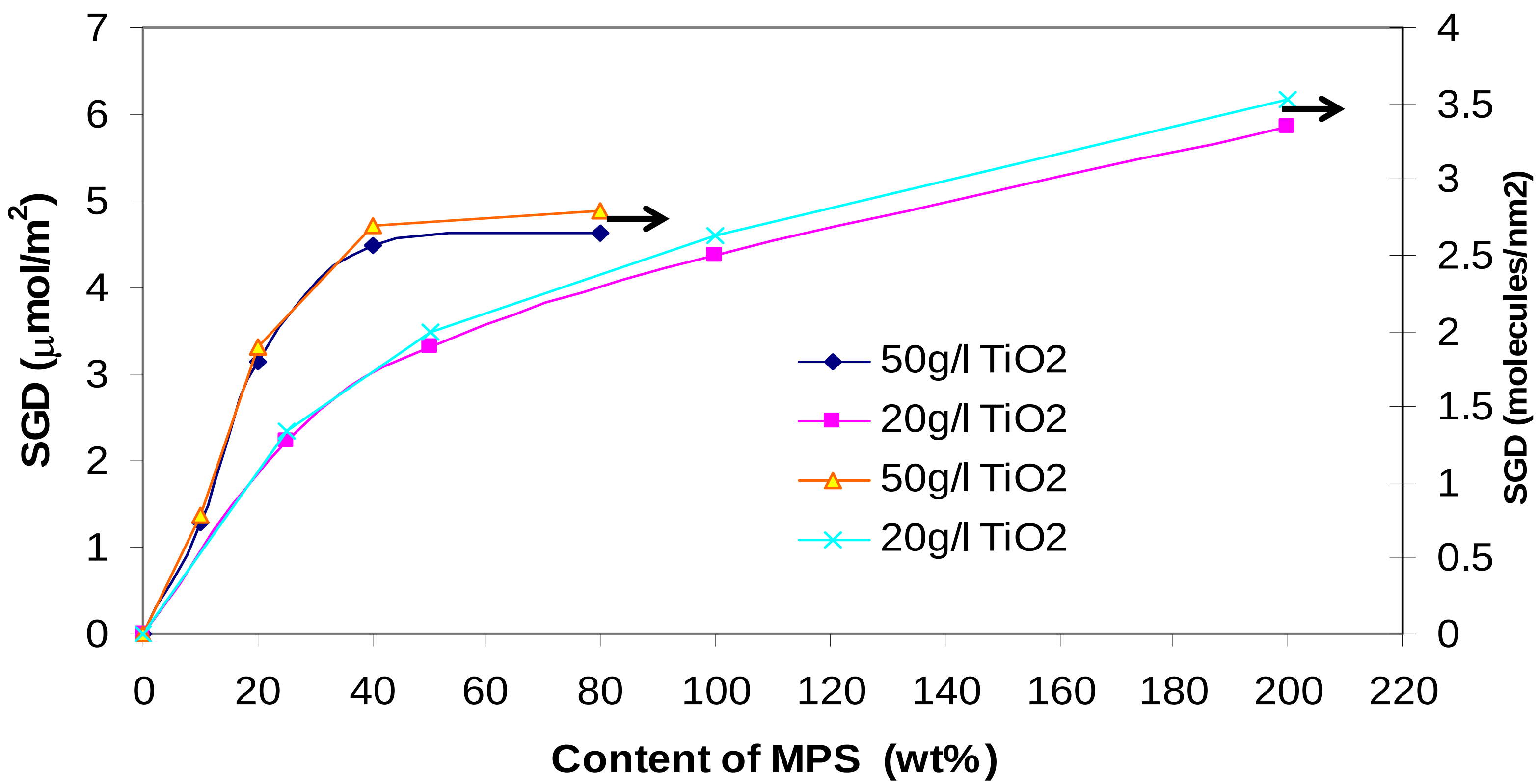


Figure 4 Surface Grafting Density vs Weight Ratio of MPS to TiO_2

How to calculate SGD

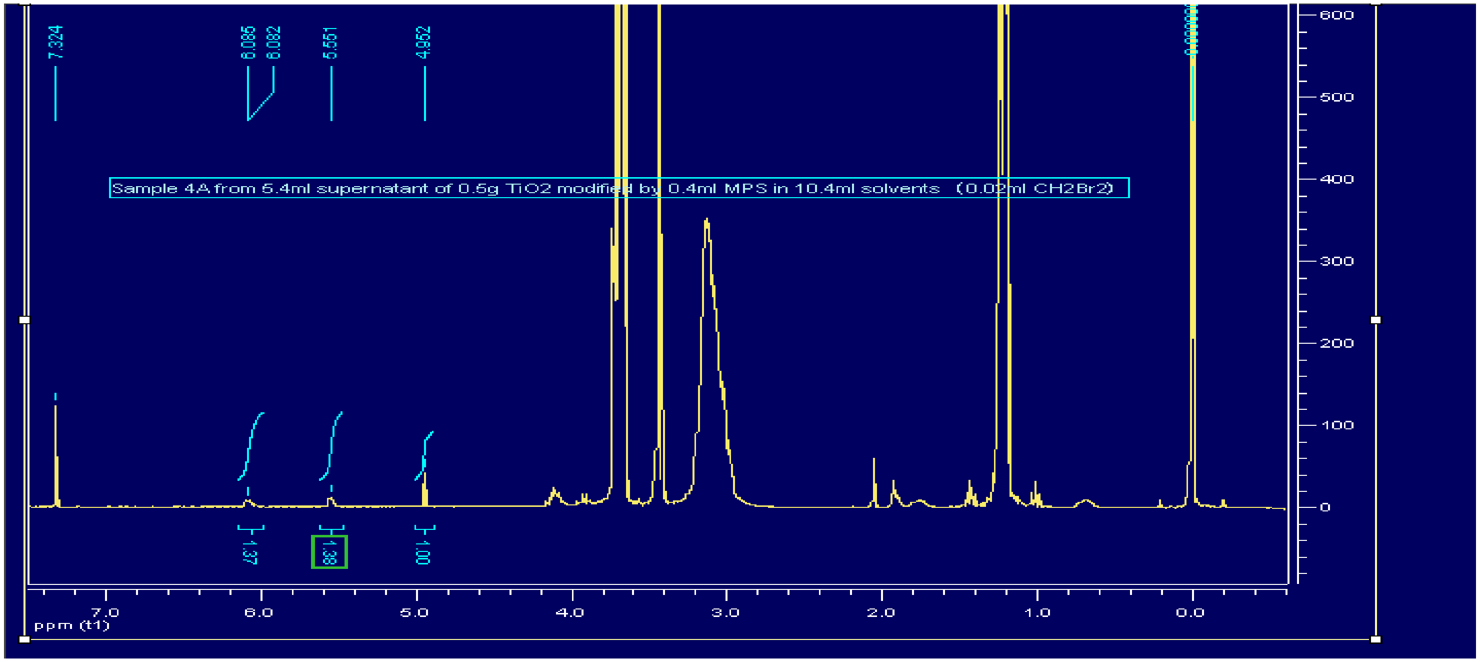


Figure 5 1H-NMR spectrum of one sample supernatant after centrifuging the modification reaction mixture

$$SGD = 10^6 \mu mol/m^2 * \frac{(\rho_M * V_{Mo}/M_{WM}) - (V_O/V_S)*(P_D/P_M)*((a+b)/c)*(\rho_D * V_D/M_{WD})}{W_T * S_T}$$

$$= 6.023*10^5 molecule/nm^2 \frac{(\rho_M * V_{Mo}/M_{WM}) - (V_O/V_S)*(P_D/P_M)*((a+b)/c)*(\rho_D * V_D/M_{WD})}{W_T * S_T}$$

Quantification of Grafting by MPS

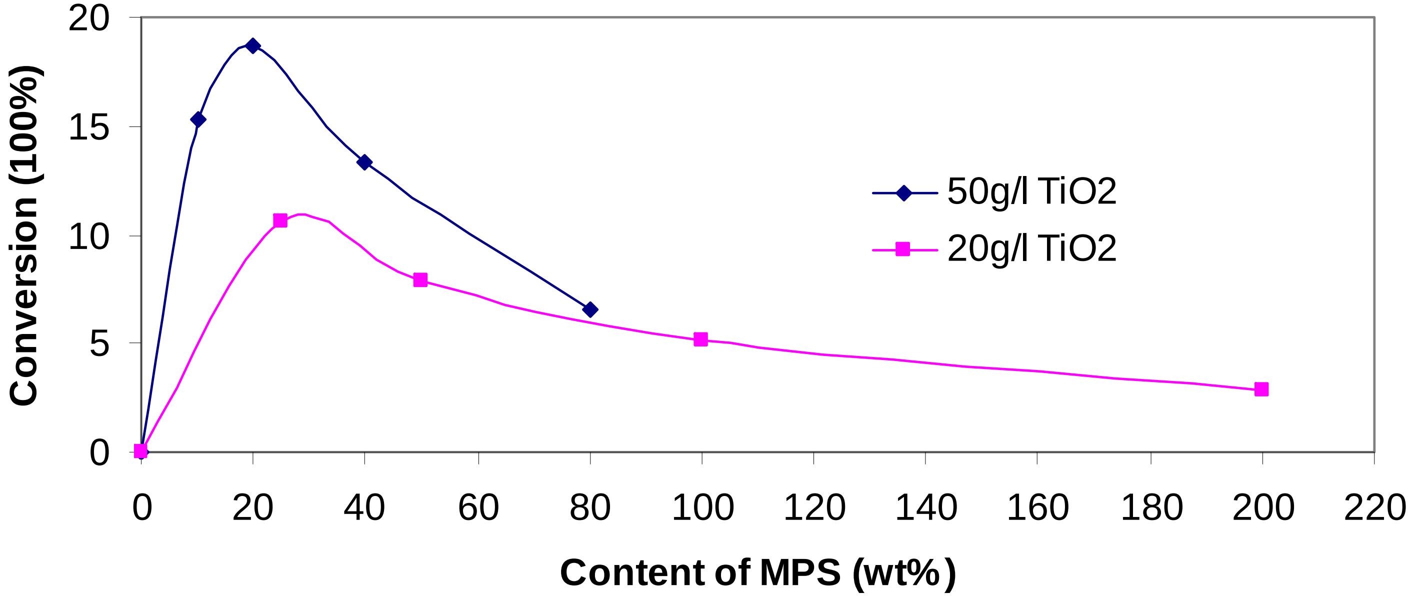


Figure 6 Surface Grafting Conversion (SGC) vs Weight Ratio of MPS to TiO_2

$$SGC = 100\% * \frac{(\rho_M * V_{Mo}/M_{WM}) - (V_O/V_S)*(P_D/P_M)*((a+b)/c)*(\rho_D * V_D/M_{WD})}{(\rho_M * V_{Mo}/M_{WM})}$$

Particle Size of modified TiO_2 in ethanol

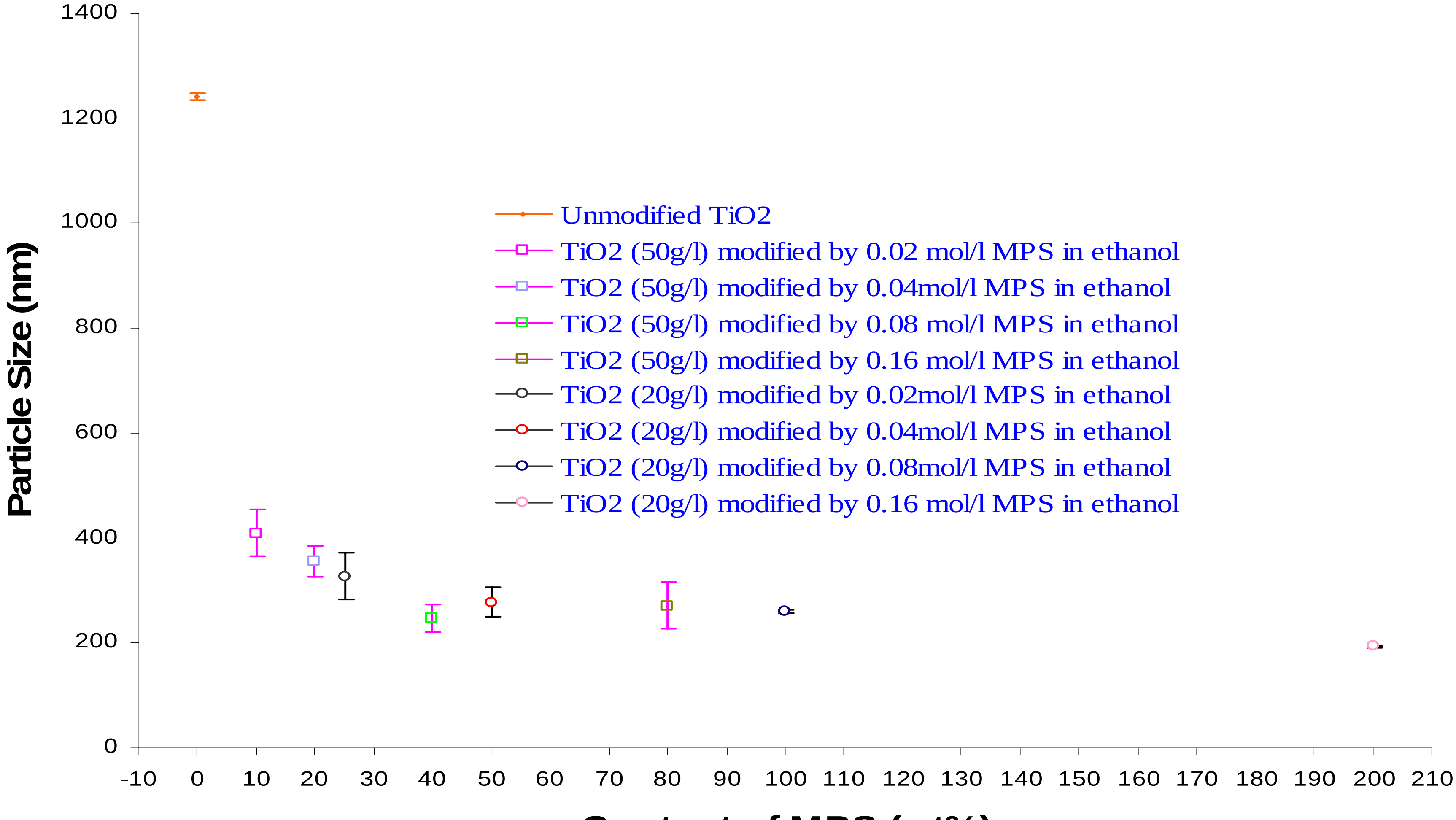


Figure 7Average Particle Size vs Weight Ratio of MPS to TiO_2

Dispersibility of modified TiO_2 in toluene

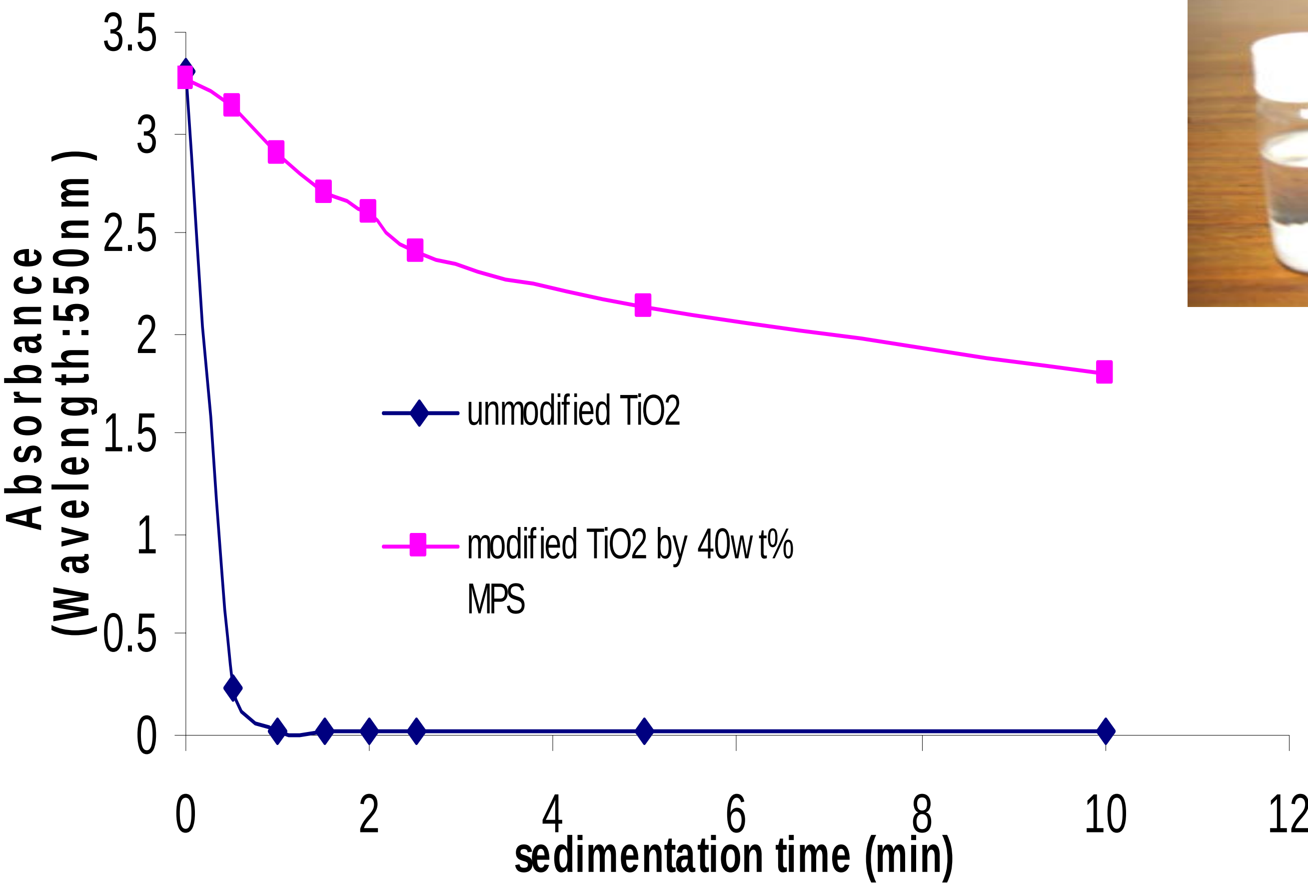


Figure 8 Dispersibility of unmodified and modified TiO_2 in toluene

Morphology of modified TiO_2 in toluene

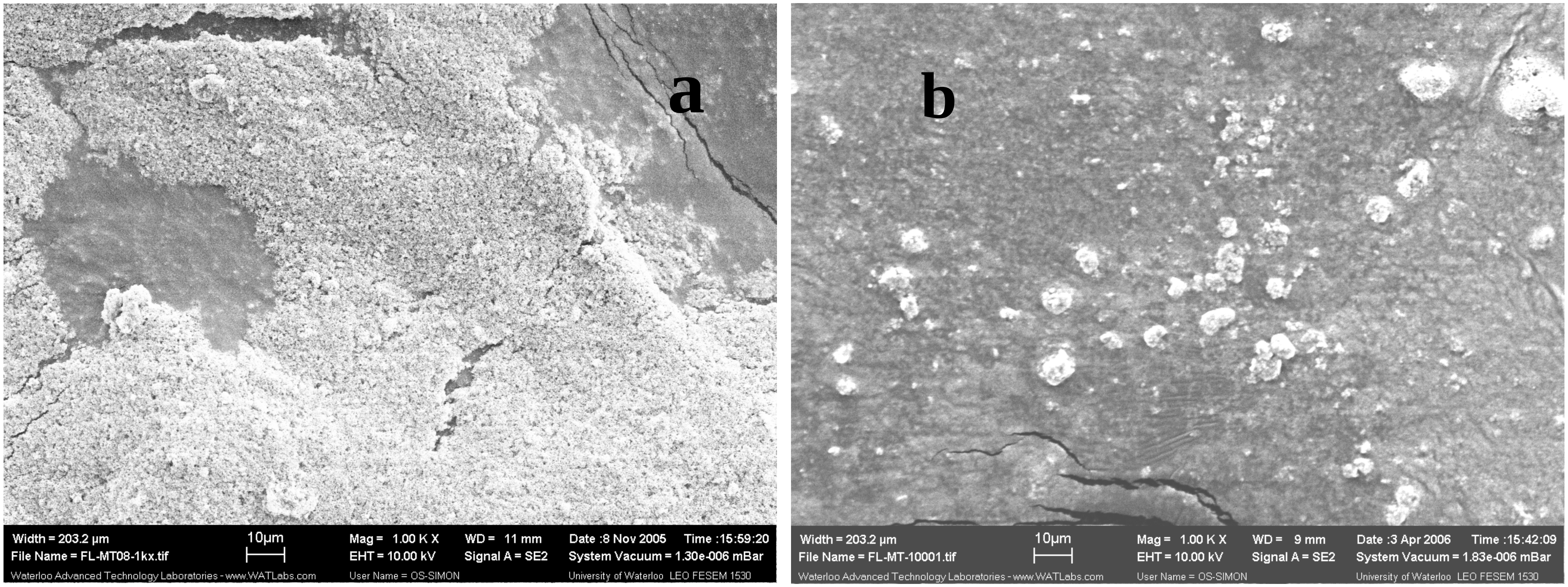


Figure 9, SEM micrographs of (a) unmodified TiO_2 ('severe agglomeration')
(b) modified TiO_2 by MPS ('light agglomeration')

FTIR Spectra of PS TiO_2 Nancomposites

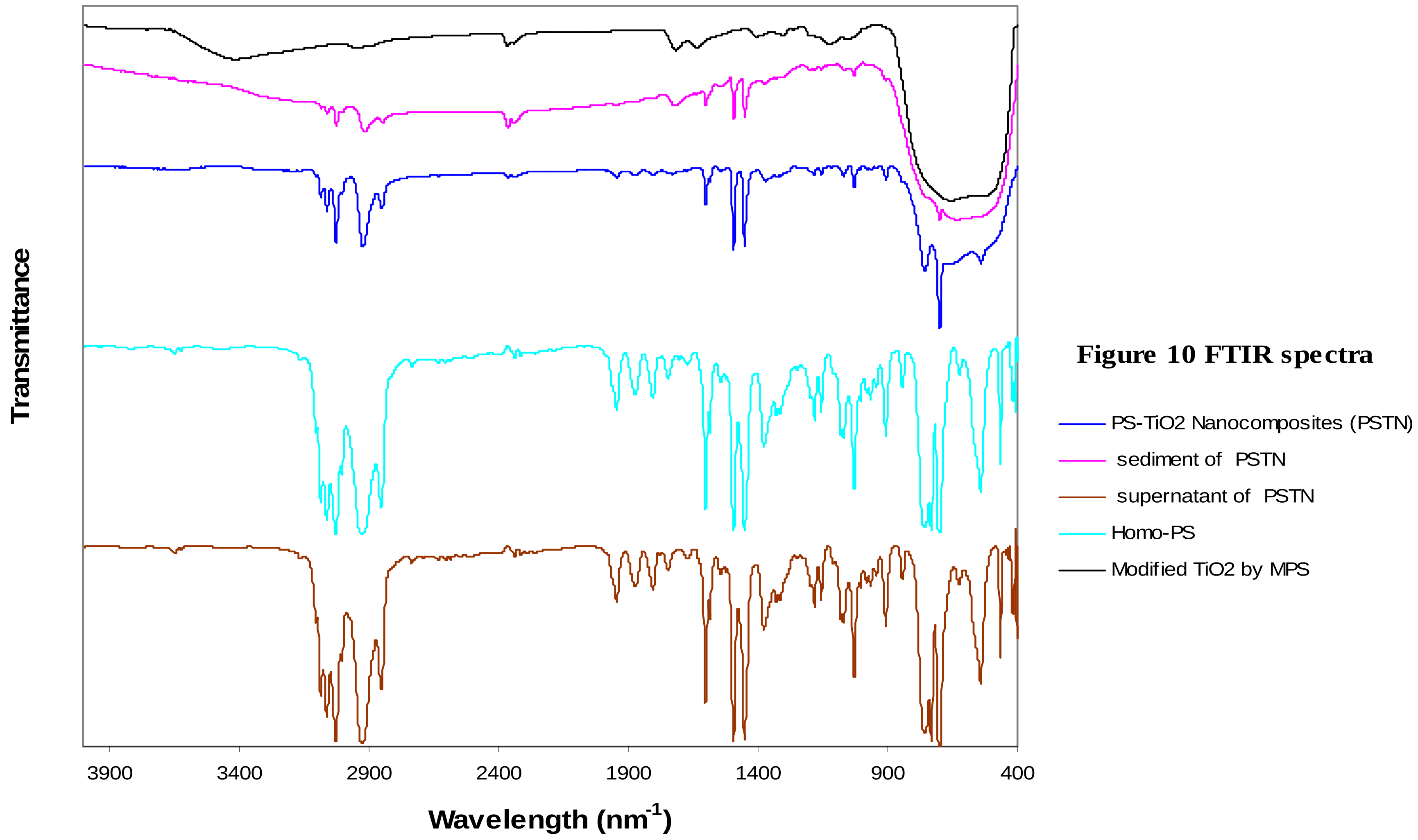
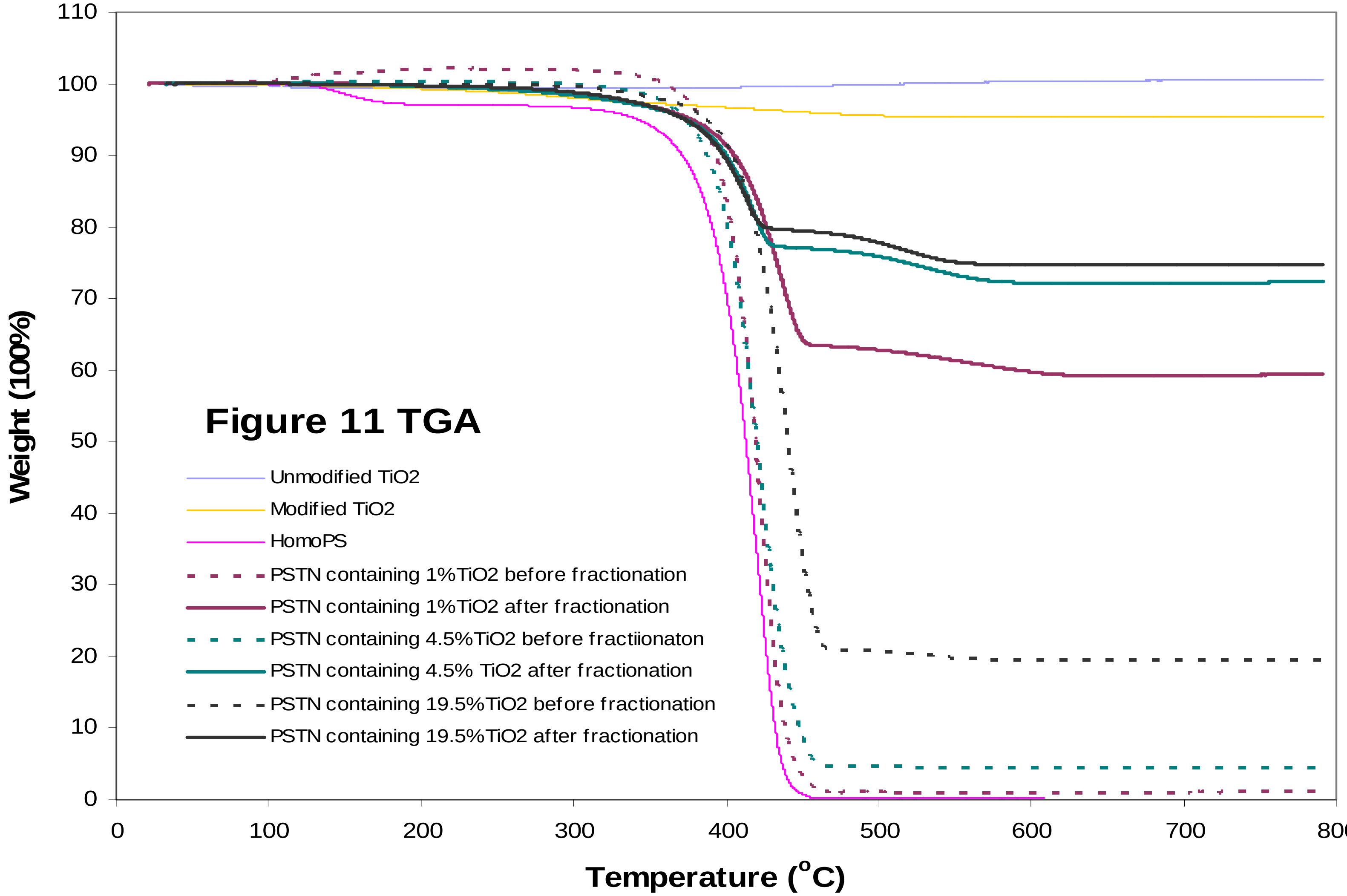


Figure 10 FTIR spectra

TGA of PS TiO_2 Nanocomposites



Quantification of PS grafting on TiO_2

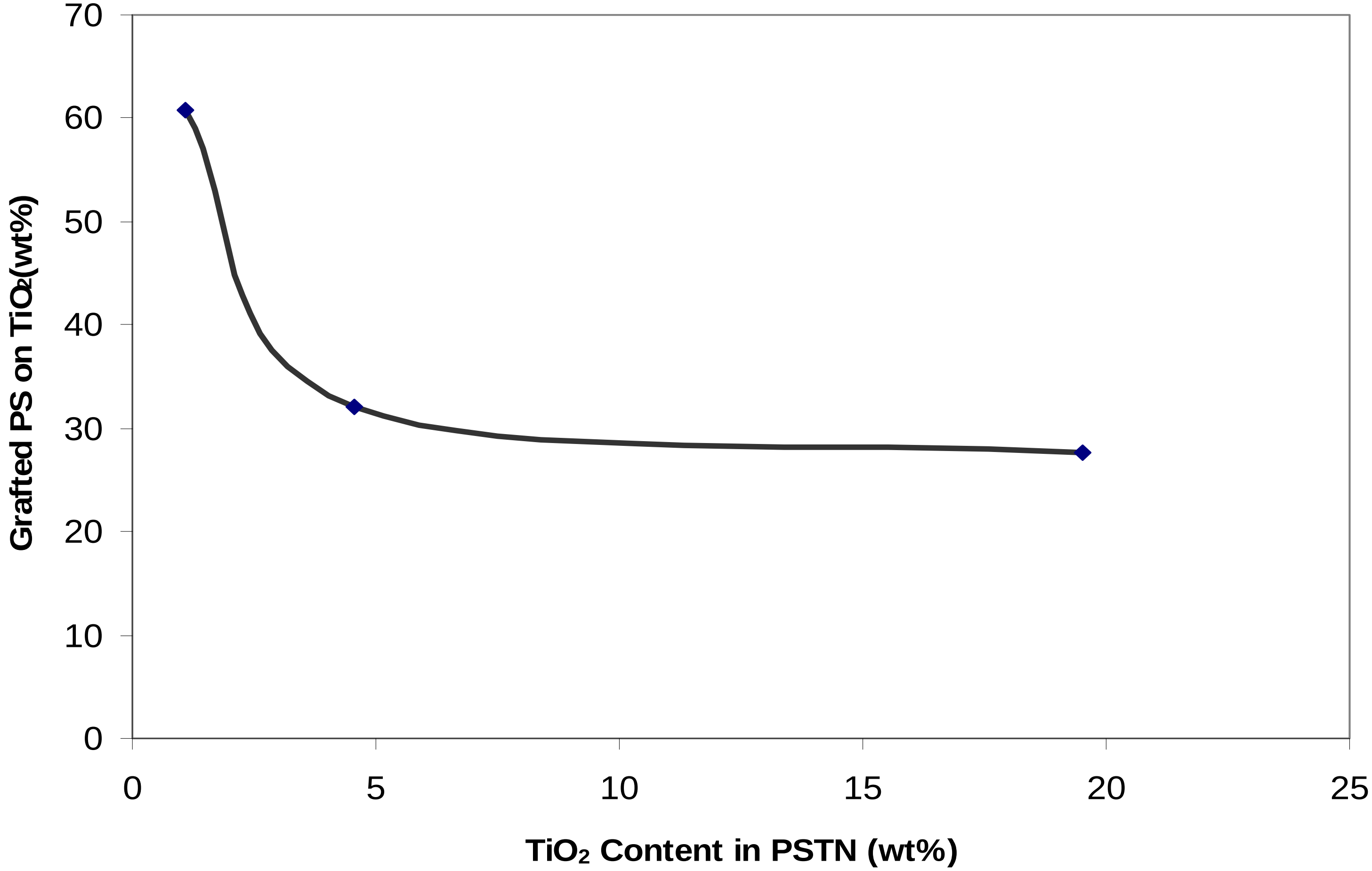
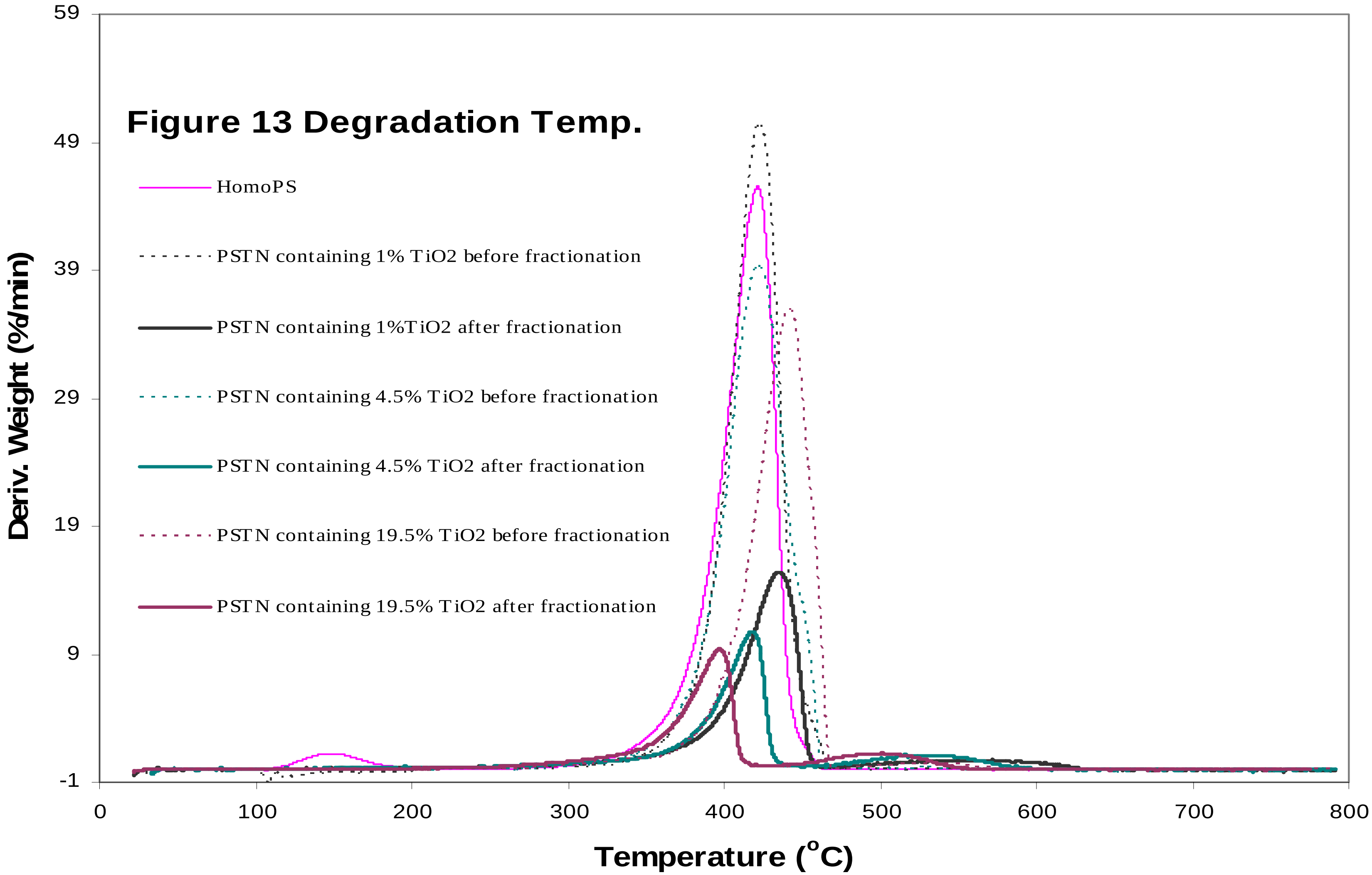


Figure 12 PS grafting efficiency vs TiO_2 concentration

T_d of PS TiO_2 Nanocomposites



Morphology of PS TiO_2 Nancomposites

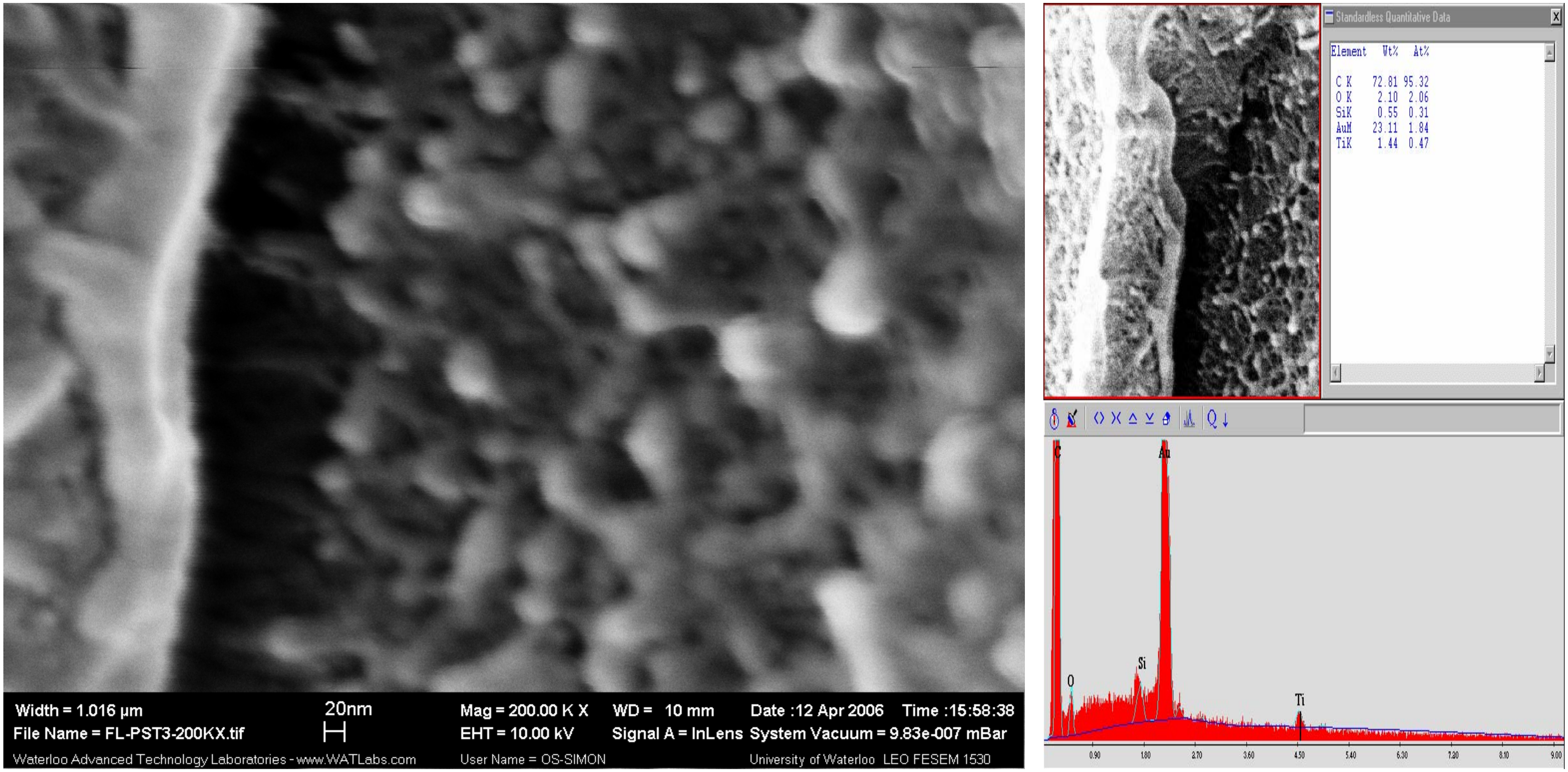
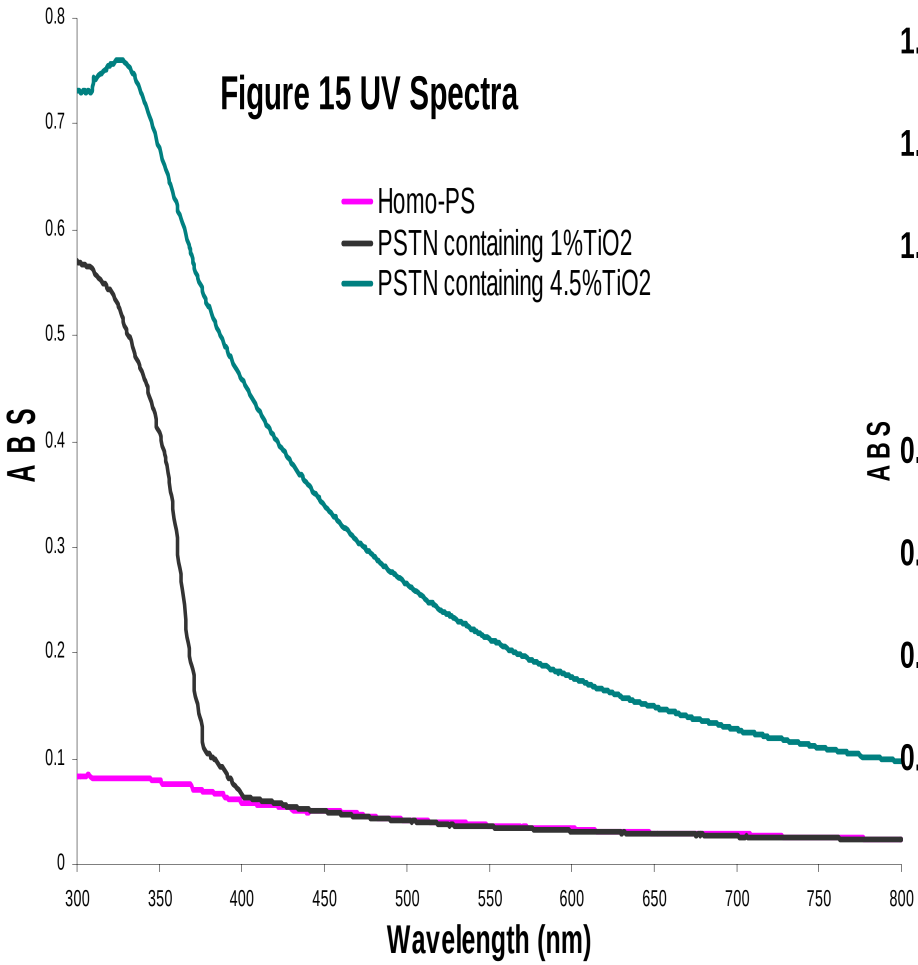
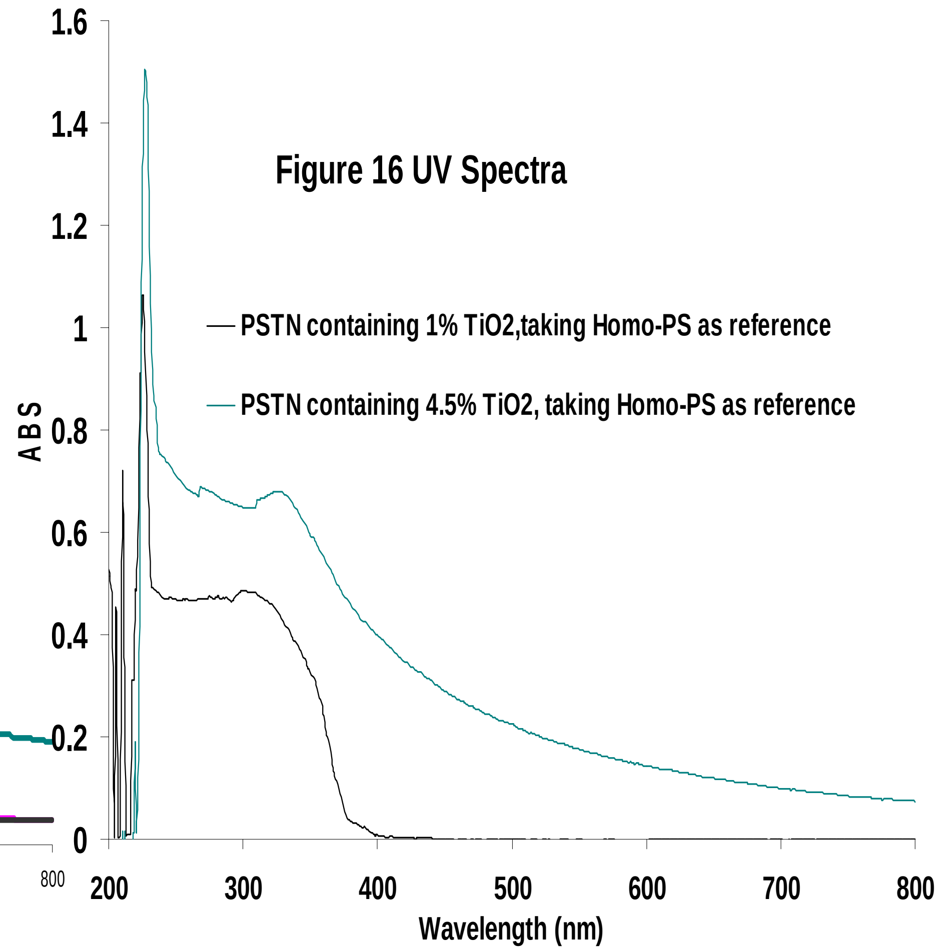


Figure 14 SEM graphs of PSTN containing 1% TiO_2 (left) Mag. 200,000x; (right) Edx

Optical Properties of PS-TiO_2 Nanocomposites





Conclusions

- Modified TiO_2 and PS-TiO_2 Nanocomposites were successfully prepared
- MPS and PS were chemically bonded on TiO_2 surface
- Surface grafting efficiency by MPS and PS were quantified
- MPS improved dispersibility of TiO_2 in nonpolar media
- TiO_2 of average particle size in the order of 20-50nm was embedded in PS matrix of the nanocomposites
- TiO_2 did not affect much the degradation temp. of the nanocomposites
- Relatively visible transparency but stronger UV absorption of the nanocomposites were observed up to TiO_2 contents of 1wt%

Future Work

- Thermal and mechanical properties of nanocomposites
- Comparison experiments: PS TiO_2 composites made by physical mixing

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Acknowledgements

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