CHAPTER IV
APPLICATION OF TITANIUM DIOXIDE NANOPARTICLES IN POLYPROPYLENE NANOCOMPOSITES

ABSTRACT

Titanium dioxide is an inorganic filler that is widely used in pigment and photocatalyst applications. This metal oxide has been intensively studied, especially in sub-micron or nanometer size which has attracted much interest because smaller particles have larger surface area per gram or per volume ratio and therefore can be more reactive. In this work, TiO_2 particles prepared via sol-gel process were introduced into polypropylene by the master batch manufacturing process and the resulting composites were compared with the blends prepared with commercial nanoparticles TiO_2. The effect of TiO_2 contents and the characteristics of TiO_2 from two sources on the properties of resulting nanocomposites were studied. Results from DSC indicated that there was no change in the crystallization exotherms of composites prepared from TiO_2 by sol-gel process whereas the composites prepared with commercial nano-TiO_2, the added TiO_2 acted as a nucleating agent. At 5wt% and 10wt% of TiO_2 in polypropylene were able to shift the crystallization exotherms by 6°C and 8°C, respectively, and therefore resulted in higher degree of crystallinity as observed from DSC and XRD. TiO_2 particles from sol-gel process were still in micro size whereas the commercial TiO_2 were much smaller, therefore it had more effect on the properties of polymer. Thermogravimetric analysis results showed that the degradation temperature of composites prepared from both sources of TiO_2 was increased by increasing contents of TiO_2, suggesting that the addition of nano-TiO_2 can improve the thermal stability of polymer. At 1-5wt% of TiO_2 from two sources in PP, there were no adverse effects on mechanical properties of the composites, whereas at 10wt% commercial TiO_2, it can increase much in Young's modulus due to higher in degree of crystallinity in this content.

(Key-words: Titanium Dioxide, Nanoparticles, Polypropylene, Masterbatch Manufacturing Process, Crystallization, Thermal Stability, Mechanical Properties)

INTRODUCTION

Nanotechnology is one of the key technologies of this century and nanoparticles inorganic filler have been intensively studied such as Si, Al, Ti and Zn. In this work we will concentrate on Titanium (Ti), this element is finding more and more applications in today's society. Over 90% of the worldwide use of titanium is in the oxide form, TiO_2 (Titanium Dioxide), thus creating a high demand. With "little effect" and "surface effect" the nanoparticle has many special properties that are different from those of other larger particles [1] because smaller particles have larger surface area per gram or per volume ratio and therefore can be more reactive.

Modification of the polymer with inorganic nanoparticles results in polymer/inorganic nanoparticle composites with excellent performance due to the combination of higher hardness, durability and thermal stability of the inorganic filler and the good flexibility, toughness and processability of the polymer [2-6]. Nanoparticle filled polymers exhibit enhanced mechanical, thermal, electrical, optical, and barrier properties at rather low nanoparticle loadings compared to traditional composites [1, 7, 8, 9]. However, in the process of preparation, there are the great number of factors affecting the properties of the resultant polymer/inorganic nanoparticle composites [10-12]. The main factors are the nanoparticle size and volume (or weight) fraction, the nature of the matrix and its adhesion to the nanoparticle, the nanoparticle dispersing into the matrix, and manufacturing technology. Among these factors, the interfacial adhesion and dispersing are of cardinal importance and markedly influence the properties of nanoparticle-filled polymers.

In this present work, attemps to "disperse" of TiO_2 nanoparticles and polymer using master batch manufacturing process. TiO_2 particles were from two sources, the first was commercial grade and the other was synthesized via sol-gel process using starting material Titanium diisopropoxide bis (acetylacetonate) 75wt% solution in 2-propanol and Triol (Pentaerythritol) as a linking agent. The effect of particle size from two sources of TiO_2 and the effect of TiO_2 content on the properties of resulting composites were studied. Isotactic Polypropylene were chosen as a polymer matrix, it is a commodity plastic, cheap, good strength and easily

process. Attentions were focused on crystallization, crystalline structure, thermal stability, mechanical porperties and morphology of the obtained composites.

EXPERIMENTAL DETAILS

Materials

Polypropylene used in this work was produced and supplied by HMC Polymers Company Limited. Some physical properties of the resin, reported by the manufacturer, are melt flow rate = 22 dg/min (ASTM D1238), density = 0.90 g/cm^3 (ASTM D792B), tensile strength at yield = 34 Mpa (ASTM D638), elongation at yield = 9% (ASTM D638), flexural modulus = 1480 Mpa (ASTM D790A), notched izod impact strength = 22 J/m (ASTM D256A), and deflection temperature = 97 °C (ASTM D648).

TiO$_2$ particles from two sources were used, the first was commercial grade supplied by JJ-Degussa Thailand and the other was synthesized via sol-gel. TiO$_2$ particles prepared via sol-gel method using starting materials titanium diisopropoxide bis(acetylacetonate) 75 wt% solution in 2-propanol and tetraol (Pentaerythritol) as a linking agent, the reaction was carried out at 70°C for 3 hours. The mole ratio between Titanium diisopropoxide bis(acetylacetonate) and tetraol was 2:1. After the reaction was completed, the titanium sol was obtained. Then HCl and H$_2$O (1:10) were added and heated at 70°C until they were homogeneous to obtain the optimized colloidal sol. The size of the sol was characterized by shining a laser light through the solution. Results from the test indicated that the size of the obtained sol was in the range of nanometer. The obtained sol was dried under vacuum and was ground before calcination. Finally, the dried titanium compound (dried gel) was calcined at 650°C for 3 hours to remove any remaining organic residues to obtain TiO$_2$ particles. Both sources of TiO$_2$ were observed to be the anatase structure by XRD.

The surface area, pore volume and pore size of the two sources of TiO2 were characterized using BET (autosorp one). The surface area, pore volume, and pore size of commercial TiO$_2$ were 56.9m^2/g, 1.84 x 10^{-2}cc/g, and 12.9 nm, respectively and the surface area, pore volume, and pore size of synthesized TiO$_2$

were $3.31 m^2/g$, 2.02×10^{-2} cc/g, and 24.4 nm, respectively. The average particle size of TiO_2 was measured by a Malvern (Masterizer X). The average particle size (D [4,3]) of commercial TiO_2 was 2.95 μm and synthesized TiO_2 was 72.95 μm. It should be noted that the particle size that observed from this equipment was the agglomerate size.

Nanocomposites Preparation

PP and TiO_2 nanoparticles were dried at 60°C for 4 hours before melt compounding. The master bacth of 10 wt% TiO_2 was prepared by using a Collin ZK25 self-wiping, co-rotating twin-screw extruder with screw speed 50 rpm. The as-prepared master batch was blended with the required amount of PP to give 1, 2, 3, 4, and 5 wt% of TiO_2 in PP. For TiO_2 from sol-gel process, due to the small amount of TiO_2 prepared, only 5wt% of TiO_2 in PP master batch was prepared. Then the as-prepared master batch was blended with the required amount of PP to give 1 and 3 wt% of TiO_2 of PP composites.

Specimen Preparation

A film of each sample was prepared from compression-molded sheet with a V50H compression press (Wabash). The obtained pellets were placed between a pair of stainless steel platens, and the mold was preheated at 200°C for 5 min between the plates without any applied pressure to allow complete melting. After that the mold was compressed under a force of 10 tons with a residence time of 5 min and this specimen was cooled at 50°C under pressure. Each film specimen was used for studying non-isothermal crystallization and subsequent melting behavior.

An ARBURG Allrounder 270M injection molding machine was used to prepare specimens for mechanical tests. The operating settings of the machine were as follow; barrel temperature = 190°C, nozzle temperature = 200°C, clamping force = 25 kN, and injection pressure = 1000 bar. Tensile specimens were prepared according to ASTM D638-91 standard test method.

Differential Scanning Calorimetry

Non-isothermal melt-crystallization and the subsequent melting behavior of neat polymer PP and PP filled with various contents of TiO_2 were investigated on a Perkin-Elmer Series 7 differential scanning calorimeter (DSC). A temperature calibration was performed on every other run using a pure indium standard (T_m = 156.6°C and ΔH_f = 28.45 J.g^{-1}). A sample of 5.0 ± 1.0 mg in weight, was sealed in an aluminium sample holder. The experimental procedure started with heating each sample from 50 to 250°C at a heating rate of 10°C.min^{-1} in order to set a similar thermal history for all the samples studied. To ensure complete melting, the sample was kept at 250°C for a holding period of 5 min, after which each sample was cooled down at a cooling rate of 10°C.min^{-1} to 50°C in order to observe non-isothermal melt crystallization behavior. As soon as the program temperature reached 50°C, the sample was immediately reheated at a heating rate of 10°C.min^{-1} to 250°C in order to observe the subsequent melting behavior. Both the non-isothermal melt-crystallization exotherm and subsequent melting endotherm were recorded for further analysis.

Wide Angle X-ray Diffratometer

A Rigaku Rint 2000 wide-angle X-ray diffractometer (WAXD) was used to determine the crystal structure and degree of crystallinity of all composites which were non-isothermally melt-crystallized at a cooling rate of 10°C.min^{-1} in DSC. Wide angle X-ray diffractometer equipped with a graphite monochrometor and a Cu tube for generating CuKα radiation (1.5046 A°). The samples were examined between 5°-90° 2θ at a scanning rate of 5° 2θ/min in 0.02° 2θ increments. CuKα radiation with λ = 0.514 nm was used as the X-ray source, operated at 40 kV and 30 mA. The digital output of the proportional X-ray detector and goniometric angle measurements were sent to an online micro computer for storing the data. Percent crystallinity was calculated using Crystallinity Multipeak Method.

Dynamic Mechanical Analysis

Dynamic mechanical of these composites were studied using a Solid Analyzer RSA Π (Rheometric scientific). The storage modulus (E') and loss modulus (E") were measured as a function of temperature. The three point bend fixture was used to mount the samples and temperature step of 4K intervals. All experiments were performed at 1Hz frequencey and 0.025% syrain amplitude using static force tracing dynamic force.

Thermogravimetric Analysis

Thermogravimetric and derivative thermogravimetric tests were carried out using TG-DTA analyzer. The experiment was done at a temperature in the range of 30-600°C under ambient atmosphere. The values of degradation temperatures were reported.

Mechanical Property Measurements

Tensile tests were performed with an Instron Universal testing machine, Model 4206, at room temperature following the procedure describe in ASTM D638-91. A crosshead speed of 40 mm.min^{-1} and 100 kN load cell was used for all measurements. The value of tensile strength at yield, percentage of elongation at yield and Young's modulus for all composites were investigated. The results from the tests were reported as an average of the data taken from 5 specimens.

Morphological Observation

Energy dispersive X-ray spectrometer (EDS), OXFORD (link ISIS series 300) composition distribution map was used to analyze and confirm Ti element in composites. Scanning electron microscope (SEM), JEOL (JSM-6400) was used to observe the dispersion of TiO_2 of the fractured surface of selected specimens which were fractured in liquid nitrogen and also use to measure particle size of TiO_2 in composites. The samples were sputtered with gold before viewing under a scanning electron microscopy (SEM) operating at 15 kV.

RESULTS AND DISCUSSION

Differential Scanning Calorimetry

Figure 4.1 and 4.2 illustrates non isothermal melt crystallization exotherms, recorded at a cooling rate of 10°C/min for neat PP and PP filled with various contents of TiO_2. For non isothermal melt crystallization, it was shown that the melt crystallization temperature of PP was increased by increasing the contents of commercial TiO_2. The temperature was shifted by 6°C and 8°C when the weight contents of commercial TiO_2 were increased from 5% to 10% (see Figure 4.1). For composites prepared from synthesized TiO_2, there was no change in melt crystalllization temperature even at 5wt% of TiO_2 (see Figure 4.2), this observation might conclude that commercial TiO_2 acted as a nucleating agent for isotactic polypropylene [13], whereas the synthesized one could not. The reason for these results derive from the differences in particle size and also surface area of two sources of TiO_2. From the agglomerate particle size as reported, the synthesized TiO_2 was much larger in size (72.95 µm) and had much smaller surface area (3.31 m^2/g) compared to the commercial TiO_2 which was much smaller in size (2.95 µm) and had larger surface area (56.9 m^2/g). Therefore commercial TiO_2 has better ability to be a nucleating agent than the synthesized one.

For the melting endotherms, the addition of both commercial and synthesized TiO_2 to PP composites did not have any effect on melting temperature and also melting peak pattern as shown in Figure 4.3, 4.4 and Table 4.1, 4.2. The values of melting enthalpy (ΔH_m) of neat PP and PP with various contents of TiO_2, obtained via DSC are also presented in Table 4.3. The values of melting enthalpy (ΔH_m) of PP tended to increase by increasing the contents of commercial TiO_2 especially at 10wt% of TiO_2, the ΔH_m was the highest at 101.16 J/g. The value of this parameter, indicating the crystallinity of a polymer [14], increases as the TiO_2 contents increase.

Wide Angle X-ray Diffractometer

In order to observe the crystal structure and the resulting apparent degree of crystallinity of neat PP and PP composites investigated, WAXD technique was utilized. Figure 4.5 illustrates WAXD pattern for neat PP and PP filled with various contents of commercial TiO_2. It should be noted that the samples were prepared in the DSC cell by cooling at a rate of 10°C/min after melt annealing at 250°C for 5 minutes. For isotactic polypropylene, the characteristic X-ray peaks were observed at the scattering angles 2θ of ca. 14.1°, 16.9°, 18.6°, 21.2° and 21.9° which are α-phase, corresponding to the reflection planes of (110), (040), (130), (111) and (041), respectively [15]. The results shown in Figure 4.5 can be seen that addition of commercial TiO_2 at 1-3 weight percent did not alter the peak pattern of PP. The peak pattern of PP was changed at 4, 5 and 10 weight percent of commercial TiO_2 composites, it was assumed that the peak at $2\theta = 16.9$ of PP may shifted to 2θ around 15.9° and the peak at 2θ around 16.9° come from the β-phase of nucleating agent or β-nucleator [16], as already discussed earlier that TiO_2 acted as nucleating agent and the intensity at $2\theta = 16.9°$ was seemed to increase by increasing the weight contents of commercial TiO_2 from 4 to 10%.. The degree of crystallinity of composites investigated from Crystallinity Multipeak Method was summarized in Table 4.3, the values tended to increase by increasing weight contents of commercial TiO_2 which corresponded to the DSC results. For synthesized TiO_2, the peak pattern was not changed with any contents of TiO_2 as shown in Figure 4.6.

Dynamic Mechanical Analysis

Results from DSC and XRD showed that the degree of crystallinity was higher when increasing TiO_2 contents, it would be expected that T_g of the PP composites should be higher because the inorganic particles should hinder segmental motions of the polymer chains. From DMA plots of loss modulus (E") against temperature to determine T_g of different composites obtained (see Figure 4.9). The composites prepared from 1-5wt% commercial TiO_2 did not show any significant effect on T_g of polypropylene. However, at 10wt% of commercial TiO_2 composite, it showed slight decreased in T_g to a lower temperature (0.38°C) when compared to the

neat PP (4.56°C). As polypropylene is the semi-crystalline polymer, therefore it is not only the crystalline part that is important but also the amorphous region which also has an effect on characteristics of polymer chains. However it was anticipated that at high contents of TiO_2, the possibility of TiO_2 particles to move to the amorphous part was higher as well therefore the steric hindrance presented by the TiO_2 particles toward the more difficult interaction between polymer chains in amorphous region can be occurred and resulted in lower T_g. As synthesized TiO_2 did not have an effect on T_g of polypropylene with the load of TiO_2 added as shown in Figure 4.10.

Thermogravimetric Analysis

TGA was used to determine the degradation temperature of the nanocomposites obtained. The degradation temperature of nanocomposites was found to increase by increasing contents of both commercial and synthesized TiO_2. The highest degradation temperature (T_d) was observed at nanocomposites prepared from 5 weight percent of commercial TiO_2 which was 378.9 °C compared to neat PP which was just 342.4°C. The addition of 5wt% of synthesized TiO_2 can also increase the degradation temperature of composites to 360.4°C (see Figure 4.11).

Tensile Property Measurements

The tensile strength at yield, percentage of elongation at yield and Young's modulus of all composites were investigated. The tensile strength of 1-5wt% commercial TiO_2 filled composites were little different from those of the neat PP. However, at 10wt% of TiO_2 in composite resulted in large reduction of tensile strength as shown in Figure 4.12. These results would suggest that it is due to the higher degree of crystallinity of nanocomposites. When it was pulling, the order structure or crystalline structure was alter and could not repack to the tensile direction therefore it could not be pulled any further and would then break with lower strength. The other reason which can make the tensile strength reduce may come from the orientation of crystals in polymer chain. They distributed unevenly like many spots in chain (TiO_2 acted as nucleating agent) and the spots could not

help the orientation in the tensile direction. The percentage of elongation was reduced by increasing the weight contents of commercial TiO_2 (see Figure 4.13). The Young's modulus were seemed to increase at 5wt% commercial TiO_2 and from the graph, it was clearly indicated that there was a large increase in Young's modulus at 10wt% commercial TiO_2, as compared to 0-4wt% of composites (see Figure 4.14), suggesting that owing to higher crystallinity at 5 and 10wt% of TiO_2 that made the increasing of modulus. The PP composites with the synthesized TiO_2 (1, 3 and 5wt%) did not affect on tensile strength and Young's modulus of composites but the percentage of elongation was reduced by increasing weight content of the synthesized of TiO_2 but the reduction was still lower when compared to the composites prepared from commercial TiO_2 (see Figure 4.15-4.17).

Scanning Electron Microscope

Energy dispersive X-ray spectrometer was used to locate Titanium element as labeled in the images. SEM micrographs of the fractured surface of PP filled with 5 and 10 wt% of commercial TiO_2 are illustrated in Figure 4.18. The contents of TiO_2 that were lower than 5wt% were not observed, due to the very small amount of the TiO_2 added. The image obtained from composites with 5wt% commercial TiO_2 showed that the TiO_2 particles were still in nanometer range, whereas the composites prepared from 10wt% was in micrometer, this may be due to the agglomeration of TiO_2 particles. The pore volume of commercial TiO_2 was 10 times larger than the synthesized one so it looked like much more content than the synthesized one when considering in same weight, therefore the probability to agglomerate was much easier. Although the agglomeration occurred but at 10wt% still had many effects on the properties of polymer as already discussed.

CONCLUSIONS

In this work, TiO_2 particles prepared via sol-gel process were introduced into polypropylene by the master batch manufacturing process. The resulting composites were compared with the blends prepared with commercial nanoparticles TiO_2. The effect of TiO_2 contents and the properties of TiO_2 from two sources of TiO_2 on the properties of resulting nanocomposites were studied. Results from DSC

indicated that there was no change in the crystallization exotherms of TiO$_2$ from sol-gel process whereas composites with commercial nano-TiO$_2$, the added TiO$_2$ acted as a nucleating agent. At 5wt% and 10wt% of TiO$_2$ in polypropylene being able to shift the crystallization exotherms by 6°C and 8°C, respectively, and therefore the commercial TiO$_2$ can increase the degree of crystallinity of nanocomposites by increasing weight contents of TiO$_2$ as observed from DSC and XRD. TiO$_2$ particles from sol-gel process were still in micro size whereas the commercial TiO$_2$ were much smaller, therefore it had more effect on the properties of polymer. Thermogravimetric analysis results showed that degradation temperature of composites was increased by increasing contents of nano-TiO$_2$ from two sources, suggesting that the addition of nano-TiO$_2$ can improve the thermal stability of polymer. At 1-5wt% of TiO$_2$ from two sources in PP, there were no adverse effects on mechanical properties of the composites, whereas at 10wt% commercial TiO$_2$ can increase much in Young's modulus due to higher in degree of crystallinity in this content.

The advantage of synthesis TiO$_2$ in sol-gel tetraol based method is the starting materials are stable in room temperature and the condition during the reaction is mild, but the obtained nanoparticles were agglomerated after calcination at high temperature. The grinding process after calcination cannot control the size of particles as expected. The author would like to suggest the improvement of systhesis of TiO$_2$ to be of smaller particles in order to have larger surface area. The first method is to try reducing the calcined temperature of TiO$_2$ to prevent the particles coming to agglomerate, but still need to make sure that it can also remove the organic substance from the compound and after calcination the particles should be sonicated in the solution instead of grinding. The other way is to find some coating compounds such as Hydroxypropyl cellulose [17] and Carboxymethyl cellulose to prevent the agglomeration of TiO$_2$ particles.

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Figure 4.1 Non isothermal melt crystallization exotherms for neat PP and PP with different amounts of commercial TiO_2: (a) neat PP, (b) 1wt% TiO_2, (c) 2wt% TiO_2, (d) 3wt% TiO_2, (e) 4wt% TiO_2, (f) 5wt% TiO_2, and (g) 10wt% TiO_2.
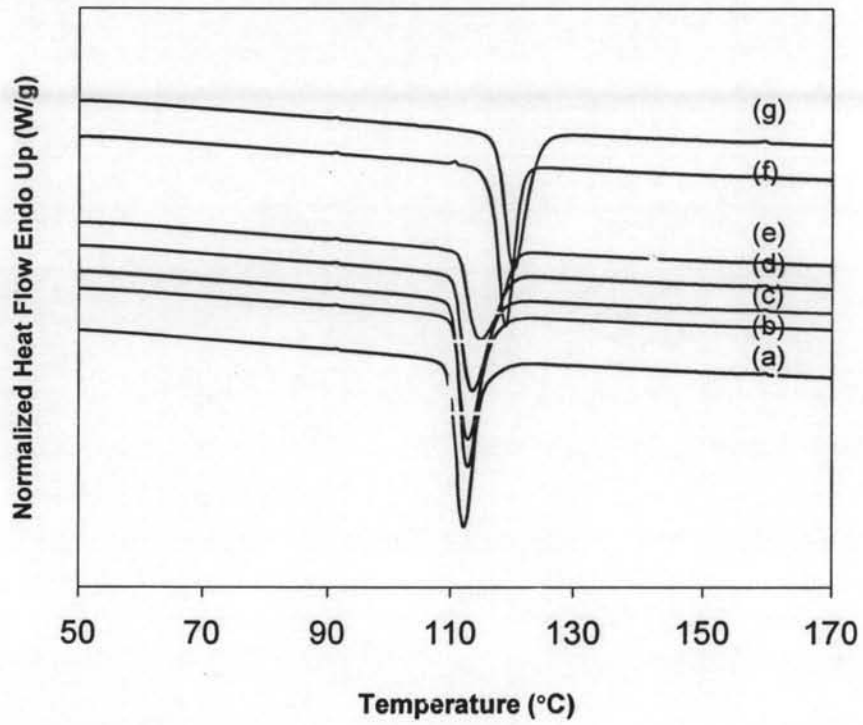
Figure 4.2 Non isothermal melt crystallization exotherms for neat PP and PP with different amounts of synthesized TiO_2: (a) neat PP, (b) 1wt% TiO_2, (c) 3wt% TiO_2, and (d) 5wt% TiO_2.
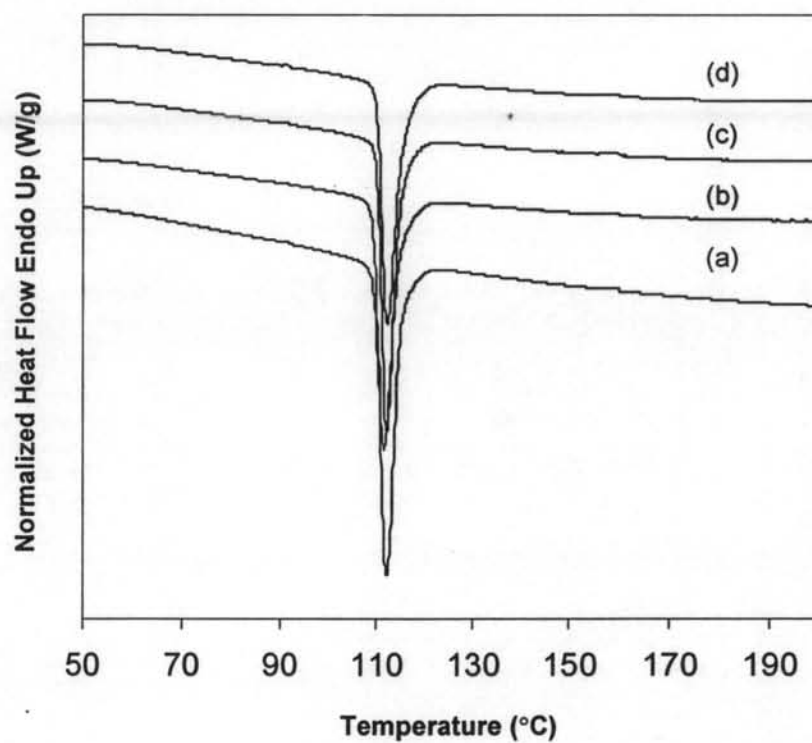
Figure 4.3 Subsequent melting endotherms for neat PP and PP with different amounts of commercial TiO_2: (a) neat PP, (b) 1wt% TiO_2, (c) 2wt% TiO_2, (d) 3wt% TiO_2, (e) 4wt% TiO_2, (f) 5wt% TiO_2, and (g) 10wt% TiO_2.
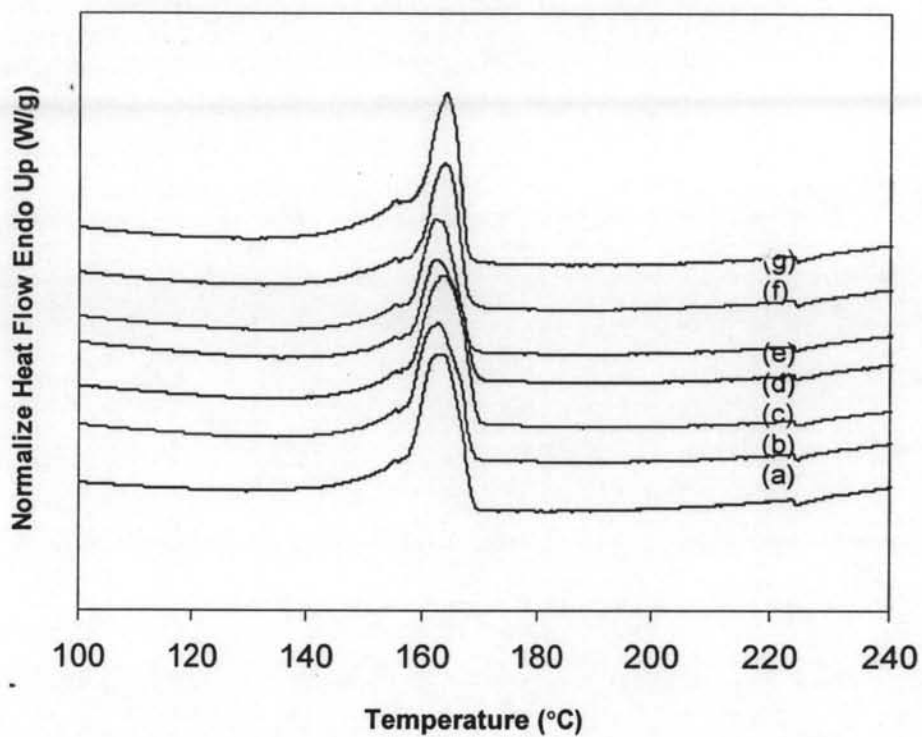
Figure 4.4 Subsequent melting endotherms for neat PP and PP with different amounts of synthesized TiO₂: (a) neat PP, (b) 1wt% TiO₂, (c) 3wt% TiO₂, and (d) 5wt% TiO₂.
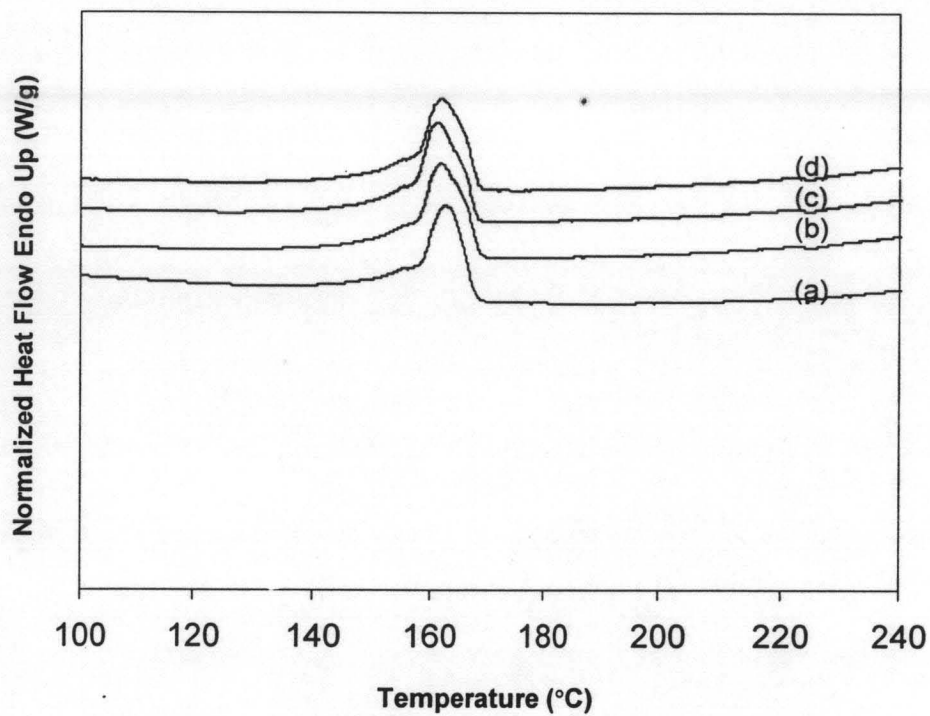
Figure 4.5 WAXD patterns for neat PP and PP filled with different amounts of commercial TiO_2: (a) neat PP, (b) 1wt% TiO_2, (c) 2wt% TiO_2, (d) 3wt% TiO_2, (e) 4wt% TiO_2, (f) 5wt% TiO_2, and (g) 10wt% TiO_2.
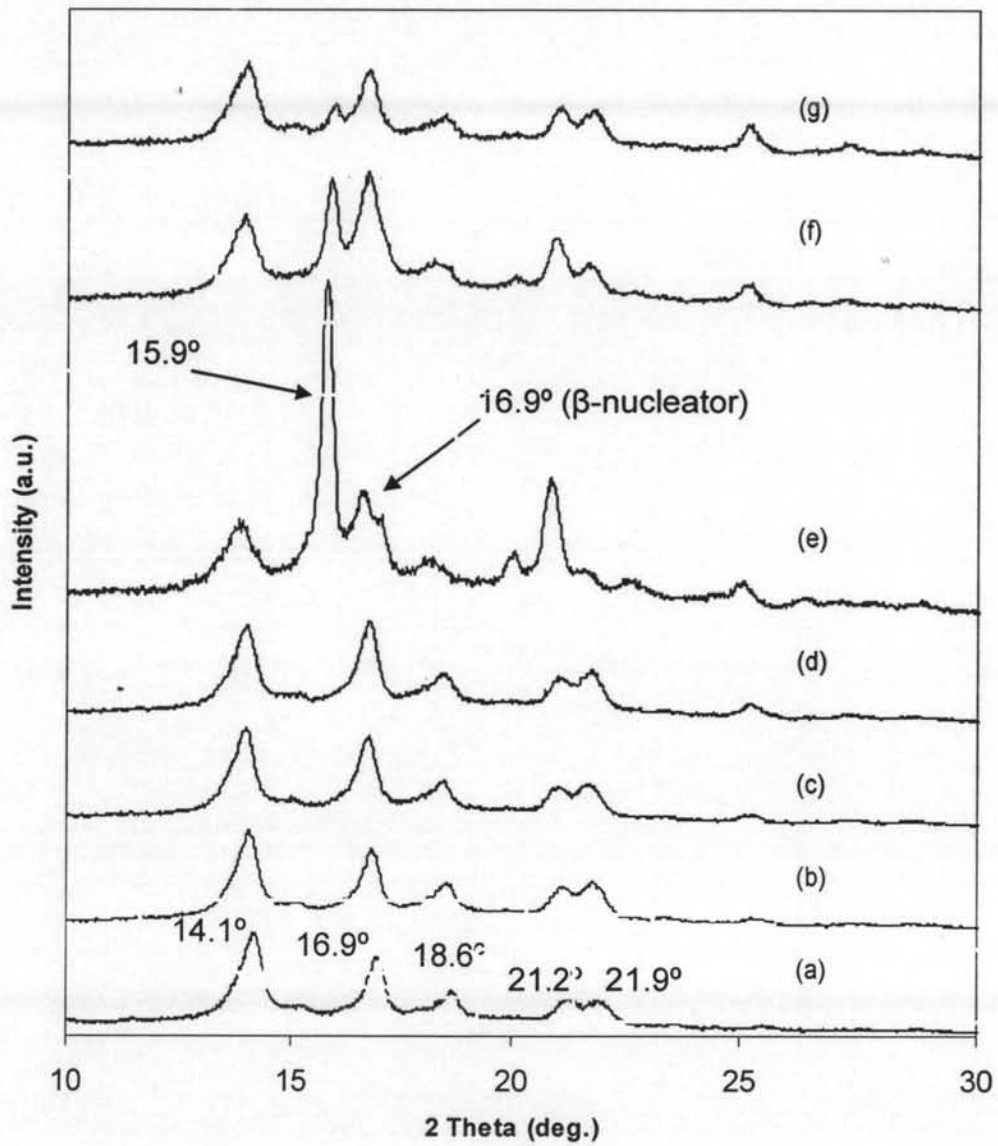
Figure 4.6 WAXD patterns for neat PP and PP filled with different amounts of synthesized TiO_2: (a) neat PP, (b) 1wt% TiO_2, (c) 3wt% TiO_2, and (d) 5wt% TiO_2.
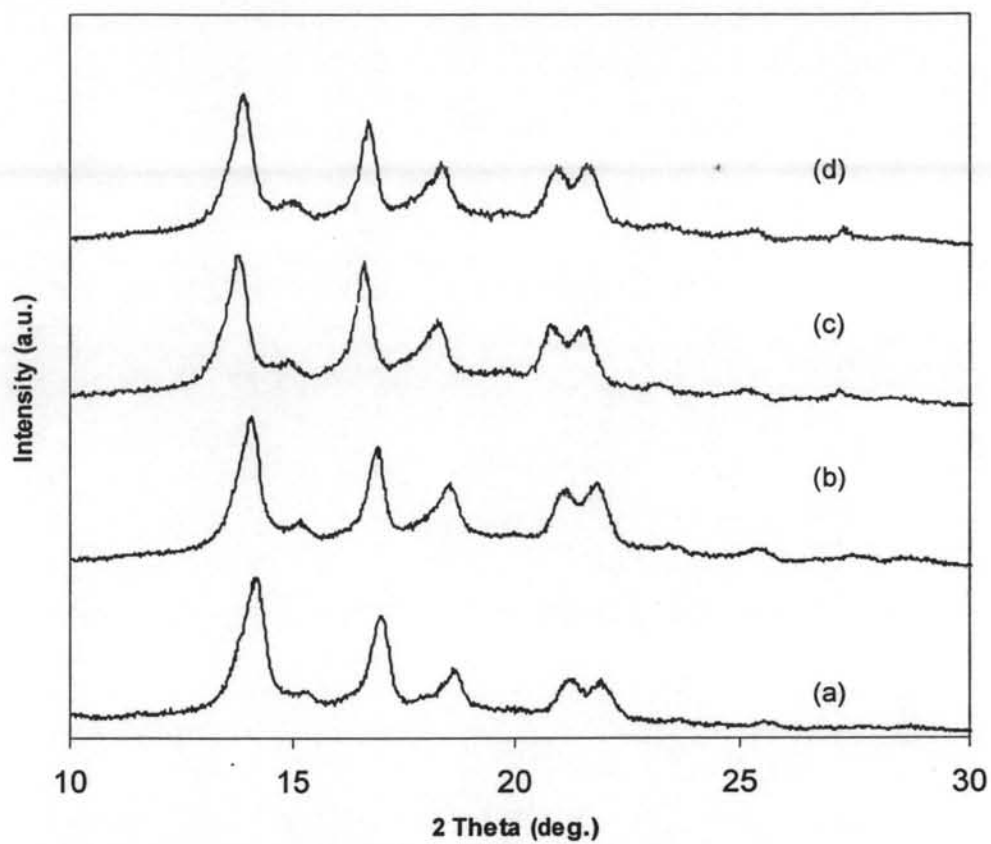
Figure 4.7 WAXD patterns of commercial TiO$_2$.
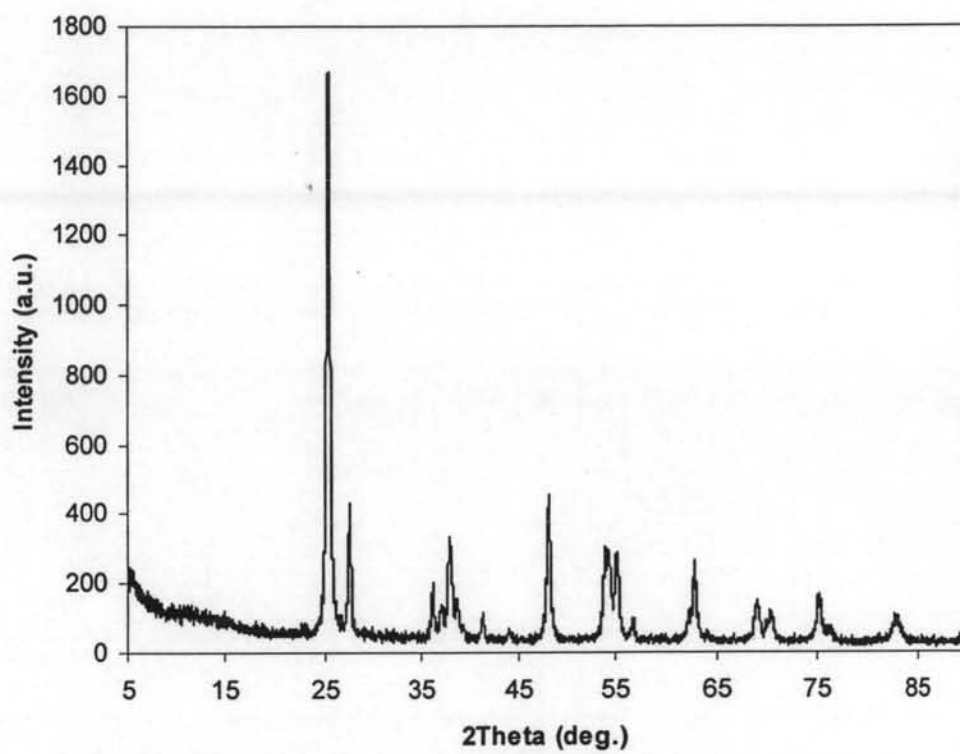
Figure 4.8 WAXD patterns of synthesized TiO$_2$.
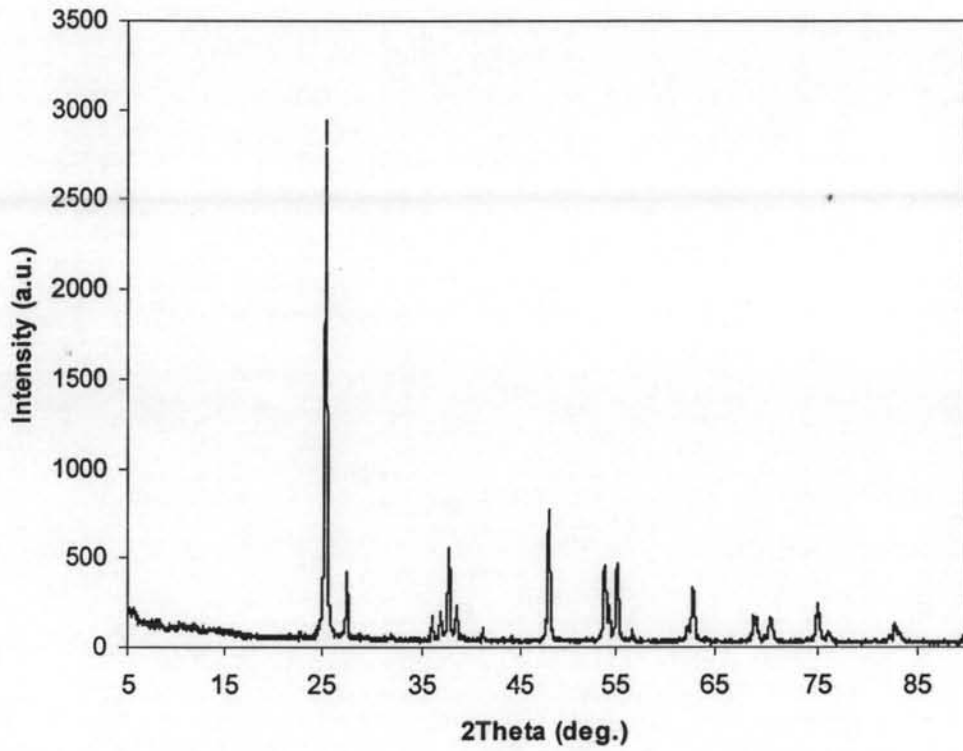
Figure 4.9 DMA results for neat PP and PP filled with different amounts of commercial TiO_2.
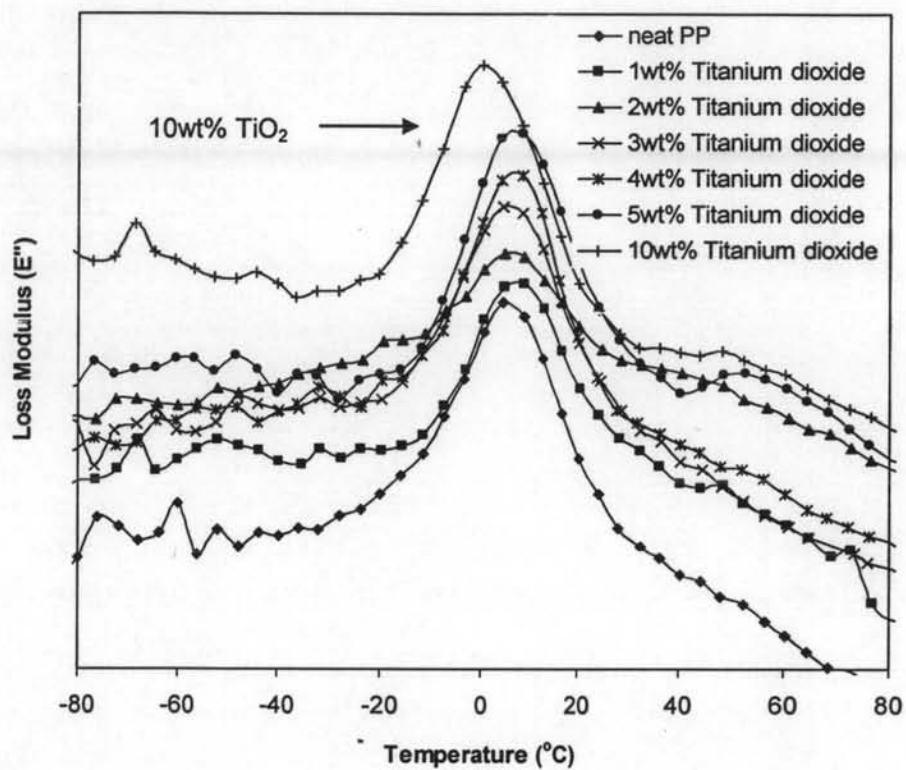
Figure 4.10 DMA results for neat PP and PP filled with different amounts of synthesized TiO_2.
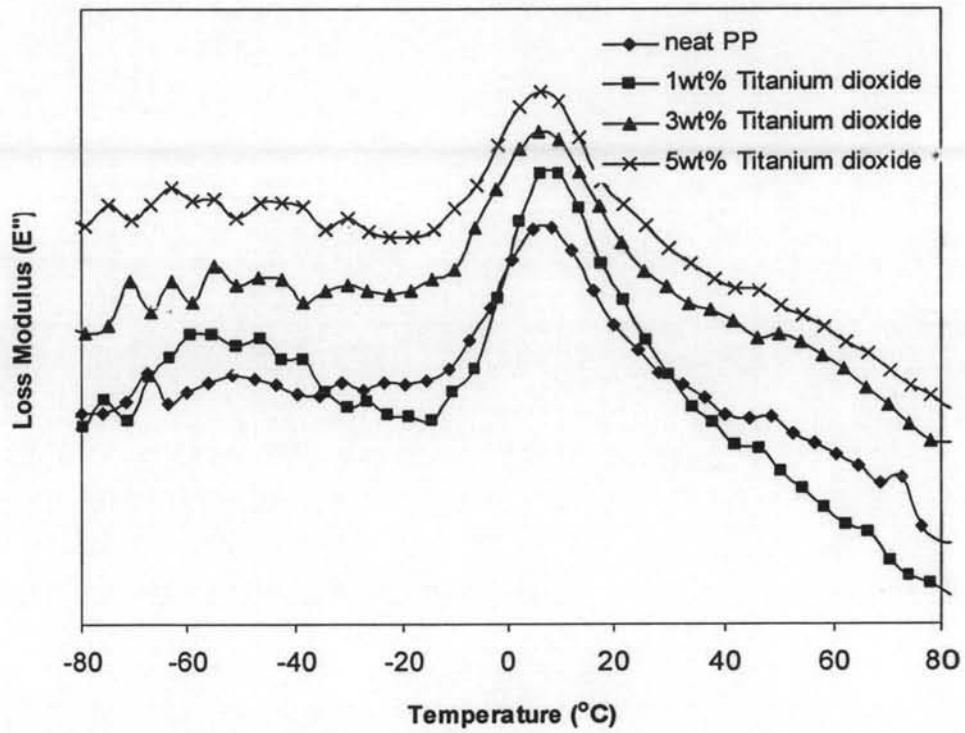
**Figure 4.11** Degradation Temperature for all PP composites prepared.
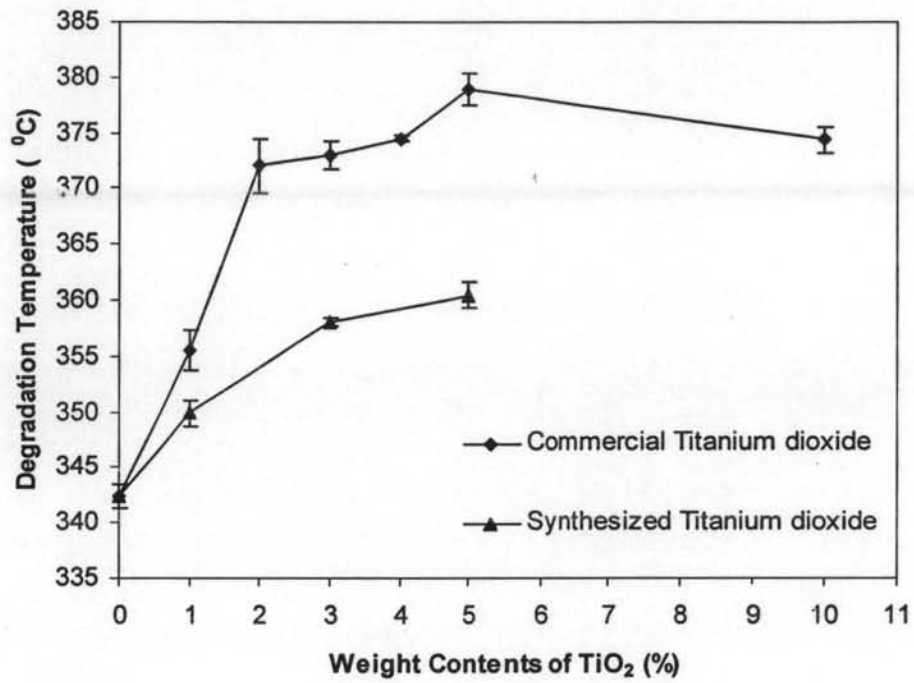
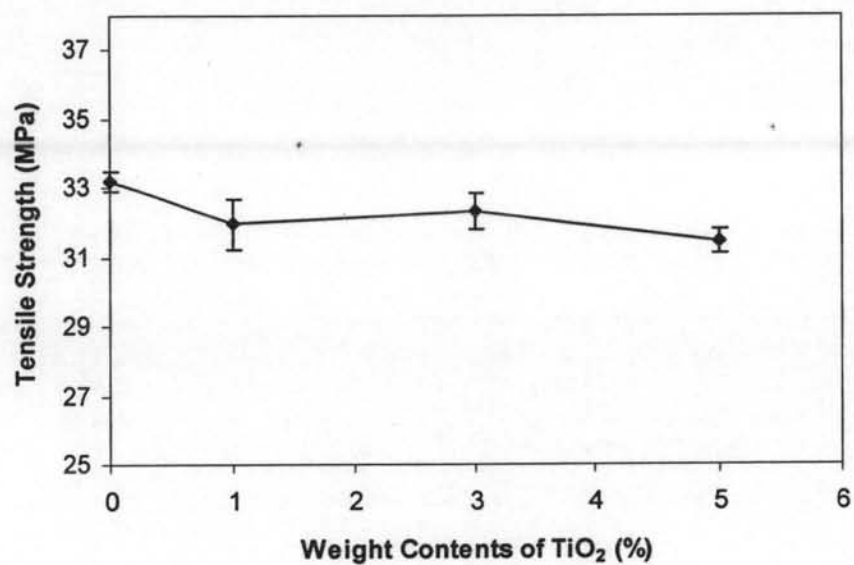**Figure 4.12** Tensile strength for neat PP and PP composites with different amounts of commercial TiO_2.
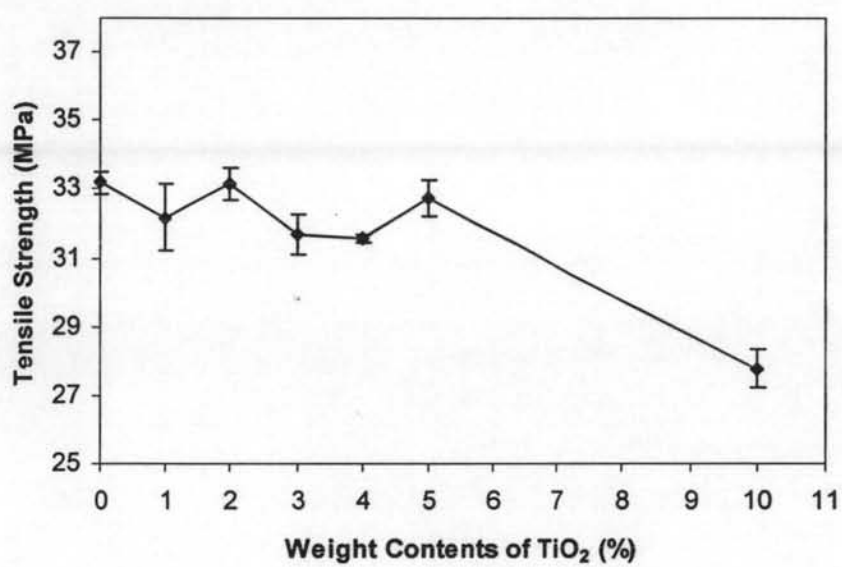
Figure 4.13 Percentage of elongation for neat PP and PP composites with different amounts of commercial TiO_2.
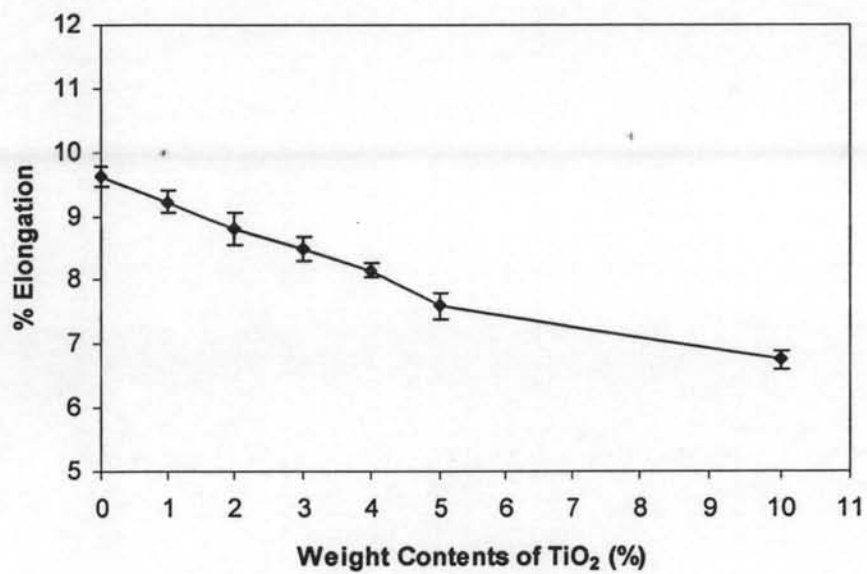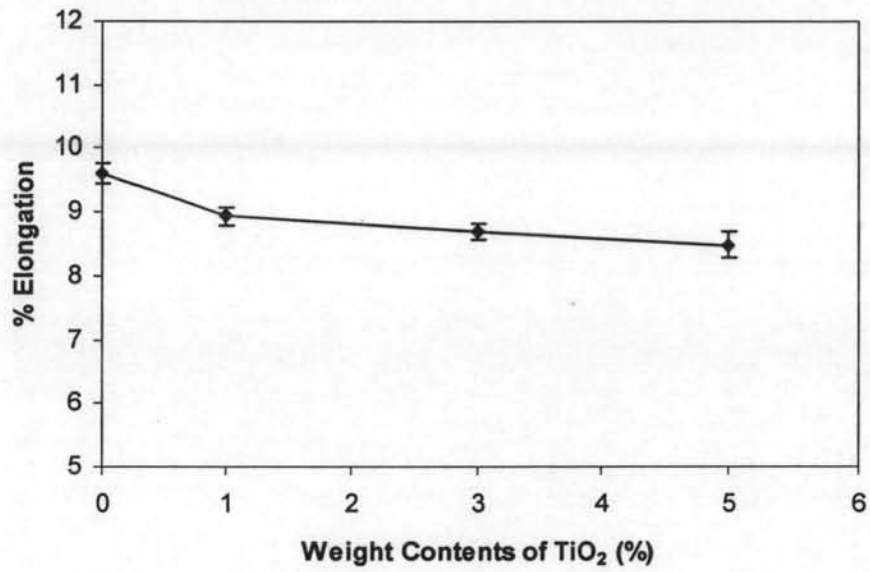
**Figure 4.14** Young's modulus for neat PP and PP composites with different amounts of commercial TiO_2.
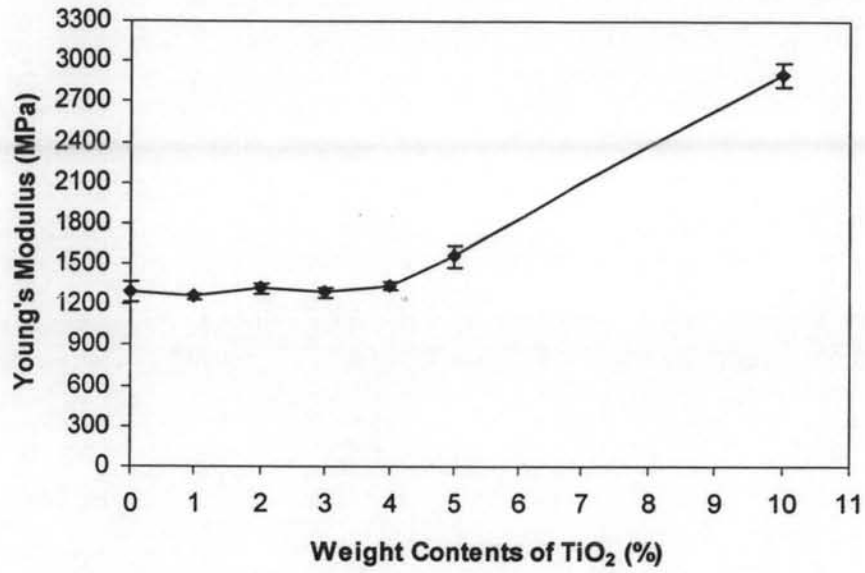
**Figure 4.15** Tensile strength for neat PP and PP composites with different amounts of synthesized TiO_2.

**Figure 4.16** Percentage of elongation for neat PP and PP composites with different amounts of synthesized TiO_2.

Figure 4.17 Young's modulus for neat PP and PP composites with different amounts of synthesized TiO_2.
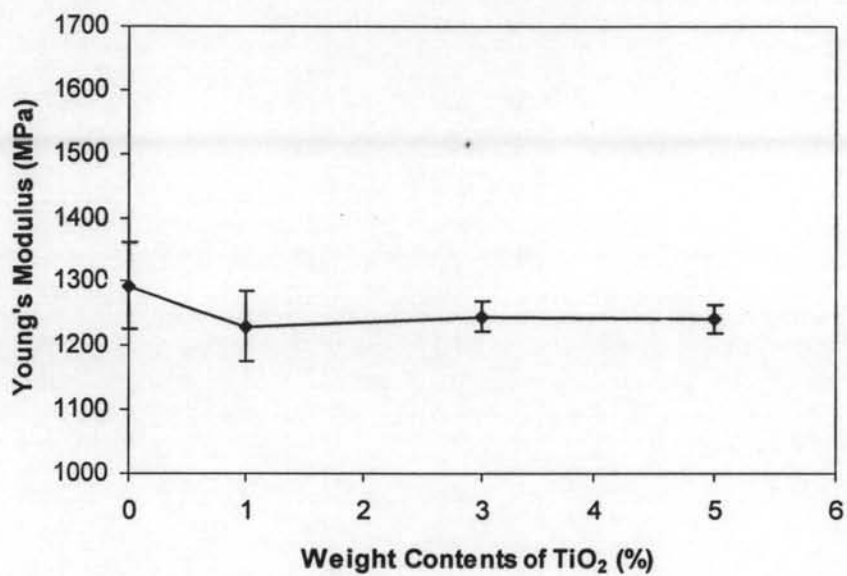
Figure 4.18 SEM micrographs of fractured surfaces of PP nanocomposites with average particle size and standard deviation: (a) 5wt% commercial TiO_2 and (b) 10wt% commercial TiO_2.
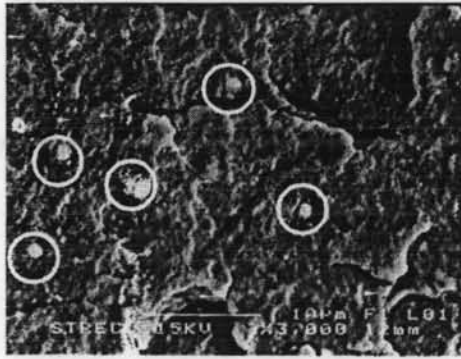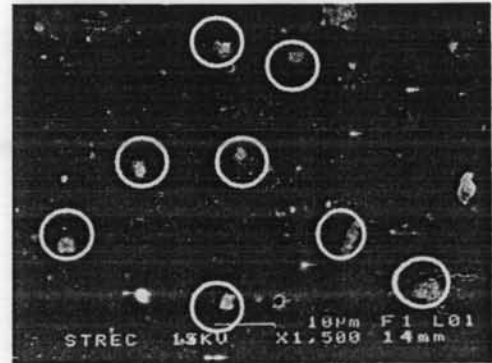
(a) 752 nm   SD 229   (b) 2161 nm   SD 484

Table 4.1 Characteristics of non isothermal melt crystallization and subsequent melting behavior observed for PP and PP filled with different amounts of commercial TiO_2

Samples	T_c (°C)	T_c (onset) (°C)	T_m (°C)	T_m (onset) (°C)	ΔH_m (J/g)
PP	112.63	115.24	163.03	157.32	74.33
1wt% TiO_2	112.80	116.45	161.86	157.21	80.86
2wt% TiO_2	112.80	116.37	163.86	156.86	78.25
3wt% TiO_2	113.63	118.71	161.70	157.40	81.63
4wt% TiO_2	114.80	120.57	162.53	157.09	86.28
5wt% TiO_2	118.80	121.54	164.03	158.19	87.23
10wt%TiO_2	120.13	124.17	164.20	157.93	101.16

Table 4.2 Characteristics of non isothermal melt crystallization and subsequent melting behavior observed for PP and PP filled with different amounts of synthesized TiO_2

Samples	T_c (°C)	T_c (onset) (°C)	T_m (°C)	T_m (onset) (°C)	ΔH_m (J/g)
PP	112.63	115.24	163.03	157.32	74.33
1wt% TiO_2	111.63	114.98	162.70	156.68	80.66
3wt% TiO_2	112.13	115.10	162.37	156.50	78.06
5wt% TiO_2	112.30	115.70	163.70	156.79	78.19

Table 4.3 The degree of crystallinity of neat PP and PP filled with different amounts of both commercial and synthesized TiO_2

Samples	Degree of crystallinity (%)
PP	57.55
1wt% commercial TiO_2	56.67
2wt% commercial TiO_2	56.11
3wt% commercial TiO_2	57.71
4wt% commercial TiO_2	58.52
5wt% commercial TiO_2	60.96
10wt% commercial TiO_2	64.13
1wt% synthesized TiO_2	57.56
3wt% synthesized TiO_2	57.62
5wt% synthesized TiO_2	58.36