

## CHAPTER II

### LITERATURE SURVEY

In recent years, there have been many studies about organic-inorganic hybrids or polymer nanocomposites, which consist of nano- or submicron- ordered inorganic phases dispersed in polymer matrices. Preparation of TiO<sub>2</sub> nanoparticle or nanopowder and the application of TiO<sub>2</sub> nanoparticles in polymer nanocomposites also have been described in the research work, as shown below.

#### 2.1 TiO<sub>2</sub> Nanoparticles Preparation

Titanium dioxide (TiO<sub>2</sub>) nanoparticles were synthesized from tetraethylorthotitanate (TEOT) dissolved in ethanol by using a semi-batch process in order to overcome difficulties in production of nanoparticles by a batch wise reaction (Kim *et al.*, 2003) In this work, a statistical experimental design method was also used to find the effect of four parameters [R (=H<sub>2</sub>O/TEOT), hydroxypropylcellulose (HPC) as a dispersant, the feed rate of reactant, and reaction temperature] on the various properties of TiO<sub>2</sub> particles. It was found that the optimal conditions for the preparation of monodispersed TiO<sub>2</sub> nanoparticles with high yield and surface area were as follows: (R: 16, HPC: 0.0028 g ml<sup>-1</sup>, feed rate of reactant: 3.3 ml min<sup>-1</sup>, and reaction temperature: 28°C). Experimental results measured by using the above optimal conditions were in agreement with theoretical data and the smallest particle size (~10 nm in diameter) was obtained. In conclusion, the main parameters affecting the properties of TiO<sub>2</sub> particles were decreased in the order of HPC > feed rate of reactant > R (=H<sub>2</sub>O/TEOT) > reaction temperature.

Sol-gel route is regarded as a good method to synthesize ultra-fine metallic oxide and has been widely employed for preparing titanium dioxide. TiO<sub>2</sub> nanopowders were prepared via a sol-gel method using tetra-n-butyl-titanate and deionized water as the starting materials (Li *et al.*, 2002). They reported the results of an investigation aiming at finding what affects the grain size of nano-TiO<sub>2</sub> powder during synthesis. Among the elements which may have effect upon the grain size and microstructure of nano-TiO<sub>2</sub> powders, the calcination temperature and pH value

were found to be more effective compared with the calcination time and concentration. The grain size tends to increase with increasing temperature and the increase in pH value. By controlling the conditions properly, nano-TiO<sub>2</sub> powders with the grain size less than 6 nm could be obtained.

## 2.2 Preparation of Nanocomposites by Sol-Gel Processes and Characterization

The preparation of nanocomposite films by sol-gel processes using titanium alkoxides as starting materials and soluble polyimides as the matrix studied by Tong *et al.* (2000). They found that the rate of hydrolysis of titanium alkoxides can be controlled by using acetic acid as a modifier. The TiO<sub>2</sub> particles in hybrid films were spherical and smaller than 60 nm. Polyimides hybrids films having the TiO<sub>2</sub> component  $\leq 10\%$  exhibited high thermal stability, high optical transparency, fairly good mechanical properties and possessed higher dielectric constants. The increase in dielectric constant results from well distributed of TiO<sub>2</sub> nanoparticles in polyimide matrix.

Lu *et al.* (2003) prepared hybrid optical films of TiO<sub>2</sub>-triethoxysilane-capped polythiourethane with high refractive index via sol-gel method. FTIR and DSC results demonstrate that the titania phase was effectively incorporated into polymer matrix by covalent bonds. AFM studies suggest that the titania phase uniformly disperse in the polymer matrix on a nanoscale and the hybrid films have excellent surface planarity. The hydrogen bonds between polymer segments or between polymer segments and titania moieties as well as the covalent bonds between them can prevent phase separation. The hybrid films exhibit high refractive index which can be tuned by the content of titania in the films and the refractive index has a better linear dependence on TiO<sub>2</sub> volume fraction. These hybrid materials can be potentially used as high refractive index optical films in the design of optics.

Organic-inorganic hybrid materials were prepared via *in situ* sol-gel process of titanium tetraisopropylate (TTIP) in polycaprolactone (PCL) and acrylic acid grafted polycaprolactone (PCL-*g*-AA) as an alternative to PCL (Wu, 2004). It was found that the interfacial forces are difference in the two hybrids: the weaker

hydrogen bonds of PCL/TiO<sub>2</sub> compared with the stronger coordination sites associated with the carboxylic acid groups of AA and the -OH of titanium-bonded isopropyl group, thus improving the properties of PCL-g-AA/TiO<sub>2</sub> nanocomposites compared with acrylic acid free counterpart. TGA tests showed that the PCL-g-AA/TiO<sub>2</sub> hybrids produced higher values of initial decomposition temperature than the equivalent PCL/TiO<sub>2</sub>. Meanwhile, maximum tensile strength and T<sub>g</sub> values occurred at about 10 wt% TiO<sub>2</sub> for PCL-g-AA/TiO<sub>2</sub> hybrids. Above this 10 wt%, it is proposed excess titania particle may cause separation between the organic and inorganic phases, so reducing compatibility between the titania network and PCL-g-AA. PCL/TiO<sub>2</sub> showed only a small change in T<sub>g</sub>, consistent with relative poor bonding between the organic and inorganic phase. The PCL-g-AA/TiO<sub>2</sub> hybrid is a significant improvement over PCL/TiO<sub>2</sub> as far as its thermal and mechanical properties are concerned.

In the same year Wu *et al.* investigated organic-inorganic polymeric nanocomposites involving TTIP in polyethylene-octene elastomer (POE). The preparation and characterization were also studied similar to the previous paper and the prepared nanocomposites (POE/TiO<sub>2</sub> and POE-g-AA/TiO<sub>2</sub>) gave the results similar to the PCL/TiO<sub>2</sub> and PCL-g-AA/TiO<sub>2</sub>.

### 2.3 Preparation of Nanocomposites by Ultrasonic Machine and Characterization

Xiao *et al.* (2002) reported on the application of nanometer-sized TiO<sub>2</sub> to the modification of unsaturated polyester resin (UP). The ultrasonic washing wave machine was used to dispersed the nanoparticles, the ultrasonic vibration can damage the coulomb and van der waals forces between agglomerate particles and make them homogeneously dispersed in the medium. When the amount of TiO<sub>2</sub> is 4 wt%, the tensile strength improves by 47%, the tensile elasticity modulus by 22%, the impact strength by 60%, and elongation at break by 48%. From DSC analysis it is concluded that nanometer-sized TiO<sub>2</sub> 4 wt% has an excellent compatibility with the UP matrix (because of the T<sub>g</sub> value of the composite is much higher than that of UP)

The friction and wear behavior of micrometer and nanometer  $\text{TiO}_2$  particle filled poly (phthalazine ether sulfone ketone) (PPESK) composites were examined by Shao *et al.* (2004). The mixture of PPESK and filler was fully mixed by ultrasonically dispersing them in acetone and the mixture then were compressed in heating mold. The results showed that micrometer  $\text{TiO}_2$  particle-filled PPESK composites exhibited increased friction coefficient and wear rate compared with unfilled PPESK. The filling nanometer  $\text{TiO}_2$  particle could greatly increase the wear resistance of PPESK in all cases under volume fractions from 0.5 to 7.5%. The nanometer  $\text{TiO}_2$  particle has good friction reduction at a filler volume fraction below 2.5%, while too high filler volume fraction corresponds to higher friction coefficient. The bonding strength between the polymeric material and the particles is weak in the case of micrometer  $\text{TiO}_2$ , while that of the nanometer  $\text{TiO}_2$  particle-filled PPESK is strong.

#### **2.4 Preparation of Nanocomposites by Master Batch Manufacturing Processes and Characterization**

Zhang *et al.* (2003) prepared HIPS/nano- $\text{TiO}_2$  nanocomposites by pretreating the surface of nano- $\text{TiO}_2$ , with a special structure dispersing agent (TAS), and using two step manufacturing technology (master batch manufacturing process). The notched impact strength, tensile strength, and tensile elastic modulus of HIPS/nano- $\text{TiO}_2$  nanocomposites increased to its maximum when nano- $\text{TiO}_2$  content was 2% and then decreased with the addition of more nano- $\text{TiO}_2$ . This is because the volume fraction of soft interfacial layer of nanocomposites increases, resulting in lower stress for the nanocomposites. The nano- $\text{TiO}_2$  has both toughening and reinforcing effects on HIPS when nano- $\text{TiO}_2$  content is 2%. The heat deflection temperature and flame retardency of HIPS/nano- $\text{TiO}_2$  nanocomposites are also improved as nano- $\text{TiO}_2$  content increased. The nanocomposites manufactured by two step method have better mechanical properties than those prepared by one step method (direct blending).

More recently, dispersion behavior of  $\text{TiO}_2$  nanocomposites was studied by Wang *et al.* (2005).  $\text{TiO}_2$  nanoparticles were introduced into LLDPE/LDPE

composite film in the form of master batch where  $\text{TiO}_2$  was pre-dispersed in LDPE by melt compounding. The viscosity of LDPE/ $\text{TiO}_2$  master batch is lower than that of LLDPE/LDPE composites. This is beneficial to the fine dispersion of LDPE/ $\text{TiO}_2$  master batch in LLDPE/LDPE composite films during the latter blow-forming process. SEM images showed that the LDPE/ $\text{TiO}_2$  master batch is crushed into micron scale dispersed phases as a result of shear stress during melt compounding process. The crystallization behavior of polyethylene is largely influenced by the introduction of  $\text{TiO}_2$  nanoparticles, the sizes of spherical crystals of polyethylene decrease while the number of the spherical crystals increases. The transparency of LLDPE/LDPE/ $\text{TiO}_2$  composite films decrease slightly but still satisfy in food packaging and agricultural applications.

## 2.5 Morphology and Crystallization of Nanocomposites

The role of  $\text{TiO}_2$  nanoparticles surfaces in affecting the crystalline structure of low-density polyethylene (LDPE) has been investigated by varying the nanoparticle surface from hydrophilic (as-received) to less hydrophilic (dried) or more hydrophylic (polar silane treated) (Ma *et al.*, 2005). It was found that the variation of the nanoparticle surfaces did not influence the LDPE crystallinity, unit cell dimensions, average lamellar thickness and average spherulite size. However, the organization of lamellar (or bundles) within the spherulites was affected by the presence of the nanoparticles in the interfibrillar regions. The neat LDPE, dried  $\text{TiO}_2$ /LDPE, AR- $\text{TiO}_2$ /LDPE, and silane treated  $\text{TiO}_2$ /LDPE possessed a decreasing degree of perfection of the spherulites. The silane treated sample, which showed nanoparticles agglomeration at the micron scale, exhibited the highest internal disorder and the most poorly developed spherulites. It appears that spherulitic organization is more disrupted when the average size of the nanoparticle aggregates is comparable to the spherulites size. The large agglomerate size in the silane sample was quite possibly due to the poor interfacial compatibility between the silane treated nanoparticles and the LDPE matrix.

Nonisothermal melt-crystallization behavior of syndiotactic polypropylene (sPP) compounded with 5% by weight (wt%) of some inorganic fillers [i.e., kaolin,

talcum, marl, titanium dioxide ( $\text{TiO}_2$ ), and silicon dioxide ( $\text{SiO}_2$ )] and 1 wt% of some organic fillers, which are some sorbital derivatives (i.e., DBS, MDBS, and DMDBS) was investigated (Charoenphol *et al.*, 2004). It was found that the ability of these fillers to nucleate sPP decreased in the following sequence: DBS > talcum > MDBS >  $\text{SiO}_2$  ~ kaolin ~ DMDBS > marl >  $\text{TiO}_2$ , with DBS being able to shift the crystallization exotherm by  $\sim 18^\circ\text{C}$  on average, while  $\text{TiO}_2$  was able to shift the crystallization exotherm by only  $\sim 6^\circ\text{C}$  on average, from that of neat sPP.

## 2.6 Electrochemical and Physical Properties of Nanocomposites

Nanocomposite polymer electrolytes based on the PEO/ $\text{LiBF}_4$  system were synthesized in which the ceramic filler,  $\text{TiO}_2$ , was formed *in situ* within the polymer host by as sol-gel process (Liu *et al.*, 2003). The morphology, crystallinity, and electrochemical properties were investigated. SEM results showed that polymer and ceramic fillers were uniformly mixed at the nanometer level. DSC confirmed the suppression of polymer crystallization in the presence of  $\text{TiO}_2$  (it is widely accepted that ion conduction occurs in the amorphous phase above  $T_g$  by a liquidlike motion of the Li cations associated with the segmental reorientations of the neighboring polymer strands). The ionic conductivity reached its maximum value with 10%  $\text{TiO}_2$  content. At  $7 \times 10^{-7}$  S/cm at  $30^\circ\text{C}$ , it is an order of magnitude higher than in the absence of  $\text{TiO}_2$ . A comparison of the activation energies for ion conduction showed enhanced  $\text{Li}^+$  ion mobility in the presence of  $\text{TiO}_2$ . Restricted anion motion and weakened polymer-lithium ion interaction both contributed to the increased transference number. The nanocomposite polymer electrolyte was also found to be electrochemically stable up to 4.5 V versus  $\text{Li}^+/\text{Li}$  from cyclic voltammetric measurements.

The electrochemical and physical properties of composite polymer electrolytes based on a blend of poly(methyl methacrylate) (PMMA) and poly(ethylene glycol diacrylate) (PEGDA) were reported by Kim *et al.* 2003. The addition of nanometer-size  $\text{TiO}_2$  filler decreases the crystallinity of the polymer electrolytes and also improves the ionic conductivity and the interfacial resistance

between the electrode and the electrolyte. In addition, this ceramic filler enhances the mechanical strength of the electrolytes. A prototype battery, which consists of a graphite anode a  $\text{LiCoO}_2$  cathode, and the composite polymer electrolyte coated on a poly(propylene) (PP) separator, shows good cycling performance at high rate.

## 2.7 Photocatalytic Properties of Nanocomposites

As a conventional plastic material, a large amount of polystyrene (PS) and the expanded polystyrene (EPS) is used in food service and retail industry, due to its inertness, polystyrene and related plastic products are non-biodegradable in natural environment. The waste PS plastics do not decompose in landfills, causing a serious environmental problem. Such the problem, photodegradable polystyrene (PS)- $\text{TiO}_2$  nanocomposite film was synthesized (Zan *et al.*, 2004). The  $\text{TiO}_2$  nanoparticles were first modified by grafting polymer on its surface (G- $\text{TiO}_2$ ), and then the PS-G- $\text{TiO}_2$  composite films were performed through polymerization. The presence of  $\text{TiO}_2$  nanoparticles in polystyrene films greatly promotes the photocatalysis degradation of the composite. The organic modification by grafting polymer on the surface of  $\text{TiO}_2$  particles has been proved to be an effective process to obtain good dispersion of  $\text{TiO}_2$  nanoparticles in polymer films.

Since ethylene is a naturally occurring gaseous hormone produced by plant tissue that in low concentrations triggers the ripening of fruits and vegetables. The photocatalytic properties of  $\text{TiO}_2$  remove ethylene gas from the air. Volatile organic compounds present in air at low concentrations can be oxidized to carbon dioxide and water when exposed to thin films of titania irradiated with near UV light. Borosilicate glass rings were coated with titania-sol generated by controlled hydrolysis of titanium isopropoxide. A reactant stream containing either 48.99 or 1055 ppm of ethylene was fed continuously to a tubular reactor packed with the coated glass rings surrounded by black light blue fluorescent bulbs. The effluent was analyzed by gas chromatography. Titania supported on glass rings exhibited higher photocatalytic activity than unsupported titania pellets (Sirisuk *et al.*, 1999).