

Poly(vinyl chloride)/TiO₂ nanocomposite resin via the synthesis of TiO₂ nanoparticles in vinyl chloride followed by *in situ* suspension polymerization

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ABSTRACT

There are various methods established and implemented to prepare polymer/TiO₂ nanocomposites, but the choice of preparation method is limited in the case of most frequently used commodity polymers because of their enormous production and low price. *In situ* suspension polymerization is rarely reported, because suspension is a severe condition to maintain the dispersion of nanoparticles in monomer phase. However, not only the incorporation of nanoparticle but also the preservation of morphology and processing condition can be attained if *in situ* suspension polymerization is achieved in the polymer resins mainly produced by suspension polymerization such as PVC. In this study, we prepared PVC/TiO₂ nanocomposite resin via the synthesis of highly dispersible TiO₂ nanoparticles in the vinyl chloride, followed by *in situ* suspension polymerization of vinyl chloride which contained the nanoparticles. Solvothermal method is applied to the nanoparticle preparation, and the prepared TiO₂ nanoparticles have controlled sizes, shapes, and crystalline phases with the types and concentrations of precursor and oxygen donor. The film samples from prepared PVC/TiO₂ nanocomposites resins are highly transparent due to the minimized visible light scattering which is an evidence of high dispersivity of TiO₂ nanoparticles.

Keywords: nanocomposite, titanium dioxide, poly(vinyl chloride), *in situ* suspension polymerization

1 INTRODUCTION

Polymer/inorganic nanocomposites have been extensively studied in the last decade. They combine the advantages of the polymer and the inorganic material, and usually contain special properties of nanofillers leading to materials with improved properties. Among the various inorganic materials, titanium dioxide (TiO₂) can be widely applied to the polymeric materials for the addition of the eco-friendly characteristics such as adsorption and catalytic degradation of various contaminations, inhibition of pathogenic microorganisms, protection of ultraviolet radiation, etc. Various methods, including melt extrusion of unmodified or organically modified TiO₂, dispersion of organically modified TiO₂ in organic solvent followed by dissolution of the matrix polymer and solvent casting, or *in*

situ polymerization, are established and implemented to prepare polymer/TiO₂ nanocomposites. However, the choice of nanocomposite preparation method is limited in the case of most frequently used commodity polymers such as poly(vinyl chloride) (PVC), because of their enormous production and low price. Moreover, there are considerable difficulties that TiO₂ nanoparticles are easily conglomerated and not simply broken apart by conventional methods. It is obvious that the most important factors which affect the properties of nanocomposites are the dispersion and the adhesion at the polymer and nanofillers [1]. The agglomerates of TiO₂ nanoparticles act as defects which inevitably result in the degradation of the mechanical properties in polymer/inorganic nanocomposites. The decrement of interface area between the polymer matrix and TiO₂ due to the agglomeration, moreover, leads to inferior catalytic activity of TiO₂. Therefore, it is necessary to find the preparation route which satisfies high performance-cost balance in the area of polymer/TiO₂ nanocomposites.

The majority of vinyl polymers are produced by heterogeneous polymerization, e.g. emulsion polymerization, dispersion polymerization, and suspension polymerization. *In situ* emulsion polymerization is the most important method for polymer encapsulation of inorganic particles by far [2]. On the other hand, *in situ* suspension polymerization is rarely reported, because the suspension obtained by shearing a system containing monomer, water, and suspending agent is a severe condition to maintain the dispersion of nanoparticles in monomer phase. However, not only the incorporation of nanoparticle but also the preservation of morphology and processing condition can be attained if *in situ* suspension polymerization is achieved in the polymer resins mainly produced by suspension polymerization such as PVC. In this study, we prepared PVC/TiO₂ nanocomposite resin via the synthesis of highly dispersible TiO₂ nanoparticles in the vinyl chloride (VC), the monomer of PVC, and *in situ* suspension polymerization of VC which contained the nanoparticles. Solvothermal method is applied to the nanoparticle preparation [3], and the prepared TiO₂ nanoparticles have controlled sizes, shapes, and crystalline phases with the types and concentrations of precursor and oxygen donor. The sizes and shapes of the nanoparticles are determined by high-resolution transmission electron microscopy (HR-TEM), and the size distributions of the nanoparticles are determined by dynamic light scattering (DLS) method. The prepared TiO₂ nanoparticles are finally incorporated in the

polymer matrix through *in situ* suspension polymerization. The film samples from prepared PVC/TiO₂ nanocomposites resins are highly transparent due to the minimized visible light scattering which is an evidence of high dispersity of TiO₂ nanoparticles. The predominant dispersions of the nanoparticles are confirmed by transmission electron microscopic and UV-visible transmittance observations of prepared PVC/TiO₂ nanocomposites.

2 EXPERIMENTAL

2.1 Materials

Titanium tetrabutoxide (Ti(OBu)₄, 98%) and titanium tetrakispropoxide (Ti(*i*Pr)₄, 98%) used in the preparation of TiO₂ were obtained from Aldrich. Lauric acid, stearic acid, oleic acid, and linoleic acid used for the surface capping of TiO₂ were also from Aldrich. Ethanol, cyclohexane, and tetrahydrofuran were of the highest purity available and purchased from Dae Jung Chem. All materials were used without further purification.

Reagents used for suspension polymerization were obtained from the following sources: vinyl chloride (VC) from Korea Gas; octyl peroxyneodecanoate (BND) and dioctyl peroxydicarbonate (OPP) from Chemex Co. Ltd.; poly(vinyl alcohol) (trade name K-420TM) from Kuraray Co. Ltd.; octadecyl dibutyl-4-hydroxyphenylpropionate (IR), dilauryl thiodipropionate (DL), and aluminum sulfate (AS) from Hanwha Chem. Corp. All of these chemicals were used as received.

2.2 Synthesis of TiO₂ nanoparticles

In the typical synthesis procedure of TiO₂ nanoparticles, Ti(OBu)₄ (2 mL), lauric acid (0.05 mol), and liquefied VC (50 g) were mixed at room temperature by mechanical stirring. After continued stirring at room temperature for 10 min, the solution was kept at 80~100 °C for 6~12 h.

Before characterization of TiO₂ nanoparticles, VC was slowly vented out and the residual VC was evaporated at room temperature. Organic-capped TiO₂ nanoparticles were easily redispersed in solvents such as cyclohexane or tetrahydrofuran. An as-obtained sol of TiO₂ nanoparticle materials could be stable for a few weeks. By adding an excess of ethanol, TiO₂ nanoparticles were precipitated at room temperature. The resulting precipitates were isolated by centrifugation and washed with ethanol to remove surfactant residuals.

2.3 Preparation of poly(vinyl chloride)/TiO₂ nanocomposite resin

In a high-pressure PVC polymerization reactor equipped with a temperature controller, a high-speed mechanical agitator, and a balance-controlled vacuum VC feeder, PVC/TiO₂ nanocomposite resin was prepared by *in-situ* suspension polymerization of VC which

contained the TiO₂ nanoparticles. A schematic illustration of the reaction procedure is shown in Figure 1. The experimental procedure was as follows. First, the reactor was charged with water and additives. The additives used in the suspension polymerization were K-420TM (as a suspending agent), BND and OPP (as initiators), IR and DL (as antioxidants), and AS (as a scale inhibitor); these additives were combined in the reactor. After TiO₂ nanoparticle dispersion in vinyl monomer is added to the dispersion, polymerization was carried out at a temperature of 57.5 ± 0.5 °C and a pressure of approximately 9.0 ± 0.5 bar while agitating the suspension at a speed of *ca.* 600 to 700 rpm until there was a pressure drop of approximately 0.5 bar from the maximum pressure attained. At the end of the reaction, the remaining gas was vented out. The crude product was then washed several times with ethanol and water, filtered, and dried overnight under vacuum.

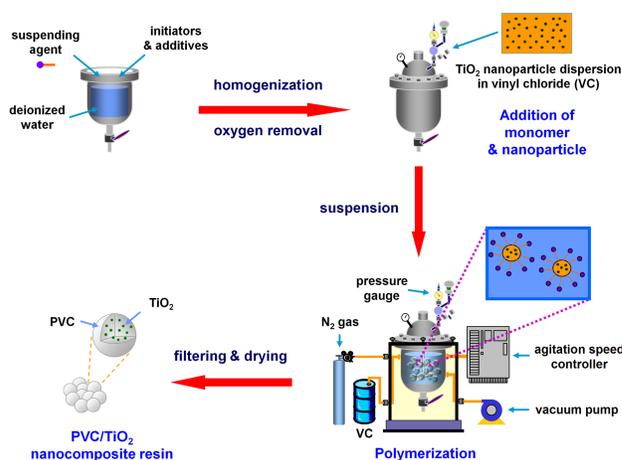


Figure 1: Schematic illustration of the synthetic pathway for the preparation of PVC/TiO₂ nanocomposite resin.

2.4 Characterization Techniques

Transmission electron microscopy (TEM). TEM images of TiO₂ nanoparticles were obtained using a JEOL JEM-3010 microscope operating at 300 kV. The samples were prepared by dropping dilute solutions of TiO₂ nanoparticles in tetrahydrofuran onto 300-mesh carbon-coated copper grids and immediately evaporating the solvent. TEM images of PVC/TiO₂ nanocomposite were obtained using a Philips CM20 microscope operating at 200 kV. Ultra-thin cross-sections of the specimens were prepared using a Leica Ultracut UCT ultramicrotome at room temperature.

Powder X-ray Diffraction (XRD). XRD patterns of TiO₂ nanocrystal powders were collected with a MAC Science Co. M18XHF-SRA diffractometer using Cu K_α radiation (λ=1.54 Å).

Dynamic light scattering (DLS). The dispersity of TiO₂ nanoparticles in hydrophobic liquid medium was estimated

by DLS using an DLS-7000 spectrophotometer coupled with a GC-1000 autocorrelator (Otsuka Electronics Co., Ltd., Osaka, Japan) by utilizing an Ar laser ($\lambda=488$ nm) at a scattering angle of 90° .

Scanning electron microscopy (SEM). The morphology of PVC/TiO₂ nanocomposite was determined with a JEOL JSM-6700F FE-SEM operating at 5 kV. The FE-SEM samples were coated with platinum for 5 min using a JEOL JFC-1100 ion sputter coater.

UV-visible transmittance. Optical properties of PVC/TiO₂ nanocomposite were observed with a PerkinElmer Lambda 25 UV-visible spectrometer.

3 RESULTS & DISCUSSION

The prepared TiO₂ nanoparticles capped with various organic ligands have controlled sizes, shapes, and crystalline phases with the types and concentrations of precursor, oxygen donor, and organic ligand. Figure 2 are the HR-TEM images of TiO₂ samples prepared with titanium tetrabutoxide as a precursor, lauric acid as an oxygen donor. In the case of L1 and L2 (Figure 2(a) and 2(b)), TiO₂ nanospheres were prepared. As the increment of precursor, nanorods appeared (Figure 2(c) and 2(d)). TiO₂ nanospheres were almost disappeared and nanorods became major products in L4. Relatively broad diffraction peaks in the X-ray diffraction patterns due to anatase structures are present for all these nanoparticles. Figure 3 is the size distribution graph of a TiO₂ nanosphere sample. The TiO₂ nanoparticles with very small size and narrow size distribution are highly dispersible in not only vinyl monomers but also various solvents such as cyclohexane or

tetrahydrofuran. The dispersibility of TiO₂ nanoparticles on the hydrophobic medium can be evaluated by analyzing the hydrodynamic diameter of dispersed nanoparticles through DLS measurement.

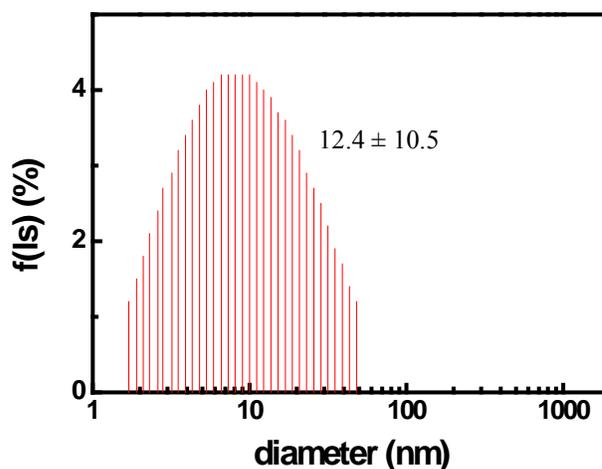


Figure 3: Size distribution graph of a prepared TiO₂ nanosphere sample (L1, dispersed in cyclohexane).

Sample code	L1	L2	L3	L4
Average Diameter (nm)	12.4	7.2	20.8	40.8
	± 10.5	± 8.4	± 54.6	± 112

Table 1: Average diameters of the synthesized TiO₂ nanoparticles measured by DLS

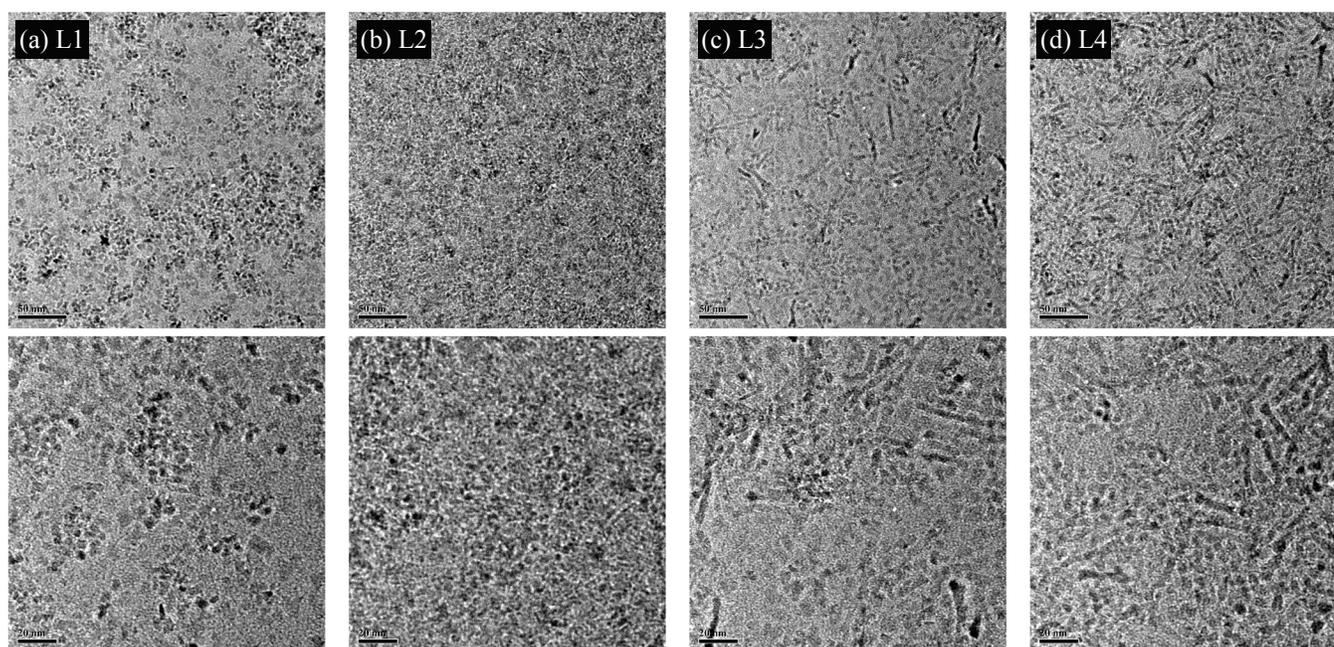


Figure 2: HR-TEM images of the prepared TiO₂ nanoparticle samples.

The preparation of PVC/TiO₂ nanocomposite resin via *in situ* suspension polymerization of VC requires no additional process step to disperse TiO₂ nanoparticles in the monomer phase, because the synthesis of TiO₂ nanoparticles and the capping of hydrophobic ligand onto the nanoparticles can be performed in liquefied VC by one step process. VC contained the nanoparticles was readily suspended in water and VC droplets containing the TiO₂ nanoparticles were subsequently polymerized to form PVC/TiO₂ nanocomposite resin. Figure 4 shows FE-SEM images of PVC/TiO₂ nanocomposite resin at various magnifications. The diameter of the grains was in the range 100–160 μm, and was thus similar to the grain size range of commercial-grade suspension PVC. The dispersion of TiO₂ nanoparticles in PVC matrix was examined by TEM, as shown in Figure 5. The TiO₂ nanoparticles were well dispersed without significant agglomeration. The degree of dispersion of nanoparticles in the polymer matrix was found to be significantly enhanced by *in situ* suspension polymerization.

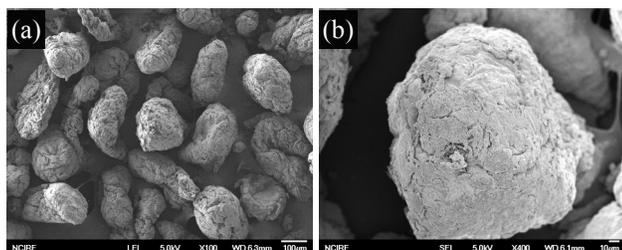


Figure 4: FE-SEM images of PVC/TiO₂ nanocomposite resin with magnifications of (a) × 100 and (b) × 400

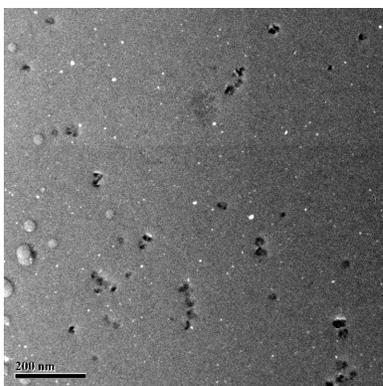


Figure 5: TEM image of PVC/TiO₂ nanocomposites resin.

The film samples from prepared PVC/TiO₂ nanocomposites resins are as transparent as pure PVC (Figure 6). PVC/TiO₂ nanocomposite are transmitting visible light (400 nm < λ < 700 nm) due to the minimized visible light scattering which is an evidence of high dispersity of TiO₂ nanoparticle. Moreover, PVC/TiO₂

nanocomposite is absorbing much of UV light which shows the potential of UV protection material (Figure 7).

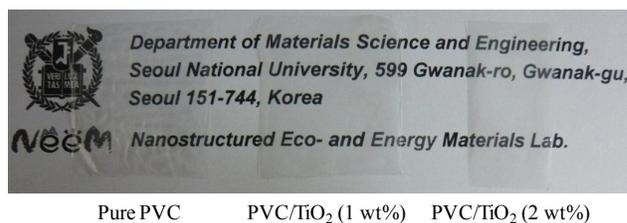


Figure 6: The film samples from pure PVC and prepared PVC/TiO₂ nanocomposites resins.

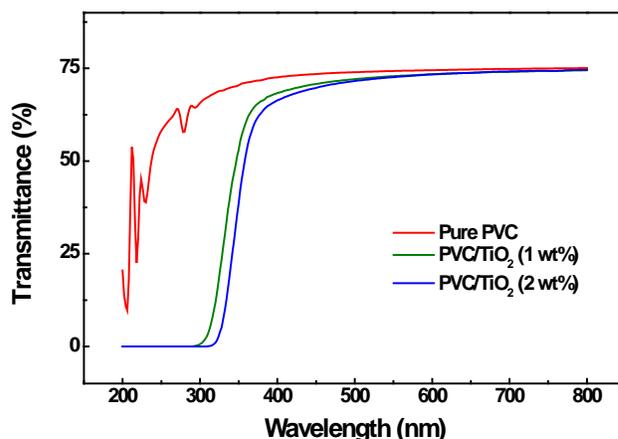


Figure 7: The film samples from pure PVC and prepared PVC/TiO₂ nanocomposites resins.

4 CONCLUSION

In this study, PVC/TiO₂ nanocomposite resin was successfully prepared via the synthesis of highly dispersible TiO₂ nanoparticles in the vinyl chloride (VC) and *in situ* suspension polymerization of VC which contained the nanoparticles. TiO₂ nanoparticles with hydrophobic surface could be synthesized in vinyl chloride directly and the sizes and shapes of TiO₂ nanoparticles were controlled in the variant of precursor concentration. The TiO₂ nanoparticles were well dispersed in PVC matrix without significant agglomeration. The films from PVC/TiO₂ nanocomposites are as transparent as pure PVC, because of the minimized visible light scattering. More investigations on their physical properties will be presented and discussed at the meeting.

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