

ORIGINAL RESEARCH PAPER

Nitroxide-Mediated Radical Polymerization of Styrene Initiated from the Surface of Titanium Oxide Nanoparticles

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ABSTRACT

Titanium dioxide (TiO₂) nanoparticles, with an average size of about 45 nm, were encapsulated by polystyrene using in situ nitroxide mediated radical polymerization in the presence of 3-aminopropyl triethoxy silane as a coupling agent and 2, 2, 6, 6-tetramethylpiperidinyl-1-oxy as a initiator. First, the initiator for nitroxide mediated radical polymerization was covalently bonded onto the surface of Titanium dioxide nanoparticles through our novel method. For this purpose, the surface of TiO₂ nanoparticle was treated with 3-aminopropyl triethoxy silane, a silane coupling agent, and then these functionalized nanoparticles was reacted with \pm -chloro phenyl acetyl chloride. The chlorine groups were converted to nitroxide mediated groups by coupling with 1-hydroxy-2, 2, 6, 6-tetramethyl piperidine. These modified TiO₂ nanoparticles were then dispersed in styrene monomers to carry out the in situ free radical polymerization.

INTRODUCTION

Recently, many researchers have attempted to utilize controlled/living polymerization methods for the preparation of nanocomposite polymers with well defined structures. Controlled/living radical polymerization (CLRP) enables synthesis of polymers with narrow molecular weight distributions (MWDs), predetermined molecular weights and various complex architectures. The past few years have witnessed a rapid development in the field of controlled radical polymerization for synthesizing tailor made polymers with well-defined architecture and predictable molecular weights [1]. A number of techniques have been explored to achieve this control: atom transfer radical polymerization (ATRP) [2-9], nitroxide-mediated radical polymerization (NMRP) [10-15], and reversible addition fragmentation process (RAFT) [16]. Nitroxide-mediated radical polymerization method is a controlled free radical

methodology, which allows the synthesis of star and graft copolymers with controlled molecular weight under mild conditions. This polymerization method is based on the use of traditional radical initiator (e.g., B.P.O) in the presence of stable nitroxide radical (e.g., TEMPO). In this type of process, the propagating species (Pn^o) reacts with a stable radical (X^o) as seen in Fig. 1. The resulting dormant species (Pn-X) can then reversibly cleave to regenerate the free radicals once again. Once Pn^o forms it can then react with a monomer, M, and propagate further. The most commonly used stable radicals have been nitroxides, especially 2, 2, 6, 6-tetramethyl tetramethylpiperidinyl-1-oxy (TEMPO).

Compared with other graft copolymerization such as anionic polymerization, an advantage of 'living' free radical polymerization (LFRP) is that in the preparation of grafted copolymers, the terminal groups are stable in air at room temperature, and pre polymers can be isolated, stored, and used as needed. Moreover, in

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anionic polymerization, stringent polymerizations conditions are required [17].

In recent years, polymer encapsulated submicron inorganic particles have attracted increasing because of their exceptional properties and use in technological applications [18-21]. Titanium dioxide (TiO_2) is one of the most important pigments and fillers used for a variety of scientific endeavors such as a dye in conjugated polymers for photo electrochemical [22] or photoconductive agents [23] a photo catalyst in a photodegradable TiO_2 -polystyrene nanocomposite films [24] and semiconductor electrodes in photo electrochemical cells [25]. However, it is difficult to disperse inorganic nanoparticles in non-polar polymers due to the incompatibility at the inter phase between the hydrophobic matrix and the hydrophilic oxide surface. Because of their extremely large surface-area/particle-size ratio, nanoparticles tend to strongly aggregate, hence reducing the mechanical properties of the resultant nanocomposite materials [27-30]. Many efforts have been taken to overcome this problem and to enhance the filler/matrix interaction, such as ultrasonic irradiation, which has been explored for dispersion of SiO_2 , TiO_2 , and Al_2O_3 nanoparticles during the synthesis of inorganic/polymer nanocomposite materials. However, this approach is restricted due to the limited interaction between the inorganic fillers and the organic matrix, compared with the very strong interaction between individual nanoparticles. Some methods have been explored to improve the dispersibility of inorganic nanoparticles in polymer such as surface modification of nanoparticles with, titanate and silane coupling agents [28-30], modification by chemisorptions of small molecules [19,31] and modification by the adsorption of polymers [32]. In addition to, polymer chains have been attached chemically to the inorganic nanoparticles. In this respect, "grafting from" and "grafting to" methods have been proposed. The "grafting from" approach relies on the immobilization of initiators for the controlled/living radical polymerization (CRP) of various monomers, followed by the chain growth from the surface and formation of polymer brush of possible high grafting density [33-35]. Currently, to the best of our knowledge, most of the reported approaches to prepare organic inorganic nanocomposites involve living radical polymerizations. Hojjati and Carpenters who used the relatively new technique of RAFT polymerization, to polymerized methyl meta crylate from TiO_2 nanoparticles [36], Zhao

and his coworkers functionalized multi walled carbon nano tubes via nitroxide-mediated radical polymerization [37], and by applying ATRP, Liu and Wang, grew polymer chains of hydroethyl acrylate from ZnO nanoparticles [38].

For the first time, synthesis and characterization of Poly styrene/ TiO_2 nanocomposite via nitroxide-mediated radical polymerization (NMRP) are reported. Firstly, TiO_2 nanoparticles were modified by 3-aminopropyl triethoxy silane coupling agent. Thereafter, these functionalization nanoparticles were reacted with α -chloro phenyl acetyl chloride. The chlorine groups were converted to nitroxide mediated groups by coupling with 1-hydroxy-2, 2, 6, 6-tetramethyl-piperidine (TEMPO-OH). These modified TiO_2 nanoparticles were then dispersed in styrene (St) monomers to carry out the in situ free radical polymerization by TEMPO iniferter.

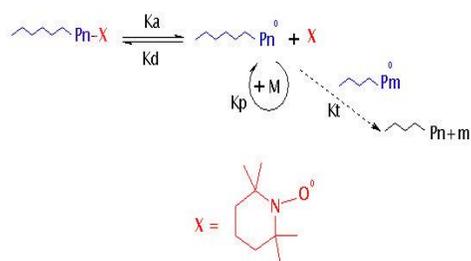


Fig. 1. Mechanism for nitroxide-mediated polymerization

MATERIALS AND METHODS

Titanium oxide (Degussa P25) dried at 150°C in inert atmosphere. 3-aminopropyl triethoxy silane (APTES) was provided by Merck Co. and used without further purification. Toluene and Tetrahydrofuran (THF) (Merck, Germany) were dried by refluxing over sodium and distilled under argon prior to use. Dimethyl formamide (DMF) dried over CaH_2 and distilled before use. Triethylamine (TEA) was dried with molecular sieves and then distilled. α -Chloro phenyl acetyl chloride was used as received. Styrene (Merck) was dried with CaH_2 and distilled before use. TEMPO was prepared in our laboratory in Tabriz Payame Nooruse. Triethylamine (TEA) was dried with molecular sieves and then distilled. α -Chloro phenyl acetyl chloride was used as received. Styrene (Merck) was dried with CaH_2 and distilled before use. TEMPO was prepared in our laboratory in Tabriz Payame Noor University [10-15].

Sodium ascorbate was provided by Aldrich Co. and

used as received. Sodium hydride was used as received).

Instrumentation

FT-IR spectra were recorded using Shimadzu FT-IR-8101M. The samples were prepared by grinding the dry powders with KBr and compressing the mixture to form disks. The disks were stored in a desiccator to avoid moisture absorption. The thermal properties of polystyrene/TiO₂ nanocomposite measurement were performed with a TGA-METTLER/ TOLEDO-SDTA 851°. Sample of about 3 mg were heated from 50 to 750 °C at rate of 10 °C min⁻¹ under nitrogen flow. DSC analysis were carried out using a DSC-METTLER/ TOLEDO 822°. The sample was first heated to 200 °C and kept for 5 min to eliminate the heat history. The sample was then cooled down at a rate of 10 °C/min. The sample was then reheated to 200 °C at a rate of 10 °C/min. Scanning electron microscopy (SEM) was performed using a FE SEM S4160-Hitachi instrument. Transmission electron microscopy (TEM) was performed using a PHILIPS CM10 TEM EPSON HP8300 Photo flat-bed scanner.

Surface modification of TiO₂ nano-particles with APTES

The grafted APTES in toluene condition was performed with 1 gr of Titanium oxide. The powder was dried at 125 °C under vacuum for 2 hr and was dispersed into anhydrous toluene (200 ml) under argon flow. The suspension was stirred for a further 1 hr and 3 ml of APTES was added slowly under argon flow. The reaction mixture was refluxed under an argon flow for a further 18 hr. The particles were recovered by centrifugation at 5000 rpm for 10 min. After separation from the suspension by centrifuging, the precipitate (APTES-grafted TiO₂ nano-particles) was washed with fresh toluene to remove the excess silane absorbed on the TiO₂ nano-particles and dried under vacuum at 125 °C for 2 hr. The reaction mechanism is illustrated in Fig. 2.

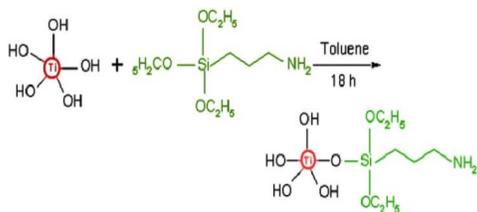


Fig . 2. Surface modification of TiO₂ nano-particles with APTES

Grafting of polymerization initiating agent to modified TiO₂ nanoparticles

The amino functionalized nanoparticle surfaces were immersed in anhydrous THF (6 mL). After this dispersion, triethylamine (0.5 mL) and α -chloro phenyl acetyl chloride (0.5 mL) were added. The reaction was allowed to proceed overnight with moderate agitation. The functionalized Titanium oxide surfaces were then purified by multiple washings with THF and dichloromethane and dried in vacuum at room temperature(. 3).

Reduction of TEMPO to 1-hydroxy-2, 2, 6, 6-tetramethylpiperidine (TEMPO-OH)

Reduction of TEMPO to 1-hydroxy-2, 2, 6, 6-tetramethylpiperidine (TEMPO-OH) was carried out. For this purpose TEMPO (0.2 gr) was suspended in a solution of sodium ascorbate (1 gr) in water (13 ml) and shaken vigorously until it was completely decolorized (0.5 h). The resulting suspension was extracted with ether. Afterwards, the ether extracts were washed with water and brine, dried (Na₂SO₄), and evaporated under reduced pressure to give a crude product (. 4).

Synthesis of TEMPO/modified-TiO₂ macro-initiator

In a two-neck round-bottom flask equipped with condenser, gas inlet/outlet, and a magnetic stirrer, 0.20 g of TEMPO-OH was dissolved in anhydrous N,N-dimethyl formamide (DMF) (30 ml) and under argon atmosphere 18 mg of NaH was added. The mixture was stirred for 30 min. Then 0.4 g of acetyl chloride-grafted TiO₂ nanoparticles was slowly added to the mixture under argon atmosphere and the mixture was stirred for 18 h at room temperature. The reaction was terminated by pouring the content of the flask into a large amount of methanol. The white solid was filtered, washed with methanol and dried in vacuum (Fig5).

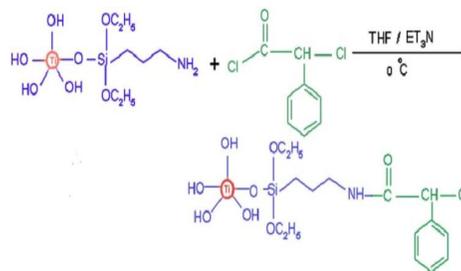


Fig. 3. Grafting of polymerization initiating agent to modified TiO₂ nanoparticles

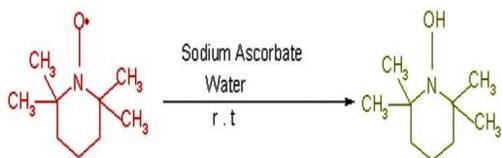


Fig. 4. Reduction of TEMPO to 1-hydroxy-2, 2, 6, 6-tetramethylpiperidine (TEMPO-OH)

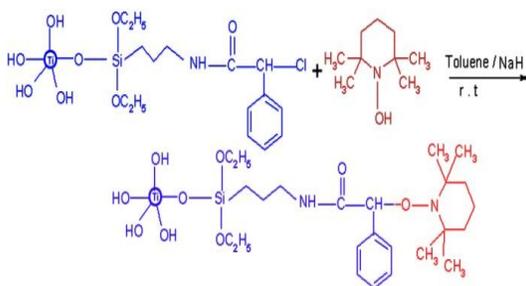


Fig. 5. Synthesis of TEMPO/modified-TiO₂ macro-initiator

Graft Polymerization of styrene onto the TEMPO/modified TiO₂ with NMRP

For preparation nano composites, 0.2 g of nanoparticles containing TEMPO initiator and 11 ml freshly distilled styrene monomer was stirred under argon gas flow and 125 °C, then a white viscous solution was obtained after 40 hours. The viscous solution was dissolved in tetrahydrofuran

and was precipitated with acidified methanol. For remove homopolymers from nanocomposites, the product were extracted with cyclohexane in Soxhlet extraction apparatus for 10 hours and then dried at room temperature.

RESULTS AND DISCUSSION

Modification of TiO₂ nano-particle with coupling agent APTES and grafting the polymerization initiator

The functional silanes have been widely used for the surface modification of metal oxides. To get evidence that coupling agent APTES was chemically bonded to TiO₂ nano-particle, FT-IR spectroscopy investigation was initially used to identify the qualitative composition of modified TiO₂. The FT-IR spectra of TiO₂ (a), APTES-grafted TiO₂ (b) and the macroinitiator (acetyl chloride grafted TiO₂ -APTES)(c) are shown in Fig. 7. FT- IR

spectra of TiO₂ sample shows that this inorganic material is non reactive because there is no functional group on its surface. The introduction of APTES to the surface of nanoparticles (NPs) is confirmed by the bands at 1108 and 1029 cm⁻¹ assigned to the Si-O-C stretching vibrations and 900 cm⁻¹ assigned to the Ti-O-Si. The broad band at 3300cm⁻¹ is referred to the N-H stretching vibration. The presence of the anchored propyl group is confirmed by C-H stretching vibrations that appear at 2860-2923 cm⁻¹. Reaction of APTES-grafted TiO₂ with chlorophenyl acetylchloride produces macroinitiator in which the presence of APTES moiety is asserted with the peak at 2929 cm⁻¹ is assigned to propyl groups and peak at 1625 cm⁻¹ is assigned to the stretching vibrations of the C=O group.

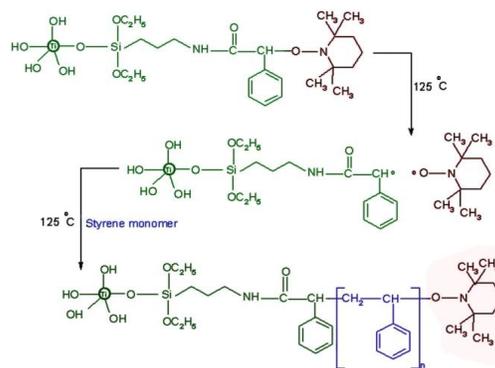


Fig. 6. Graft Polymerization of styrene onto the TEMPO/modified TiO₂ with NMRP

Synthesis of TEMPO/modified-TiO₂ macro-initiator

For synthesis TEMPO/modified-TiO₂ macro-initiator, first the TEMPO initiator was synthesized and then TEMPO was reduction to TEMPO-OH, then the TEMPO/modified-TiO₂ macro-initiator were synthesized. . 8 shows the TEMPO (a), TEMPO-OH(b) and TEMPO/modified-TiO₂ macro-initiator (c). In TEMPO spectrum, absorption band in the region 978 cm⁻¹ is assigned to the stretching vibrations of N-O, and stretching vibrations of C-H (aliphatic) bands has appeared in the region 2984cm⁻¹. After the reduction of TEMPO to 1- hydroxy-2,2,6,6-tetramethyl piperidine (TEMPO-OH), the peak in 3407 cm⁻¹ represent OH group. Stretching vibrations of CH₃ group is appears in 2975 and 2933 cm⁻¹, and also bending vibrations of CH₃ groups are visible in 1380 cm⁻¹. After

synthesis the TEMPO / modified -TiO₂ macro - initiator, Stretching vibrations of aliphatic groups in the TEMPO can be seen in 2925 cm⁻¹. Also in the range of 1461 cm⁻¹ bending vibrations of methyl groups can be seen as weak and O-N bonds are also appears in 1000 cm⁻¹ as weak.

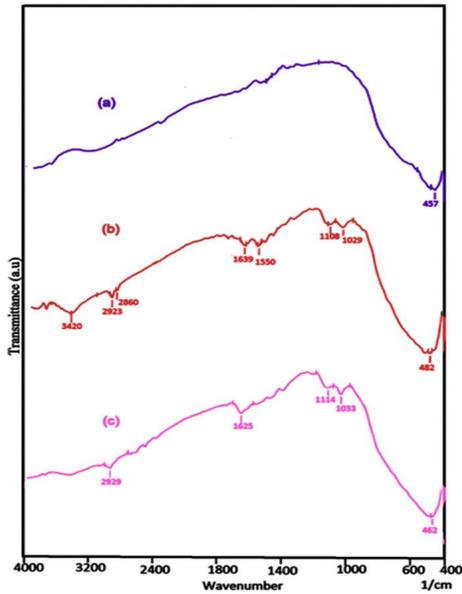


Fig. 7. FT-IR spectra of TiO₂ (a), APTES-grafted TiO₂ (b) and the macroinitiator (acetyl chloride grafted TiO₂ - APTES)(c)

Encapsulation of modified TiO₂ nano-particle by polystyrene

Fig. 8 (d) shows the FT-IR spectra of TiO₂ nanoparticles encapsulated by polystyrene. The peak at 1490 and 1660 cm⁻¹ is assigned to the stretching vibrations of the C-C from benzene ring and bending vibrations of the C-H from benzene ring were appears at 754 cm⁻¹ and also bending vibrations(offset) of the C-H from benzene ring were appears at 698 cm⁻¹. Stretching vibrations of the C-H from PS are appears between 2850-3026 cm⁻¹.

vibrations of the C-H from PS are appears between 2850-3026 cm⁻¹.

SEM characterization of nanocomposite

Scanning electron microscope (SEM) provides an actual image of the morphology of the nanocomposite. Fig. 9 shows the SEM image of the titanium oxide nanoparticles(a) and PS-TiO₂ nanocomposite(b). TiO₂

nanoparticles show the spherical morphology and most of the particles have tendency to aggregate, and the average particle size is about 39 nm. Fig 9(b) shows SEM images of PS-TiO₂ nanocomposite. In these images, a sheet of polymer is created, In addition, the polymers exist as a piece, this indicates that the polymerization has begun separately of each particle and dispersion is better.

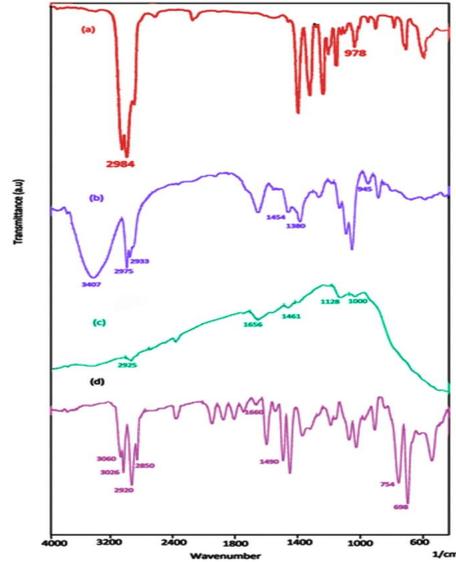


Fig. 8. FT-IR spectra of TEMPO (a), TEMPO OH (b), TEMPO/modified-TiO₂ macro-initiator (c) and TiO₂ - polystyrene nanocomposites (d)

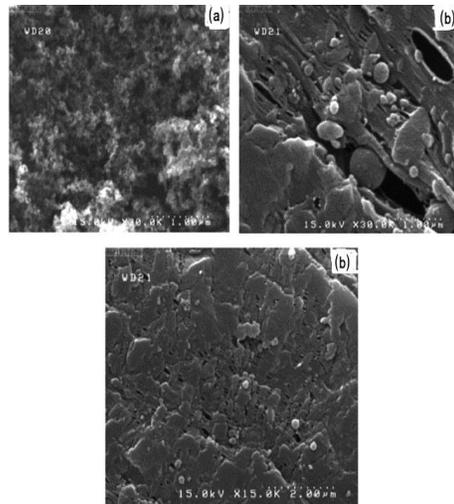


Fig. 9. SEM image of the titanium oxide nanoparticles (a) and PS-TiO₂ nanocomposite (b)

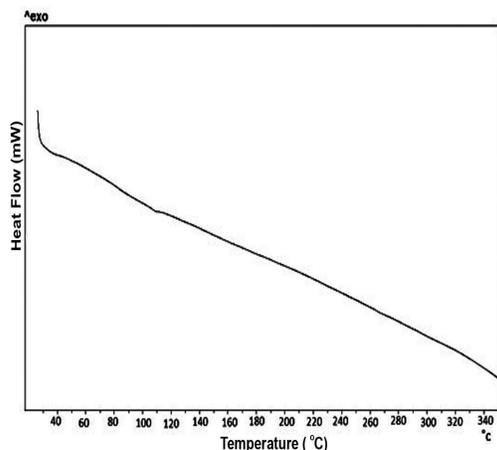


Fig. 10. DSC traces of the PS/TiO₂ nano-composite

Thermal property study

DSC measurements

Thermal behaviors of the obtained nano-composites were investigated by differential scanning calorimetric (DSC) and thermo gravimetric analysis (TGA). Fig. 10 shows the DSC traces of the PS-TiO₂ nano-composite. Polystyrene is non-crystalline and therefore does not exhibit any crystallization or melting transitions. Polystyrene exhibits an endothermic peak approximately at 83 °C, corresponding to the glass transition temperature. In Fig. 10, the endothermic peak seen at 76 °C has been attributed to the evaporation of any residual water and solvent. The DSC measurements indicate that the PS-TiO₂ nanocomposites have only one endothermic step based on glass transition temperatures (T_g) at 121°C. The former T_g temperature is higher than that of the PS (83 °C). Perhaps in the PS/TiO₂ nanocomposites, the TiO₂ nanoparticles disperse homogeneously in the polystyrene matrix. Strong interfacial bonding between the modified TiO₂ nanoparticles and polymer chains leads to an increase of glass transition temperature of nano-composite by impeding the chain flexibility.

Thermal stability of PS/TiO₂ nanocomposite

The thermal degradation of the nanocomposites was studied using TGA. Fig. 11 presents TG curve obtained under nitrogen environment for PS/TiO₂ nanocomposites. TGA results indicate improvement of the thermal stability for PS/TiO₂ compared to neat polystyrene. According to Fig. 11 we can conclude that the weight-loss at 332 and 476 °C in the TGA curve

of PS/TiO₂ is a result of polystyrene chains decomposition that was covalently attached to TiO₂ nano-particles. Higher decomposition temperature of PS/TiO₂ composites (332°C) compared with pure PS (250 °C) indicated that no polymer was adsorbed noncovalently onto the surface of TiO₂ nanoparticles. It appears from these data (TG curves) that in inert atmosphere, the presence of TiO₂ nanoparticles have significant effect on the thermal degradation of PS.

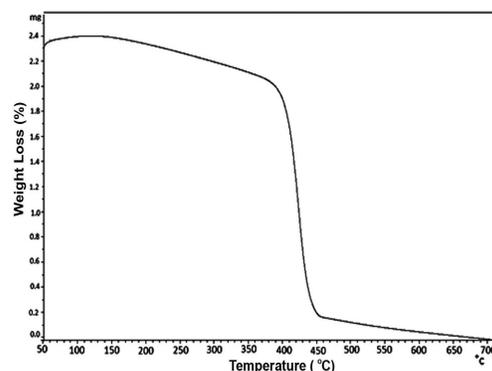


Fig. 11. TGA curves of the PS/TiO₂ nano-composite

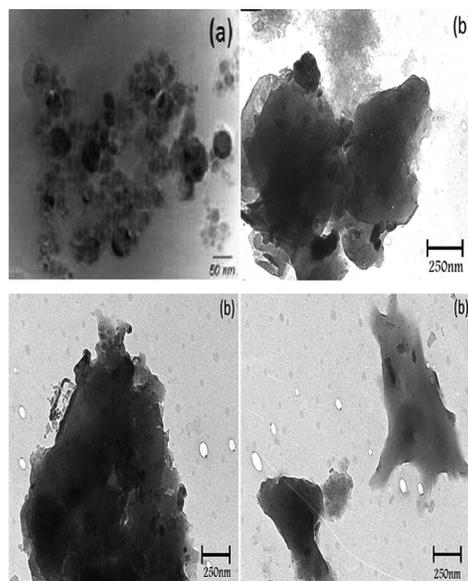


Fig. 12. Transmission electron micrographs (TEM) of the bare TiO₂ nanoparticles(a) and PS grafted TiO₂ (b)

3.6. Transmission electron microscopy

The transmission electron micrographs (TEM) of the bare TiO₂ nanoparticles and PS grafted TiO₂ are shown in Fig. 12. It is clear in Fig. 12(a) that the TiO₂

nanoparticles show spherical morphology. Due to the large specific surface area and high surface energy, some nanoparticles aggregate. The aggregation occurred probably during the process of drying. In order to check whether or not the polymer was encapsulated on the surface of nano TiO₂, the composite particles were characterized by TEM. As is shown in . 12(b), the black and translucent parts in the micrographs represent nano-TiO₂ and PS polymer, respectively. It was obviously revealed that nano- TiO₂ particle was embedded into the polymer. The nano-TiO₂ particle is too small and irregular to ensure that there is only one nano-TiO₂ particle in a composite and their diameter is about 45 nm. . 12(b) shows that aggregation was alleviated and dispersion was improved. Besides, one can also observe that around the TiO₂ nanoparticles there encircle some shadows, implying the existence of the grafted polymer layers.

CONCLUSION

Nano-TiO₂/Polystyrene nanocomposite had been prepared through nitroxide-mediated radical polymerization. For this purpose to reduce the aggregation among TiO₂ nanoparticles an effective surface modification method was proposed. Firstly, TiO₂ nano-particles were modified by APTES coupling agent, then the amine groups from coupling agent reacted with the initiator. After purification, the modified particles were treated with TEMPO. Then polystyrene chains were grown from the functionalized nanoparticles surface in the presence of a TEMPO. After characterization, DSC results showed the increase glass transition temperature of composites compared to pure polymer. TGA results showed the increase thermal stability of composites than that of pure polymer. Scanning electron microscopy and transmission electron microscopy showed the growth of polymers on particle surfaces and core-shell hybrid structures for composites.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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