

The Preparation of CNTs/PE Nanocomposites Particles with Coral Shape and Core-Shell Structure *In Situ* Produced via Nanotemplate Catalyst Based on MWCNTs

Jing Wang¹, Jiangping Guo¹, Yang Zhou¹, Qigu Huang^{1*}, Jianjun Yi², Hongming Li², Yunfang Liu¹, Kejing Gao² and Wantai Yang¹

¹State Key Laboratory of Chemical Resource Engineering, Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, People's Republic of China

²Lab for Synthetic Resin Research Institution of Petrochemical Technology, China National Petroleum Corporation, People's Republic of China

Abstract

A kind of nano template catalyst was prepared through loading the active compound (m-CH₃PhO)TiCl₃ on carbon nanotubes (CNTs). This catalyst can catalyze (co)polymerization of ethylene to form CNTs/polyethylene (PE) nanocomposites particles. The nano template catalyst showed high catalytic activity up to 5.8 kg/(gTi.h.p) for the copolymerization of ethylene with 1-hexene. The results revealed that the nascent CNTs/PE nanocomposites particles looked like coral shape and featured with the core-shell structure which CNTs as the core and polyethylene as the shell.

Keywords: Carbon nanotubes; Nanocomposites; Microstructure

Introduction

Porous materials such as SiO₂, MgCl₂ and Al₂O₃ have been applied as supports for heterogeneous Ziegler-Natta catalysts in olefins polymerization. Many reports on the use of porous materials as supports for Ziegler-Natta catalysts, metallocene catalysts and nickel diimine catalysts in the olefin polymerization have appeared in the literature [1-8].

Carbon materials have been attracted much attention on promising fillers in various polymers because of their excellent mechanical, thermal and electrical properties. Carbon nanofibers [9] and graphene oxide [10] are treated with methylaluminoxane and then loaded the active species on the surface for ethylene/propylene polymerization. All most previous works report that the efficient active sites are directly anchored on the supports surface without chemical bond between the active site and the support. Zhu [11] utilized two methods for the impregnation of Ni-diimine complexes on silicate-based nanotubes, which were carried out for ethylene polymerization. Wanke [12] studied the morphology of polyethylene particle catalyzed by MgCl₂-supported Ziegler-Natta catalyst. He found that the polymer particle was a perfect replica of the catalyst particle. The obtained milli-scaled polyethylene particles were spherical. Young [13] used a thermally pretreated bimetallic MgCl₂/tetrahydrofuran (THF)/TiCl₄ catalyst for producing polyethylene particles with regular and homogeneous globule. Mao [14,15] developed MgCl₂-supported Ziegler-Natta catalysts for ethylene and propylene polymerization to produce the polymer particles with good spherical morphology. Choi [7] synthesized MgCl₂-supported nickel diimine catalysts for ethylene polymerization with high catalytic activity, and the obtained polymer particles had good spherical morphology. Kanellopoulos [16] studied the single particle growth in heterogeneous olefin polymerization according to the random pore polymeric flow model. Our previous work [8] reported that MgCl₂-supported Ziegler-Natta catalysts with different structure ligands had efficient catalytic activity for the copolymerization of ethylene with 1-octene. The comonomer incorporation content of the copolymer was relative to the catalysts' ligand structure. Carbon nanotubes (CNTs) have been attracted much attention because of their excellent mechanical, thermal and electrical properties. Based on these distinctive advantages, they were considered

to be promising fillers in various polymers. Huang [10] prepared the polypropylene/graphene oxide nanocomposites by *in situ* Ziegler-Natta polymerization. The active site TiCl₄ was anchored to the support graphene oxide through MgCl₂. Milani [17] obtained polypropylene (PP)/graphene nanosheet (GNS) nanocomposites with good molecular weight, thermal properties, and tacticity by *in situ* polymerization using metallocene catalysts. Kaminsky [9] reported that carbon black (CB), carbon nanofibers (CNFs) and different types of CNTs were separated by ultra sound and then treated with methylaluminoxane (MAO). These catalytic active centers efficiently promoted ethylene/propylene polymerization and polyolefin nanocomposites were obtained after mixing zirconocenes or other transition metal complexes with the fillers. Pinheiro [18] prepared linear low-density polyethylene nanocomposites containing different types of nanofiller (TiO₂, MWCNT, expanded graphite, and boehmite) by *in situ* polymerization using a Zirconium-Nickel tandem catalyst system. All most previous works reported that the efficient active sites were directly anchored on the supports surface without chemical bond between the active site and the support. The active sites included TiCl₄, metallocene catalysts, α - and β -diimine complexes, FI catalyst, Cr-based catalyst and et al. The supports included MgCl₂, SiO₂, carbon nanotubes; graphene oxide and et al. Recently, Wang [19] reveal that the active site TiCl₄ is directly bonded with the support oxidized nanosized carbon spheres through Ti-O bond. Coperet [20] investigated SiO₂-supported dinuclear CrIII sites to polymerize olefins forming polymers initiated by C-H bond activation, the active site is directly bonded with the support through Cr-O-Si bond.

*Corresponding author: Qigu Huang, State Key Laboratory of Chemical Resource Engineering, Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China, Tel: +86-10-64433856; Fax: +86-10-64433856; E-mail: huangqg@mail.buct.edu.cn

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In this work, we report that the CNTs/PE nanocomposites particles with the coral-shaped and core-shell structure *in situ* produced by the nano template catalyst (*m*-CH₃PhO)TiCl₃/CNTs which is directly bonded to the oxidized multiwalled carbon nanotubes (MWCNTs) through Ti-O bond, AlEt₃ used as a co-catalyst. The morphology and structure of the nano template catalyst and the obtained CNTs/PE nanocomposites particles, as well as the performance of the polymerization, are investigated.

Experimental Section

General remarks

All operations of air- and moisture-sensitive materials were performed using the rigorous repellency of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line under a nitrogen atmosphere. CH₃MgCl with 22 wt% in tetrahydrofuran (THF) and triethylaluminum (AlEt₃) with 1.0 M in hexane were purchased from Acros Organics Agent in China. MgCl₂ (water included<0.01%), AlEt₃ (2.0 M in n-hexane) and *m*-cresol were purchased from Acros in China. 1-hexene were from Fluka in China. Other chemicals were from Beijing chemical agent company. 3-Chloro-1,2-epoxypropane and tributyl phosphate were treated with activated 5 Å molecular sieves under high-purity nitrogen for one week before use. Toluene, THF and n-hexane were further purified by refluxing over metal sodium under nitrogen for 48 h and distilled before use. Ethylene (polymerization grade) was from Sino-petrochemical Company, and used without further purification.

Synthesis of non-metallocene catalyst

To a stirred solution of TiCl₄ (11.0 mL, 0.10 mol) in toluene (30 mL), one equivalent of *m*-cresol (10.5 mL, 0.10 mol) was added with a syringe at -25°C. The mixture was gradually warmed to 30°C for 4 h. The mixture was filtrated and extracted by toluene. The solvent was removed, brown solid (*m*-CH₃PhO)TiCl₃ was obtained with yield 22.40 g (89.6%). (*m*-CH₃PhO)TiCl₃ (M_w=261.3) compound: ¹H NMR: δ 7.13 (tri, 1H), δ 6.75 (m, 1H), δ 6.65 (m, 2H), 2.30 (s, 3H); ELEM.ANAL, Calcd: C, 32.12; H, 2.68. Found: C, 32.20; H, 2.59. ¹³C NMR: δ 169.54 (C1), 119.42 (C2), δ 139.57 (C3), δ 126.71 (C4), δ 128.92 (C5), δ 115.96 (C6), δ 21.18 (CH₃).

Preparation of oxidized MWCNTs

Two grams (2.0 g) MWCNTs and 100 mL of concentrated nitric acid were added into a 250 mL Schlenk flask. The mixture was subjected to ultrasonic washing for 5 min with an ultrasonic washer and was stirred for 5 h with a stirring bar at 80°C. The obtained residue after filtrating was washed twice with distilled water and anhydrous ethanol, respectively, and then it was further purified by vacuum for 1 h to obtain black bulk solid, oxidized MWCNTs with diameter of 50 nm and length of *ca* 20 μm. The yield was 1.70 g.

Preparation of MWCNTs supported catalyst

Oxidized MWCNTs (1.5 g) and n-hexane (100 mL) were added into a 250 mL schlenk flask. The mixture was stirred in high speed with a dripping of 21.0 mL of CH₃MgCl (0.06 mol). The reaction was carried out for 2 h at room temperature, the reactant was filtrated and the residue was washed twice with 50 mL of n-hexane to remove the remnant Grignard reagent. The obtained solid and 50 mL of n-hexane were added into a 250 mL schlenk flask, followed by adding 15.0 g of (*m*-CH₃PhO)TiCl₃ at 0°C. Then the reaction system was stirred for 1 h at the same temperature. Warming to 60°C slowly, the mixture was maintained for 2 h at 60°C. After that, the reaction system was filtrated.

The residue was washed in turn with toluene and n-hexane (50 mL each time) at 50°C until no titanium in the filtrate was determined by Inductively Coupled Plasma (ICP) and drying under vacuum for 2 h. Black powder product was obtained with yield of 1.83 g. The titanium content of the catalyst was 4.0 wt% confirmed by ICP, *i.e.* (*m*-CH₃PhO)TiCl₃ content was 21.8 wt%. The number of the active sites on CNTs presented with (*m*-CH₃PhO)TiCl₃ was 63%, estimated by the result of the poisoning experiment according to the literature [21].

Preparation of MgCl₂ supported catalyst

The supported catalyst (*m*-CH₃PhO)TiCl₃/MgCl₂ was prepared according to the literature [8]. To a mixing solution of MgCl₂ (solid, 1.0 g) dissolved in toluene (60 mL), 3-chloro-1,2-epoxypropane and tributyl phosphate, 11.0 g of (*m*-CH₃PhO)TiCl₃ in toluene (Mg:Ti=1:4 in mol) were added by a syringe at -10°C over a period of 1 h in a 300 mL Schlenk flask with a magnetic bar. Then the mixture was enhanced to 60°C and kept it for 3 h at the temperature. Adding n-hexane 20 mL, spherical precipitate was given. The mixture was filtrated and washed in turn with toluene and n-hexane for times (40 mL each time) at 50°C until no titanium in the filtrate was determined by ICP, then dried by vacuum. Spherical catalyst particles were obtained in yield of 1.31 g with brown color. The titanium content of the catalyst was 3.8 wt %, as determined by ICP analysis, *i.e.* (*m*-CH₃PhO)TiCl₃ content was 20.7 wt %. The number of the active sites on CNTs presented with (*m*-CH₃PhO)TiCl₃ was 51.6% which was also estimated according to the literature [21].

Polymerization procedure

All polymerizations were carried out in a 2000 mL stainless steel reactor equipped with a magnetic stirrer after purging all moisture and oxygen by a high-vacuum pump, the reactor was sealed under a nitrogen atmosphere. Freshly distilled hexane (1000 mL), along with the desired amounts of heterogeneous non-metallocene catalyst and AlEt₃, were added in the order. The mixture was stirred for 15 min for preactivation, and heating to 80°C, comonomer 1-hexene was charged into the reactor and the copolymerization was initiated by the introduction of ethylene and ethylene pressure was kept at 0.2 MPa for a desired time. The monomer pressure was kept constant during the polymerization by continuously charging with ethylene. The reaction was stirred for a desired time. Finally, the polymerization was terminated with 10 wt% HCl in alcohol. The obtained polymer was filtered, washing with alcohol and water, and then drying overnight in a vacuum oven at 50°C. Ethylene consumption was automatically recorded by a flowmeter. Ethylene polymerization followed the same procedure, but there was no comonomer added.

Characterization

¹³C NMR spectra were recorded on an INOVA500 MHz instrument operating at 125 MHz. The condition used for quantitative ¹³C NMR was of the copolymer content up to 15 wt% in solution, using *ortho*-dichlorobezene (*d*₄) as the solvent at 125°C. Tetramethylsilane was used as internal chemical shifts reference. The 1-hexene incorporation was estimated from ¹³C NMR spectra according to the literature [22-24]. The average molecular weight and molecular weight distribution were measured by a PL-GPC220 instrument using standard polystyrene as a reference and 1,2,4-trichlorobenzene as a solvent at 150°C. DSC thermograms were recorded with a PA5000-DSC instrument at a rate of 10 K/min. Scanning electron microscopy (SEM), morphological observation for the catalyst particle and polymer particle was performed on SUPRA 55/55VP field emission scanning electron microscope. The samples (the catalyst particle and polymer particle) for SEM were

obtained by immobilized on a film, and were sputter coated with gold to *c.a.* 15 nm thicknesses. Micrographs were taken at 20 kV HR-TEM. The titanium content in the catalyst was determined using a Shimadzu ICPS-5000 inductively coupled plasma emission spectrometer. ¹H NMR spectra was measured on an INOVA500MHz instrument. ¹H chemical shifts were reported in ppm relative to proton resonance in chloroform-d at δ 7.26 ppm. Elemental analyses were performed on a Perkin-Elmer 2400 microanalyzer at the College of Material Science and Technology, Beijing University of Chemical Technology.

Results and Discussion

Properties of the heterogeneous nano template catalyst

The kinetic curves of the catalyst (*m*-CH₃PhO)TiCl₃/CNTs, AlEt₃ used as a cocatalyst, for the copolymerization of ethylene with 1-hexene is shown in Figure 1. From Figure 1a, the catalyst (*m*-CH₃PhO)TiCl₃/CNTs exhibited much higher catalytic activity than that of catalyst (*m*-CH₃PhO)TiCl₃/MgCl₂. The catalytic activity of the catalyst system (*m*-CH₃PhO)TiCl₃/CNTs/AlEt₃ maintains nearly constant at 80°C over 2 h even at fairly low titanium concentration, such as 5.4×10^{-5} M in 1000 mL of solvent. The polymer mass increases linearly with increasing polymerization time within 2 h (Figure 1a'). The results indicate that the catalyst (*m*-CH₃PhO)TiCl₃/CNTs is stable even at 80°C for 2 h. Thus a low rate of deactivation of the catalyst (*m*-CH₃PhO)TiCl₃/CNTs might be attributable to the enhanced steric hindrance of the support CNTs bond with (*m*-CH₃PhO)TiCl₃. But the activity of catalyst (*m*-CH₃PhO)TiCl₃/MgCl₂ showed obviously decline for the copolymerization of ethylene with 1-hexene under the same conditions (Figure 1b). The polymer mass increases not linearity with increasing polymerization time within 2 h (Figure 1b). The discovery indicated that the support of CNTs is more efficient for non-metallocene catalyst for the copolymerization of ethylene with 1-hexene than MgCl₂. The data recording started at temperature 80°C (t=0 min), before the temperature, the product mass was 1.9 g for line a'.

The HR-TEM image of the catalyst (*m*-CH₃PhO)TiCl₃/CNTs and low magnification TEM image of MWCNTs are shown in Figure 2. As shown in Figure 2, the CNTs have an outer average diameter of 30-60 nm, multilayer arrays and many defects on the surface; exhibiting the nano template catalyst has a rough surface. It is believed that to some extent, the surface structure is damaged during the treatment with acid. The rough surface of the CNTs should be the result of the reaction between the functional group located on the surface and the transition metal compound (*m*-CH₃PhO)TiCl₃, which is in favor of the attachment for the active sites for ethylene polymerization.

Morphology of CNTs/PE nanocomposites particles

HR-TEM result reveals that the polymeric shell covers around the CNTs core of the CNTs/PE nanocomposites particles. As ethylene was charged continuously in feed, the polymerization didn't quit within the polymerization time, the particle size increased with the polymerization time. It is about 35 nm at 2 min of polymerization time (Figure 3a), 70-80 nm at 10 min (Figure 3b) and 500 nm at 20 min (Figure 3c). It is interesting, the SEM images confirm that the CNTs/PE composite particles produced by the nano template catalyst (*m*-CH₃PhO)TiCl₃/CNTs, look like coral shape with about 8-10 μ m in diameter and about 30 μ m in length when the polymerization time is 120 min (Figure 3d). The SEM image of the cryo-fracture surface of the CNTs/PE nanocomposites is shown in Figure 3d. The sample *in situ* produced by (*m*-CH₃PhO)TiCl₃/CNTs/AlEt₃ after 2 min of polymerization time exhibits a lot of nano fibers in PE matrix. The result reveals that CNTs of the CNTs/PE nanocomposites are well-distributed in PE matrix.

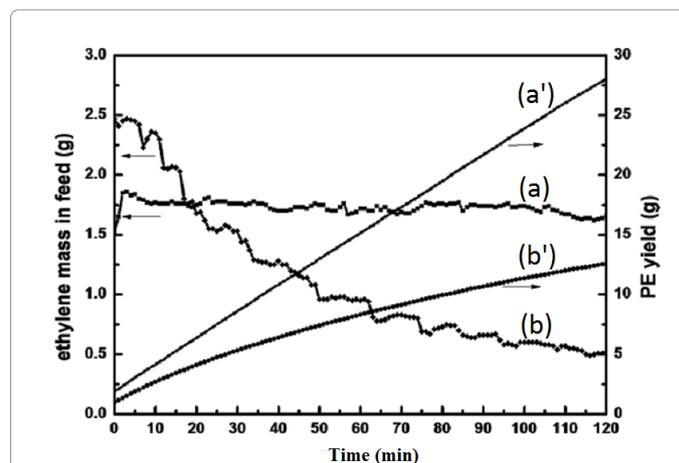


Figure 1: Ethylene mass in feed in polymerization catalyzed by catalyst systems of (a) (*m*-CH₃PhO)TiCl₃/CNTs and (b) (*m*-CH₃PhO)TiCl₃/MgCl₂, PE yield obtained by catalyst systems of (a') (*m*-CH₃PhO)TiCl₃/CNTs and (b') (*m*-CH₃PhO)TiCl₃/MgCl₂

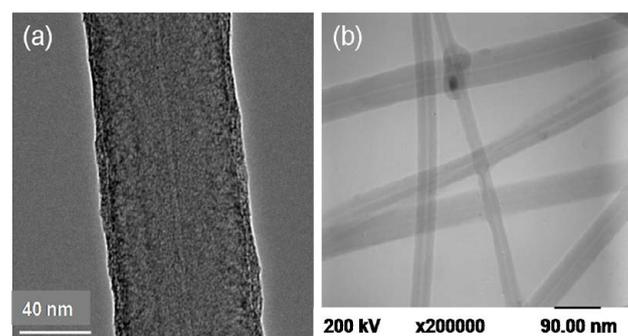


Figure 2: (a) HR-TEM image of the nano template catalyst of (*m*-CH₃PhO)TiCl₃/CNTs and (b) low magnification TEM image of MWCNTs

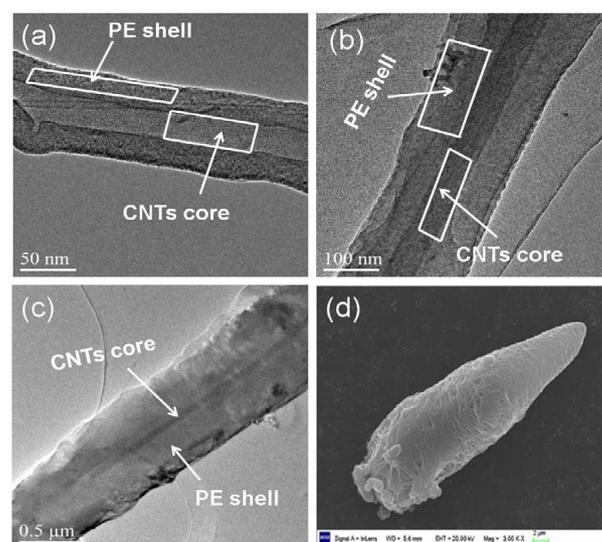


Figure 3: HR-TEM images of the CNTs/PE nanocomposites particles with polymerization time of (a) 2 min, (b) 10 min and (c) 20 min, and SEM image of the CNTs/PE nanocomposites particles with polymerization time of (d) 120 min

The SEM micrographs taken from the cryo-fracture surfaces of coPE/CNTs nanocomposites samples are shown in Figure 4. Figure 4a shows the fracture surface of pure polyethylene which has a flat crack propagation region in addition to some wrinkle. But no CNTs can be seen on it. However, the coPE/CNTs nanocomposites sample *in situ* produced by the catalyst system (*m*-CH₃PhO)TiCl₃/CNTs/AlEt₃ after polymerization time of 2 min, exhibiting a lot of nano CNTs in coPE matrix (Figure 4b). From Figure 4b, the distribution of the nano CNTs is fairly uniform. The result reveals that CNTs of the coPE/CNTs nanocomposites are well distributed in coPE matrix. With increasing polymerization time up to 10 min, the size of coPE shell of the coPE/CNTs nanocomposites reaches about 75 nm, coPE component is aggregated (Figure 4c). When the polymerization time is 120 min, the size of coPE shell of the coPE/CNTs nanocomposites is about 5 μm (Figure 4d); the cryo-fracture surface of the coPE/CNTs nanocomposites sample is similar to that of pure PE.

TGA analyses were performed for both conventional polyethylene and PE/MWCNTs nanocomposites in Figure 5. From Figure 5, it shows that conventional polyethylene and PE/MWCNTs nanocomposites have the same starting decomposition temperature of ca. 300°C, the decomposition temperature of loss 5 wt% of them is ca. 360°C. Furthermore, the conventional polyethylene and the PE/MWCNTs nanocomposites have the similar sharp decomposition temperature at ca. 450°C. The results indicate that the PE fraction of the PE/MWCNTs nanocomposites is thermally stable. From Figure 5, we can also find that for the conventional polyethylene, the complete decomposition temperature is 500°C (Figure 5a), while the PE/MWCNTs nanocomposites has approximately 75°C higher complete decomposition temperature at ca. 575°C (Figure 5b). MWCNTs can be decomposed at the temperature range from 500°C to 600°C.

Conclusion

Nano template catalyst (*m*-CH₃PhO)TiCl₃/CNTs was prepared through (*m*-CH₃PhO)TiCl₃ bonded directly to the oxidized MWCNTs. The kinetics of the copolymerization of ethylene with 1-hexene catalyzed by the nano template catalyst revealed that the composite mass increased linearly with increasing of the polymerization time. CNTs/PE nanocomposites particles with coral-shaped and core-shell structure were formed *in situ*. CNTs of the CNTs/PE nanocomposites were well-distributed in the matrix confirmed by SEM.

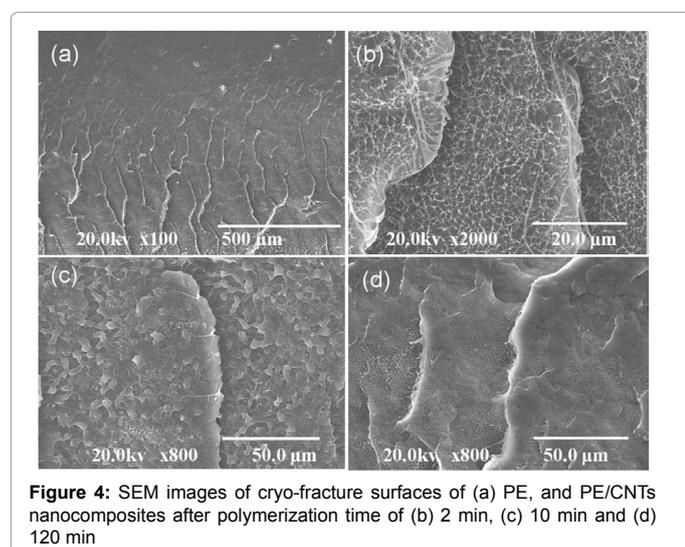


Figure 4: SEM images of cryo-fracture surfaces of (a) PE, and PE/CNTs nanocomposites after polymerization time of (b) 2 min, (c) 10 min and (d) 120 min

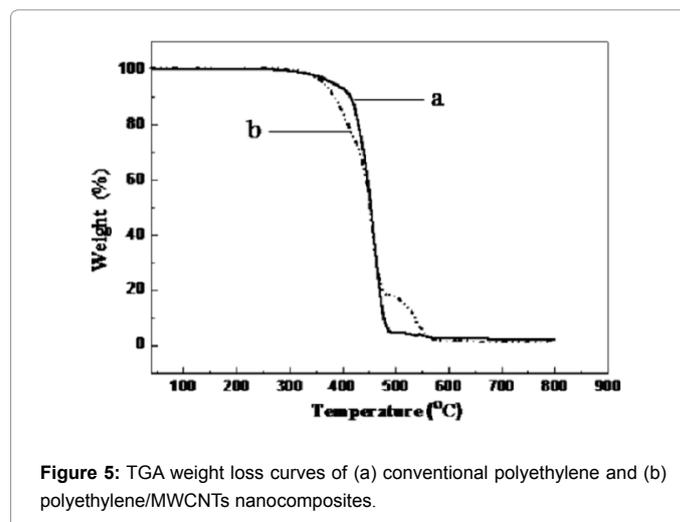


Figure 5: TGA weight loss curves of (a) conventional polyethylene and (b) polyethylene/MWCNTs nanocomposites.

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