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Short communication

Iron oxide/cassava starch-supported Ziegler–Natta catalysts for *in situ* ethylene polymerization

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ABSTRACT

Iron oxide nanoparticles were used as supporters for *in situ* polymerization to produce polymer nanocomposites with well-dispersed fillers in polymer matrix. Iron oxide could be sustained as colloidal solutions by cassava starch to produce a good dispersion of iron oxide in the matrix. New supports based on iron oxide/cassava starch or cassava starch for Ziegler–Natta catalysts were utilized as heterogeneous supporters for partially hydrolyzed triethylaluminum. Then, $TiCl_4$ was immobilized on the supports as catalysts for polymerization of ethylene. High-density polyethylene (HDPE) composites were obtained by the synthesized catalysts. A good dispersion of iron oxide/cassava starch particles was observed in the synthesized polymer matrix promoting to good mechanical properties of HDPE.

1. Introduction

Polyolefins are widely used in many applications in our daily life such as packaging films, plastic bags, food packages, construction and automobiles (Kaminsky, 2008; Makio, Terao, Iwashita, & Fujita, 2011). However, the unsatisfied properties of polyethylene such as tear strength, impact strength and low thermal stability are limited in its applications. To overcome those problems, composites or fillers were considered as additives to improve mechanical properties. In polymer industry, blending between polyolefins and other substances was widely accepted as a general method for the preparation of polymer composites (Gorrasi, Di Lieto, Patimo, De Pasquale, & Sorrentino, 2011; Yan, Lin, & Bhattacharyya, 2006). However, it is difficult to disperse additives into polyethylene, especially in non-polar segments. Alternatively, nanoparticles or fibers can be used as supporters for *in situ* polymerization to produce polymer nanocomposites with well-dispersed fillers in polymer matrix (Cheng, Wang, Ren, Chen, & Tang, 2007; Kaminsky, Funck, & Klinke, 2008; Köppl, Alt, & Phillips, 2001).

Iron oxide nanoparticles are considered as fillers in polymer composites due to their good mechanical properties, magnetic properties and biocompatibility. They can be prepared by different methods such as coprecipitation, hydrothermal reaction, thermal decomposition, sol–gel reactions, polyol methods and electrochemical methods (Laurent et al., 2008). The aggregation of iron oxide nanoparticles is usually prevented by adding surfactants or dispersants (Burke, Stöver, & Dawson, 2002). Stabilized polymers with functional group are important for controlling monodispersion of iron oxide nanoparticles (Wang, Liao, Yang, & Guo, 2012). Polyethylene is the most common polymer but iron oxide nanoparticles stabilized by polyethylene were reported by only one method in which the nanoparticles were prepared by the thermal decomposition of organometallic precursors (He et al., 2012). Furthermore, this method required the dissolution of polyethylene in a high-boiling point organic solvent such as xylene and the facile decomposition of toxic organometallic precursors such as $Fe(CO)_5$. In this report, the alternative preparation of iron oxide nanoparticles stabilized by polyethylene was proposed by using well-known Ziegler–Natta typed catalysis. Recently, our groups studied the interactions between iron oxide and starch (Somsook et al., 2005) and starch vermicelli could be used as a template for iron oxide nanostructures (Chairam & Somsook, 2008). Iron oxide could be sustained as colloidal solutions by arrow root starch and cassava starch (Mophan, Vinitnantharat, & Somsook, 2010). The multiple

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hydroxyl groups of arrowroot starch and cassava starch may bind tightly to the surface of iron oxide to prevent the further hydrolysis and precipitation and also the fine structures of starch may prevent the aggregation and control the size of nanoparticles. In addition, the partial hydrolysis of trimethylaluminum by starch has been reported as generating supporters for metallocene polymerization of ethylene (Köppl et al., 2001). Herein, cassava starch was used to govern the dispersity of iron oxide particles as iron oxide/cassava starch and supporters were generated by the partial hydrolysis of triethylaluminum by cassava starch or iron-oxide/cassava starch for the immobilization of $TiCl_4$ on those supporters. The partial hydrolysis of triethylaluminum was assumed to proceed the similar fashion as trimethylaluminum.

2. Experimental

2.1. Preparations of catalysts and supports

All reactions were performed under purified argon atmospheres using a standard glove box and Schlenk techniques.

Catalyst **A** ($MgCl_2/TiCl_4$): $MgCl_2$ (2 g, 0.02 mol) was dispersed in *n*-hexane (20 cm^3) in a Schlenk flask. Then, THF (3.4 cm^3, 0.04 mol) was added dropwise at 0 °C. The mixture was refluxed at 65 °C for 2 h. The THF adduct was washed by *n*-hexane and dried under vacuum. Dried THF adduct (1.5 g) was dispersed in *n*-hexane (20 cm^3) in a Schlenk flask. $TiCl_4$ (7.7 cm^3, 0.07 mol) was added dropwise to the THF adduct at 0 °C. The mixture was stirred for 24 h at room temperature. Catalyst **A** was washed by *n*-hexane (50 cm^3) six times and dried under vacuum.

Iron oxide/cassava starch support: iron oxide/cassava starch was prepared by the previous report (Mophan et al., 2010). 0.2 g of cassava starch was added to 100 cm^3 of distilled water and the mixture was heated at 90 °C until the mixture was clear. Then 2 cm^3 of 5 mol/dm^3 NaOH was added into the mixture. Then 100 cm^3 of 0.1 mol/dm^3 $FeCl_3$ solution was added into the hot mixture as vigorously stirred and then heated the mixture at 90 °C for 10 min. Adjust the pH of the mixture until the pH of the mixture was 12. The mixture was filtered to remove larger particles than the pore size of Whatman filter paper no. 1. Then the filtrate was heated at 100 °C to evaporate water and then the sample was dried in an oven at 120 °C.

Catalyst **B** (cassava starch/$TiCl_4$) and **C** (iron oxide/cassava starch/$TiCl_4$): cassava starch or the prepared iron oxide/cassava starch (1.00 g) and *n*-hexane (50 cm^3) were added to a Schlenk flask. At 0 °C, triethylaluminum (15 mmol) was added dropwise to the solid support and stirred at ambient temperature for 1 h and at 60 °C for 2 h. The supports were washed and filtrated by hexane three times. Next, $TiCl_4$ (3.3 cm^3, 30 mmol) was added dropwise to the solution and stirred at ambient temperature for 30 min and at 60 °C for 2 h. Finally, the catalysts were washed by *n*-hexane three times at 60 °C.

2.2. Polymerization of ethylene

Polymerization of ethylene was carried out in a 2-dm^3 reactor at 8 bar of ethylene. First, the prepared catalyst was added into a Schlenk flask with *n*-hexane (20 cm^3) as solvent. *n*-Hexane (500 cm^3) was transferred from a solvent purification equipment to the reactor. Triisobutylaluminum (TIBA) as a cocatalyst and a scavenger was added to reactor and the solution was stirred for 10 min. At 75 °C, ethylene was fed to reactor at 8 bars. The polymerization was controlled at 80 °C for 1 h. At the end of polymerization time, ethylene feed was stopped and the reaction was cool down at RT. Polyethylene was isolated and dried under vacuum.

2.3. Composites characterization

Polyethylene composites were characterized by FT-IR and ^{13}CNMR spectroscopy. Thermal properties of samples were analyzed using differential scanning calorimetry (DSC) with heating from 25 to 200 °C at a heating rate of 20 °C/min and then cooled at 0 °C. The melting temperature and crystallinity of the sample was recorded in the step of the second heating rate of 20 °C/min. For thermogravimetric analysis, it was performed under N_2 atmosphere and heating rate 20 °C/min and temperature range from 0 to 700 °C. The morphology of catalysts precursor and polyethylene composites was studied by scanning electron microscopy (SEM). Polyethylene composites were molded into small sheets (1 mm) by compression molding under pressure at 160 bars at 200 °C for 10 min. Polymer sheets were measured by SEM and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDX) to test dispersion of iron-oxide/cassava starch in HDPE matrix. For dynamic mechanical analysis (DMA, Gabo Explexor 25N), the polymer samples (1 cm × 3 cm × 1 mm) were measured at a fixed frequency of 5 MHz with heating range −80 °C to 100 °C. Tensile strength and percentage elongation were measured by using an Instron universal testing machine (Model 5569) and tested on dumbbells operated according to ISO 527 with control rate: 50 mm/min.

3. Results and discussion

The partial hydrolysis of trimethylaluminum by carriers such as silica, starch, and cellulose was reported to substitute methylaluminoxane (MAO) cocatalyst in the metallocene polymerization of ethylene (Köppl et al., 2001). In our report, ethylene polymerization was successfully carried out in the presence of classical Ziegler–Natta catalysts and also Ziegler–Natta catalysts on cassava starch and iron–cassava starch supported as shown in Table 1. As a reference (entry 1), polymer **1** was prepared by catalyst **A**, Ziegler–Natta catalyst ($MgCl_2/TiCl_4$, Ti = 2 wt%) and TIBA as cocatalyst. The immobilization of $TiCl_4$ on cassava starch and iron oxide/cassava starch was successfully achieved by partial hydrolysis of triethylaluminum by cassava starch or iron oxide. Both catalyst **B** and catalyst **C** were active for ethylene polymerization (entries 2–6). The catalytic activity of polyethylene was improved by loading higher amount of catalysts (entries 2–3). Catalyst **C** showed comparable catalytic activities as catalyst **B** (entries 3–6) indicating that active species were not deteriorated by iron oxide. Polymers **1**, **2** and **3** were successfully prepared with a characteristic of high-density polyethylene (HDPE) by catalysts **A**, **B** and **C**, respectively. The DSC results showed that the melting temperature and crystallinity of polymer **1**, **2** and **3** are approximately 135–140 °C and 47–60%, respectively, indicating to HDPE characteristics. Furthermore, ^{13}CNMR spectroscopy of prepared HDPE showed only one peak at 30 ppm of methylene protons indicating no branching in the polymer chain (Kaji, Akitomo, & Murano, 1991). All polymers showed FT-IR spectra (not shown) with a strong CH stretching peak at 2800–2900 cm^{-1} corresponding to CH_2 groups in polyethylene (Pagès, Carrasco, Surina, & Colom, 1996). The broad peak of FeO stretching at 600 cm^{-1} was observed for polymer **3** indicating the bounding of iron oxide by HDPE.

As shown in Fig. 1, the morphology of catalyst **A** showed fibrous structures leading to fibrous structures of polymer **1**. In contrast, the morphology of catalyst **B** showed good spherical shapes leading to a spherical shape of polymer **2** while irregular shapes of both catalyst **C** and polymer **3** were observed. The bigger size and roughly spherical shape of polymer **2** indicated that polyethylene was grown from the surface of the catalyst. To test physical and mechanical properties, all polymers were then compressed into small sheets. SEM

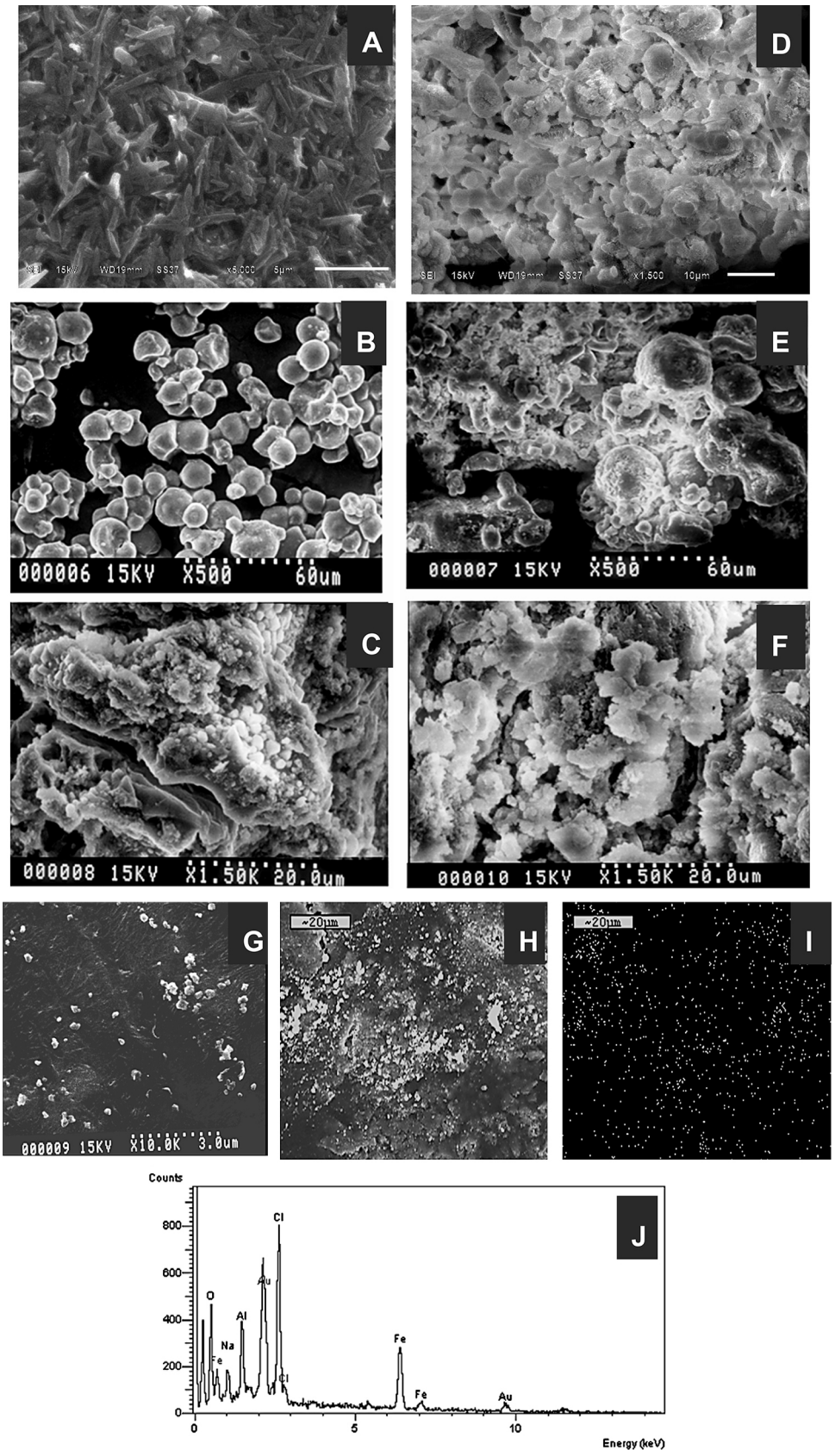

Fig. 1. SEM images: (a) catalyst **A**, (b) catalyst **B**, (c) catalyst **C**, (d) polymer **1**, (e) polymer **2**, (f) polymer **3**, (g) SEM image: sheets polymer **3**, (h–j) SEM-EDX images: sheets polymer **3**.

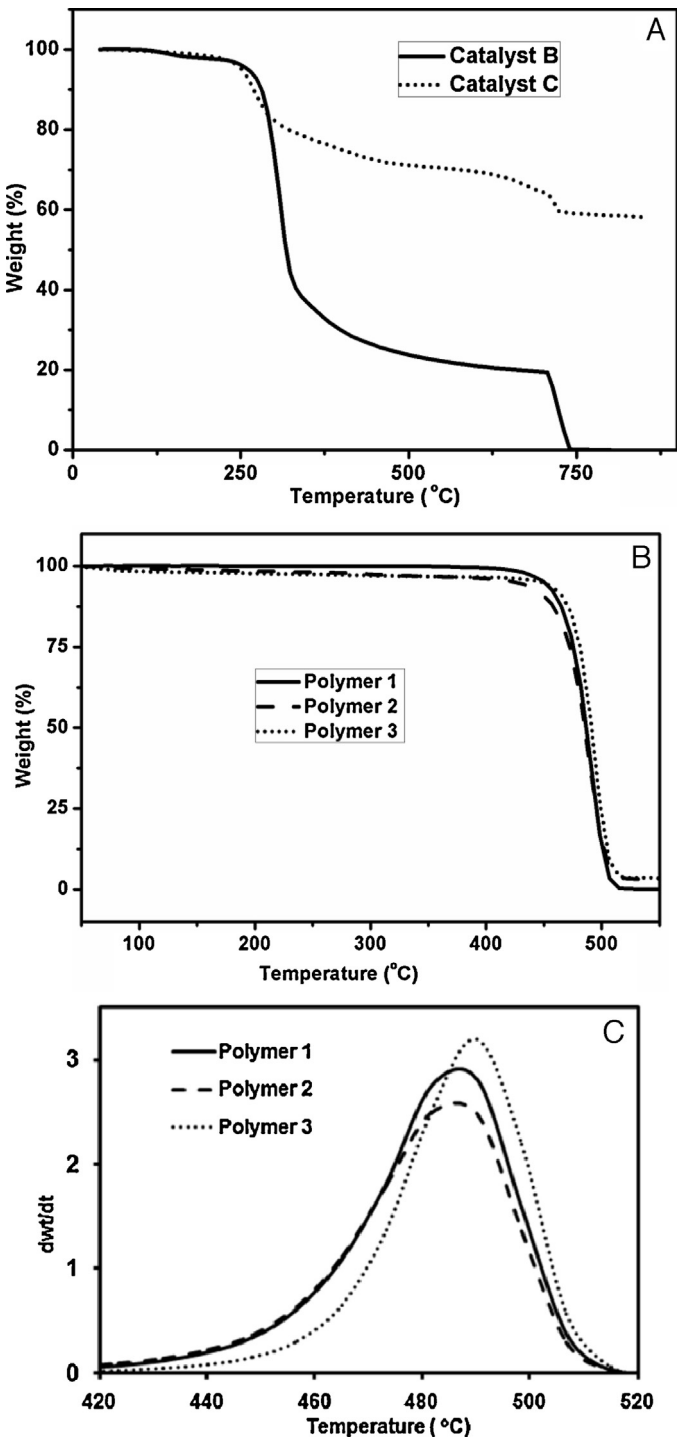

Fig. 2. TGA thermograms: (a) catalysts **B–C**, (b) polymers **1**–**3**. First derivative of TGA thermogram: (c) polymers **1**–**3**.

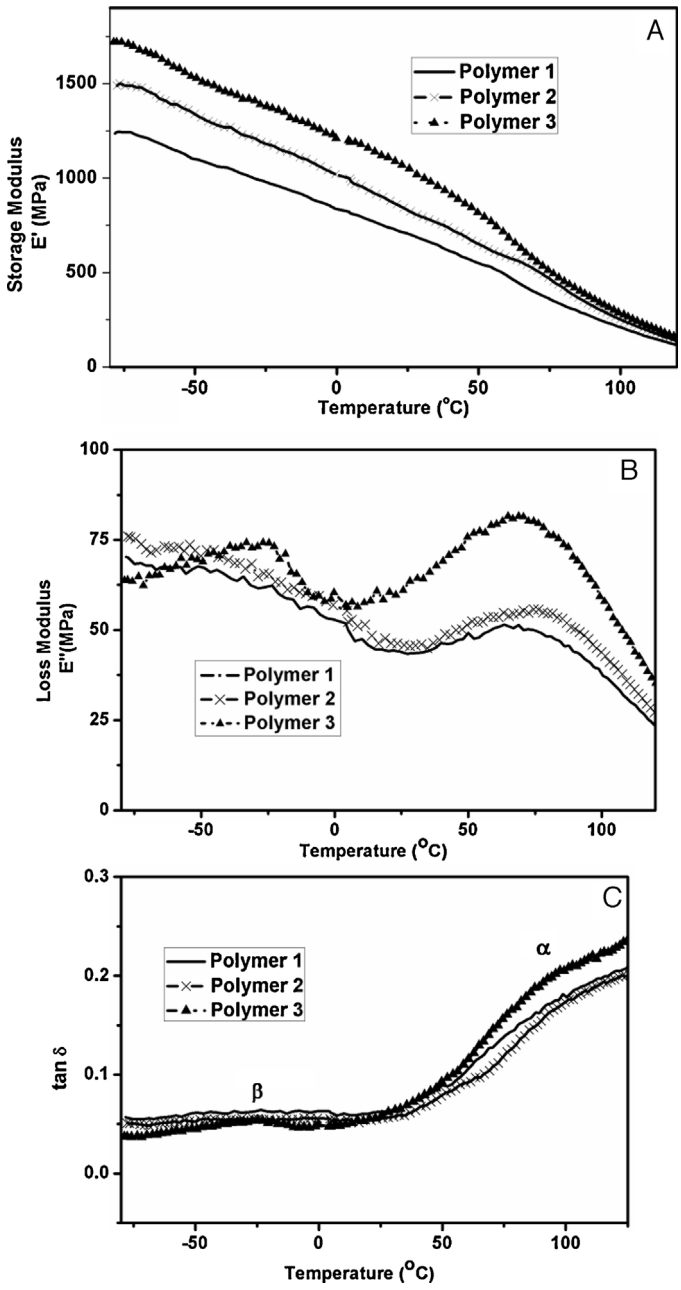

Fig. 3. Temperature dependence of (a) storage modulus (E'), (b) loss modulus (E'') and (c) loss tangent (tan δ) for all polymers.

and SEM-EDX images (mapping of Fe) of polymer sheets confirmed the presence of iron oxide with a good dispersion in HDPE matrix with particle size of approximately 100–200 nm as shown in Fig. 1.

TGA thermograms of catalysts and polymers are shown in Fig. 2. Catalyst **B** and **C** showed the decomposition of starch at 250–300 °C as previous report (Kim, Lee, Kim, & Kim, 2010). All polymers exhibited a single degradation in the range of 420–520 °C. The first-derivative TGA curves displayed the maximum decomposition temperature (T_C) in which polymer **3** showed the T_C higher than polymer **1** and **2** indicating that the improvement of thermal stability by iron oxide in polymer **3**. Dynamic mechanical analysis (DMA) with plots of storage modulus (E') and tan δ versus temperature is shown in Fig. 3. The storage modulus (E') of polymer **3** was higher than both polymer **1** and **2**. The improvement of storage modulus in polymer **3** showed the good compatibility and reinforcement of iron oxide/cassava starch composites in HDPE matrix. Generally, the relaxation process of polyethylene is observed at −115, −25, 70 °C assigning to γ-, β-, α-relaxation, respectively. The β-relaxation is represented to glass–rubber transition of constrained non-crystalline chain segments indicating the relaxation of branching point in polyethylene. In our study, β-transition of all polymers was not observed indicating the characteristic of HDPE. The α-process indicates the intracrystalline relaxation and sliding of tied chain within crystalline blocks (Li, Adams, Wang, Blümich, & Yang, 2010). In polymer **3**, α-relaxation was shifted due to catalyst **C** suggesting that the influence of iron oxide on the properties of

Table 1
Polymerization of ethylene[a].

Entry	Catalysts	Loading cat. (mg)	Polymer yield (g)	Activity[b]	T_m[c] (°C)	X_c[c] (%)
1	Ziegler–Natta ($MgCl_2/TiCl_4$) (**A**)	20	75.3	3765	141	60
2	Cassava starch/$TiCl_4$ (**B**)	60	3.3	55	135	47
3	Cassava starch/$TiCl_4$ (**B**)	120	8.4	70	136	47
4	Cassava starch/$TiCl_4$ (**B**)	120	9.8	82	136	51
5	Iron oxide/cassava starch/$TiCl_4$ (**C**)	120	8.8	74	135	49
6	Iron oxide/cassava starch/$TiCl_4$ (**C**)	120	11.3	94	136	55

[a] Polymerization temperature at 80 °C and time 1 h, TIBA 2.5 cm^3.
[b] Activity (g polymer/g support cat).
[c] Melting temperature (°C) was measured by DSC technique, and percentage of crystallinity (X_c) were estimated by ΔH_f/293 J/g.

Table 2
Tensile results of all polymers.

Polymer	Tensile at maximum load (MPa)	Tensile at break (MPa)	% Strain at break	Young modulus (Automatic, MPa)
1	32.6	29.6	542	3992
2	20.1	11.4	63	3430
3	42.4	42.4	367	7382

crystalline regions. As shown in Table 2, the tensile strength and tensile strain of polymer **2** were lower than polymer **1** which tensile strength and strain of HDPE is normally dropped by starch and biopolymer as fillers (Walker, Tao, & Torkelson, 2007). Surprisingly, the tensile strength and modulus of polymer **3** exhibited higher than ones of polymer **1** but the percentage of elongation was lower. This showed the advantage of iron oxide as reinforcement for improving the tensile properties of HDPE.

4. Conclusion

High-density polyethylene composites without branching were successfully synthesized by catalysts **B** and **C** with a good dispersion in HDPE matrix and improved mechanical properties (tensile strength and modulus). These demonstrated that *in situ* ethylene polymerization by $TiCl_4$ immobilized on heterogeneous supporters for partial hydrolyzed triethylaluminum is one challenge method to prepare well-dispersion of metal oxide filler in HDPE matrix.

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