

# Polymerization-Filled Composites Prepared with Highly Active Filler-Supported Al/Ti/Mg Catalysts. I. Synthesis of Homogeneous Polyethylene-Based Composites

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**ABSTRACT:** When it is attached onto the surface of an inorganic filler (kaolin, barite), the  $(\text{BuO})_4\text{Ti}/\text{BuMgOct}/\text{EtAlCl}_2/\text{Et}_3\text{Al}$  system is a highly efficient and very promising catalyst for the production of high-performance polyethylene-based composites. The surface concentration of the hydroxyl groups, the Al/Ti/Mg ratio, and the purity of the reagents have a major effect on the catalyst efficiency and molecular weight, crystallinity, and physico-mechanical properties of the final composite. Under ca. 4 bar partial pressure of ethylene in heptane at 60°C, the optimum Al/Ti/Mg catalyst composition is 120/0.75/10, the efficiency of which is as high as 300 kgPE/(gTi × h) in the presence of kaolin particles (Satintone W/W). The effect of transfer agents, such as hydrogen and 1-octene, and purity of the  $\alpha$ -olefin has been investigated. Actually, the catalyst efficiency is increased in the presence of both hydrogen and octene. Scanning Electron Microscopy (SEM) has shown that the ethylene was polymerized from the filler surface. Special attention has also been paid to the effect of size, density, and surface acidity of the filler particles. The surface of basic filler has to be treated in order to become an efficient catalyst carrier. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 423–438, 1997

**Key words:** composites synthesis; polyethylene; polymerization-filling technique; supported catalysts; molecular weight control

## INTRODUCTION

The academic and industrial interest for filled polymers is steadily increasing as the result of an appreciable reduction of cost and the opportunity of producing materials with a new set of selected properties.

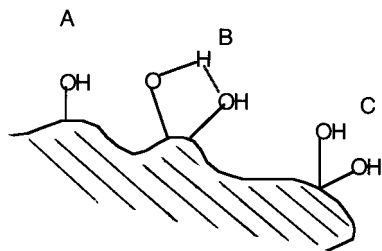
The filled elastomer technology is currently based on the dispersion of a high level of fillers (especially carbon black), which increases tensile strength, modulus, and hardness. In contrast, the

addition of mineral fillers into a semicrystalline thermoplastic, such as a polyolefin or a polyamide, is associated with a detrimental effect on the mechanical performances, due to a weak interfacial adhesion. Actually, the mechanical properties of composites depend on the complex interplay of the characteristic features of the filler (nature, shape, size, size distribution, . . .) and the polymer matrix (nature, melting temperature, crystallinity degree, ductility, molecular weight, polydispersity, . . .), the filler content, the dispersion technique, and, above all, the interfacial adhesion.

The preparation of composites by melt blending the polymeric matrix and the filler is a straight-

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**Figure 1** Hydroxyl groups on the silica surface; (A) isolated; (B) hydrogen bonded hydroxyl groups; (C) geminated hydroxyl groups (from the same Si atom).

forward procedure but is poorly efficient when the resulting composite properties are concerned. In order to overcome these limitations, a first strategy has been proposed that is based on the filler encapsulation by a polymer coating.<sup>1</sup> A second approach relies upon the chemical modification of the filler surface by functional silanes and titanate esters able to promote adhesion to the polymer.<sup>2,3</sup> In addition to these two rather complex and expensive techniques, the polymerization-filling technique has been developed by Enikolopian et al.<sup>4</sup> and Howard et al.<sup>5-9</sup> It consists of attaching a Ziegler-Natta-type catalyst onto the surface of an inorganic filler, so that olefin can be polymerized from the filler surface,<sup>10-12</sup> which allows a very high filler loading (up to 95 vol %) to be reached together with acceptable mechanical properties. Indeed, the polymer structure and molecular weight (ultrahigh molecular weight polyethylene: UHMWPE) and the high filling degree are the basis of completely new composition materials that cannot be produced by the standard mixing method.<sup>13</sup> Both the Russian and American teams have considered methods to generate active polymerization sites on the filler surface. As a rule, the transition metal compounds have been either merely deposited on the surface and possibly within the pores of the particles,<sup>11,14</sup> or the organometallic compounds have been reacted with some functional groups, for example, hydroxyls, available on the filler surface.<sup>10,15,16</sup> As far as silica is concerned, three kinds of OH groups, i.e., isolated, hydrogen bonded, and geminated double hydroxyl groups as sketched in Figure 1, have been recently identified by IR and NMR spectroscopy.<sup>17</sup> Nowlin et al.<sup>18</sup> have accordingly quantified the amount of dibutyl-magnesium (DBM) or triethylaluminum (TEA) that react with the surface OH groups of silica. The surface density of reactive hydroxyl groups can be easily modified by chemical<sup>17</sup> and thermal treatment.<sup>19,20</sup> In the case

of nonreactive particle surfaces, a pretreatment with a reagent bearing functional groups has been proposed.<sup>21</sup>

Table I reports the main filler/coordination catalyst pairs that have been used in the polymerization-filling technique, together with the catalyst efficiency. Among the investigated fillers, kaolin has received special attention more likely because it is known as a strong reinforcing agent.<sup>32,33</sup> Polymerization-filled composites (PFC) have been prepared by using various transition metals ( $Tm$ ) based catalysts, mostly Zr, Ti, V, and Cr. The reported catalyst efficiency ranges from 14 up to 936 kgPE/mol  $Tm \times h$ , depending on the addition or not of a cocatalyst, the size, type, and pretreatment of kaolin (Table I, entries 1-8).

Catalysts supported onto dolomite, alumina, and wollastonite appear to be of a relatively high efficiency, higher than 1000 kgPE/mol  $Tm \times h$  (entries 14, 17, and 25). The method used to associate the catalyst with the filler (entries 16 and 17) and the choice of the transition metal clearly affect the catalyst efficiency, for example, from 1 to 282 kgPE/mol  $Tm \times h$  in the particular case of silica (entries 18 and 19). It is worth pointing out that traces of a transition metal (Ti, V, and/or Cr) in some mineral particles, for example, kaolin, are able to initiate the olefin polymerization upon thermal activation (up to 1200°C) and addition of an alkylaluminum compound as cocatalyst (entry 9). The catalyst efficiency is, however, rather low in relation to the  $Tm$  concentration and distribution on the filler surface, and coating of the filler particles is nonhomogeneous, which leads to poor mechanical performance.

From Table I, the most active catalyst would be the  $CaSO_4$ -MAO- $Cp_2ZrMe_2$  system reported by Kaminsky et al. (entry 22). The activity of all the Zr atoms would explain this high efficiency, i.e., 36,500 kgPE/g mol Zr.<sup>30</sup> Nevertheless, the amount of MAO is prohibitively large (312,500 mol Al per mol Zr).

The latest development in the heterogeneous polymerization of ethylene has to be found in the incorporation of  $MgCl_2$  as a "support" for the coordination catalyst. Accordingly, Damyanov et al.<sup>25</sup> have succeeded in producing polyethylene composites with a catalyst efficiency in the range of 600 to 1300 kgPE/mol  $Tm \times h$ , depending on the filler (entries 5, 14, 15). The filler is first added with a known amount of diethyl aluminum chloride (DEAC), so as to form a monolayer, followed by the respective deposition of  $TiCl_4$  at 60°C,

**Table I State of the Art in Polymerization Filling Technique**

No.	Filler	Al/Tm/Mg	$T_m$	Catalyst Efficiency		Ref.
				kgPE/(mol $T_m \times h$ )	kgPE/(g $T_m \times h$ )	
1	Kaolin	20/1/0	Zr	936	10.2	22
2	Kaolin	0/1/0	Zr	280	3.0	23
3	Kaolin	0/1/0	Ti	44	0.9	19
4	Kaolin	133/1/0	Ti	745	15.5	24
5	Kaolin	120/1/10	Ti	612	12.5	25
6	Kaolin	3/1/0	Ti	14	0.3	26
7	Kaolin	0/1/0	Cr	140	2.7	23
8	Kaolin	5/1/0	V	336	6.6	26
9	Kaolin	1/0/0	Al	26	—	27
10	Tufa	0/1/0	Zr	112	1.2	19
11	Tufa	0/1/0	Zr	115	1.2	23
12	Tufa	30/1/0	Ti	649	13.5	23
13	Tufa	0/1/0	Cr	104	2.0	23
14	Dolomite	104/1/10	Ti	1,331	27.8	25
15	Perlite	100/1/10	Ti	813	17.0	25
16 <sup>a</sup>	Al <sub>2</sub> O <sub>3</sub>	40/1/0	Zr	545	6.0	28
17 <sup>b</sup>	Al <sub>2</sub> O <sub>3</sub>	0/1/0	Zr	1,320	14.5	19
18	SiO <sub>2</sub>	1/1/0	Ti	1	<0.1	29
19	SiO <sub>2</sub>	0/1/0	Zr	282	3.1	19
20	Marl	0/1/0	Zr	20	0.2	19
21	Fumice	0/1/0	Zr	136	1.5	19
22	CaSO <sub>4</sub> <sup>c</sup>	312,500/1/0	Zr	36,488	401.0	30
23	Mica	660/3/1	Ti	6	0.1	14
24	Asbestos	7/1/0	Ti	429	9.0	31
25	Wollastonite	1/1/0	Ti	2,020	42.2	32

<sup>a</sup> Calcinated Al<sub>2</sub>O<sub>3</sub> treated with 5  $10^{-5}$  mol (iso-Bu)<sub>3</sub>Al/g filler and 1  $10^6$  mol tetrabenzylzirconium/g filler. Polymerization at 50°C.

<sup>b</sup> Calcinated Al<sub>2</sub>O<sub>3</sub> treated with tetrabenzylzirconium (0.3 mmol/g filler) by the gas phase method. Polymerization at 80°C.

<sup>c</sup> Soluble catalyst system.

DEAC and diphenyl magnesium (DPM) as cocatalysts, the final Al/Ti/Mg ratio being 120/1/10.

Little success has been reported for the preparation of mica-based composites by direct adsorption of Mg containing compounds on the mica surface. Quite a low catalyst efficiency has been reported (entry 23) for that approach, which disregarded the hydroxyl functions present on the filler surface.

The purpose of this article is to produce homogeneous composites by the ethylene polymerization initiated by a novel (BuO)<sub>4</sub>Ti–BuMgOct–EtAlCl<sub>2</sub>–Et<sub>3</sub>Al catalyst attached onto the filler by using the hydroxyl groups present at the filler surface. This research is in line with a previous article dealing with the very efficient slurry polymerization of ethylene promoted by a Al/Ti/Mg–*n*-propanol catalyst. A catalyst efficiency as high as 7.950 kgPE/gTi  $\times$  h was reported.<sup>35</sup> The herein reported strategy for the preparation of a high

efficiency filler-anchored catalyst relies upon the substitution of the aliphatic alcohol for the hydroxyl functions present on the filler surface and/or pores. As already mentioned, kaolin is currently referred to as an efficient reinforcing agent for polyethylene,<sup>36–38</sup> the acidic surface of which allows the catalyst to be directly prepared (after the filler drying stage) without any previous surface treatment. For the sake of comparison, a basic filler, such as barite, has also been studied, which requires a preliminary acidic coating. This article, which is the first of a series,<sup>39</sup> is mainly devoted to the surface treatment of the filler, the Al/Ti/Mg catalyst preparation, and anchoring onto kaolin and barite. A special attention will also be paid to the effect that catalyst composition, monomer purity, and addition of transfer agents (H<sub>2</sub>,  $\alpha$ -olefin) can have on catalyst efficiency and melting temperature, crystallinity degree, melt index, and molecular weight of the final poly-

**Table II** Main Characteristics of the Kaolin and Barite

Composition	Kaolin Al <sub>2</sub> O <sub>3</sub> · SiO <sub>2</sub>		Barite BaSO <sub>4</sub>
	Satintone W/W	Satintone 5	Blanc fixe N
Trade name	Satintone W/W	Satintone 5	Blanc fixe N
Specific area (m <sup>2</sup> /g)	12	12	—
Mean particle size (μm)	1.4	0.8	3
Density	2.63	2.63	4.4
pH	5–6	5–6	9
OH content (10 <sup>-4</sup> mol/g) <sup>a</sup>	2.3	2.5	2.4 <sup>b</sup>

<sup>a</sup> Measured by volumetric titration.<sup>b</sup> Measured after surface treatment.

olefin. The physico-mechanical properties of the polymerization-filled composites (PFC) will be the topic of a forthcoming article.<sup>39</sup>

## EXPERIMENTAL

Kaolin (Satintone W/W and Satintone 5) and barite (Blanc Fixe N) were used as fillers and their main characteristics are listed in Table II. All the experiments were performed under nitrogen and standard inert-atmosphere polymerization conditions.<sup>39</sup> All gases were purchased from Air Liquide. Nitrogen (N55, 99.9999%, 2 ppm H<sub>2</sub>O, 0.5 ppm O<sub>2</sub>) and heptane were dried on a column of 4 Å molecular sieves. Butyl-octyl magnesium (BOMAG), (n-C<sub>4</sub>H<sub>9</sub>)<sub>1.5</sub>(n-C<sub>8</sub>H<sub>17</sub>)<sub>0.5</sub> Mg, was used as a 15 wt % (0.643 mol/L) solution in heptane, as purchased from Witco. Triethyl aluminum (TEA, Witco) was used as 1.00 mol/L or 0.10 mol/L solution in heptane. Ethylaluminum dichloride (EADC, Witco) was used as 0.916 mol/L heptane solution. Tetrabutyl titanate (TBT, Dynamit Nobel Chemkalien) (n-C<sub>4</sub>H<sub>9</sub>O)<sub>4</sub> Ti, was used as a 0.49 mol/L or 0.05 mol/L solution in heptane. Concentrations of TEA, EADC, TBT, and BOMAG solutions were measured by complexometric titration as previously reported.<sup>35</sup>

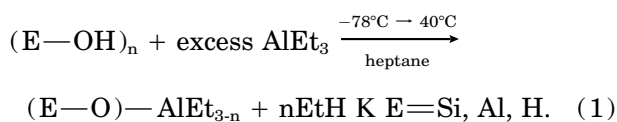
### Purification of 1-Octene

1-Octene (99%, Aldrich) was dried by stirring overnight over activated alumina previously heated at 240°C for 24 h and further treated overnight with CaH<sub>2</sub> powder and freshly distilled under vacuum just prior to use.

### Titration of the Surface Hydroxyl Groups

Kaolin and barite were previously heated overnight at 100°C under vacuum (10<sup>-2</sup> mmHg). The

content of hydroxyl groups and adsorbed water was volumetrically titrated according to eq. (1):



A Pyrex flask (250 mL, 2 outlets) equipped with rubber septa, connected to a gas burette and previously flamed and purged with N<sub>2</sub> was filled with 10 g of filler (Satintone W/W, Satintone 5, or barite) dried under reduced pressure (10<sup>-2</sup> mmHg) overnight. It was subsequently dispersed in 100 mL of dry and oxygen free *n*-heptane and cooled to -78°C. After the addition of 4.02 mmol of TEA (4.0 mL; 1.004M), the reaction mixture was heated to 40°C and kept at that temperature until no gas evolution was observed. The hydroxyl content was, in fact, equal to the total of ethyl group consumed and, therefore, to the quantity of ethane evolved (taking into account the dead volume of the device).

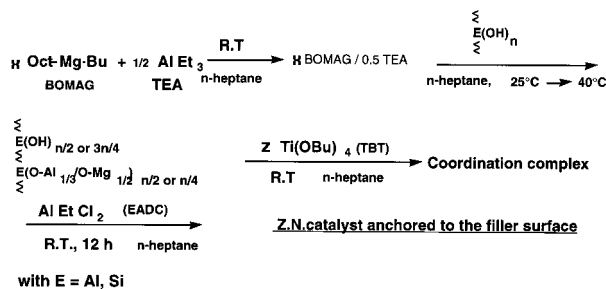
The value obtained was confirmed by the volumetric measurement of the ethane produced by hydrolysis of the unreacted ethyl groups of the TEA excess.

## Catalyst Preparation

### Kaolin Filler

The catalyst was attached onto the filler in such a way that either 50 or 25% of the kaolin OH groups were consumed (Fig. 2).

Under anhydrous conditions, 250 mL of dry and deoxygenated *n*-heptane were added to 20 g of Satintone W/W previously dried at 100°C for 18 h under 10<sup>-2</sup> mmHg pressure. In case of 25% of the filler OH groups (1.15 · 10<sup>-3</sup> mol), 1.65 · 10<sup>-4</sup>

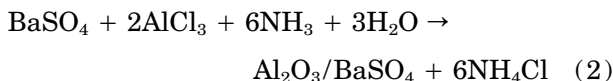


**Figure 2** Reaction pathway for the preparation of the highly efficient polymerization-filling Mg/Ti/Al based catalyst.

mol triethylaluminum in *n*-heptane (TEA) (1.6 mL;  $0.1 \text{ mol} \cdot \text{L}^{-1}$ ), and  $3.29 \cdot 10^{-4}$  mol Butyl-octyl magnesium in *n*-heptane (BOMAG) (0.5 mL;  $0.643 \text{ mol} \cdot \text{L}^{-1}$ ) were added, respectively, at room temperature and under stirring. The temperature was then raised up to  $40^\circ\text{C}$  for 0.5 h while ethane was released and continuously replaced by nitrogen inert gas. After cooling down to room temperature,  $2.45 \cdot 10^{-5}$  mol tetrabutyltitanate in *n*-heptane (TBT) (0.5 mL;  $0.049 \text{ mol} \cdot \text{L}^{-1}$ ) followed by  $1.65 \cdot 10^{-3}$  mol ethylaluminumdichloride in *n*-heptane (EADC) (1.8 mL;  $0.916 \text{ mol} \cdot \text{L}^{-1}$ ) were then added. The mixture was further aged for 18 h at room temperature. The Al/Ti/Mg composition was accordingly 55/z/10, with z the desired Ti amount, and it was used to identify the anchored catalyst. In this case, the catalyst Al/Ti/Mg composition was accordingly 55/0.75/10.

### Barite Filler

Prior to the catalyst preparation, barite particles were coated with alumina to form an acidic surface in agreement with a treatment previously reported by Howard et al. [eq. (2)].<sup>5</sup>



Six grams of  $\text{AlCl}_3$  ( $0.18 \cdot 10^{-3}$  mol Al/g  $\text{BaSO}_4$ ) were added to 231 g of a  $\text{BaSO}_4$  slurry in 2.3 L of water. Fifty milliliters of  $\text{NH}_3$  (25 wt % in  $\text{H}_2\text{O}$ ) were then added, and the surface treated particles were filtered and dried under vacuum at  $70^\circ\text{C}$ . The number of hydroxyl groups was measured by volumetric titration as  $2.4 \cdot 10^{-4}$  mol —OH groups/g ( $\text{Al}_2\text{O}_3/\text{BaSO}_4$ ). The catalyst was prepared by reaction of 25% of the filler hydroxyl groups, i.e.,  $0.6 \cdot 10^{-4}$  mol OH/g filler.

TEA ( $0.17 \cdot 10^{-3}$  mol) (1.71 mL;  $0.1 \text{ mol} \cdot \text{L}^{-1}$ )

and  $3.2 \cdot 10^{-4}$  mol BOMAG (0.5 mL;  $0.65 \text{ mol} \cdot \text{L}^{-1}$ ) were added to 20 g of previously dried  $\text{Al}_2\text{O}_3/\text{BaSO}_4$  [at  $100^\circ\text{C}$  for 18 h, under reduced pressure ( $10^{-2}$  mmHg)] dispersed in 250 mL of dry and oxygen-free *n*-heptane. The temperature was increased up to  $40^\circ\text{C}$  for 30 min and then decreased down to room temperature. The slurry was added with  $4.09 \cdot 10^{-5}$  mol TBT (0.8 mL;  $4.9 \cdot 10^{-2}$  mol  $\cdot \text{L}^{-1}$ ) and of  $1.64 \cdot 10^{-3}$  mol EADC (1.8 mL;  $0.91 \text{ mol} \cdot \text{L}^{-1}$ ). The catalyst was aged at room temperature for ca. 17 h prior to polymerization. The Al/Ti/Mg composition was 55/0.75/10.

### Polymerization

Ethylene was polymerized in a batch mode in a 2 L stainless steel Autoclave Engineers reactor equipped with a magnetic coupled stirrer, with a variable stirring speed and an external jacket heater. Hydrogen (N50, 99.999%) was used as received and ethylene (N35, 99.5%) additionally dried on a column of 4 Å molecular sieves.

The dry and oxygen-free reactor was heated up to  $60^\circ\text{C}$  and loaded with 1.5 L of dried and deoxygenated *n*-heptane containing the required amount of cocatalyst (TEA) so as to reach a final Al/Ti ratio of 120/0.75, 120/1, 120/1.5, or 120/2 (see Results and Discussion). If needed, 1-octene was added, for example,  $6.36 \cdot 10^{-3}$  mol of 1-octene compared to 1.57 mol of ethylene, eventually polymerized leading to a  $4.04 \cdot 10^{-3}$  octene/ethylene molar ratio. Slurry of the filler-supported catalyst was then added under  $\text{N}_2$ . The reactor headspace was repeatedly purged with hydrogen and the desired hydrogen pressure was set up (0 to 6 bar). Polymerization started upon the ethylene feeding. Ethylene consumption was measured with a Weva thermal mass flow-meter, since the ethylene pressure was kept constant at 4 bar. The ethylene feeding was stopped when the desired filling level was reached (e.g., 32 wt %), by addition of a small amount of methanol. The polymerization-filled composite was filtered off, vacuum dried at  $60^\circ\text{C}$  and weighed.

### Measurements

The filler content was calculated from the ash weight released by a well-known amount of composite (ca. 0.5 g) upon air calcination in an electric oven heated up to  $500^\circ\text{C}$ . The filler content is obtained from the weight difference before and after sample calcination.

The melting endotherms were measured with

**Table III** Experimental Errors in SEC Analysis of HDPE and PE Extracted from PFC (Average on Five Samples)

Sample	$\bar{M}_n$	$\bar{M}_w$	$M_p^a$	MWD
	$10^{-3}$			
HDPE 10062 <sup>b</sup>	20 ± 14%	71 ± 12%	45 ± 9%	3.2 ± 24%
PFC <sup>c</sup>	37 ± 18%	175 ± 22%	109 ± 17%	7.1 ± 70%

<sup>a</sup> Molecular weight at the maximum of the SEC elution peak.

<sup>b</sup> Commercial HDPE purchased from Dow Company (Terneuzen).

<sup>c</sup> PFC prepared as reported in Table VI (entry 2).

a Dupont 2000 calorimeter. Melting Temperature ( $T_m$ ) and degree of crystallinity ( $X_c$ ) were reported from both the first heating scan ( $T_{m1}$ ,  $X_{c1}$ ) and the second scan recorded after the sample quenching in liquid nitrogen ( $T_{m2}$ ,  $X_{c2}$ ). The heating rate was 25°C/min. The crystallinity degree was calculated from the melting peak area and melting enthalpy of 2.93 10<sup>5</sup>J·kg<sup>-1</sup> for 100% crystalline polyethylene.<sup>28</sup>  $T_m$  was reported as the temperature at the maximum of the melting endotherm.

Melt flow measurements were carried out at 190°C with a CEAST 6542 apparatus, according to the ASTM D 1238 norm. Three different loads were used: 2.16, 10.00, and 21.60 kg, as referred to as MI<sub>2</sub>, MI<sub>10</sub>, and MI<sub>21</sub>, respectively. The results were expressed in g/10 min. The MI<sub>10</sub>/MI<sub>2</sub> ratio was referred to as the melt flow ratio (MFR).

Molecular weight ( $M_n$ ,  $M_w$ ,  $M_p$ ) and molecular weight distribution (MWD) were measured in 1,2,4-trichlorobenzene, with a SEC equipment operating at 160°C and calibrated with PS standards. The experimental error on the molecular parameters of polyethylene was estimated by using a commercially available HDPE (DOW 10062) (Table III). The molecular weight values are the average of five measurements. The quantitative extraction of PE from PFCs by dissolution in 1,2,4-trichlorobenzene at 160°C for 10 to 24 h and filtration, was carried out in case of sample No. 2 in Table VI.

Deagglomeration of the filler particles that occurred upon the addition of the organometallic compounds was measured by sedimentation experiments before and after addition of increasing amounts of TEA. In a previously flame-dried 500 mL round-bottom flask (max. i.d. 10 cm) containing a 5 cm magnetic bar, 20 g of filler (Santone W/W, Santone 5 or barite) were dried for ca. 17 h at 100°C under reduced pressure (10<sup>-2</sup> mmHg). Then 250 mL of dried *n*-heptane were added under nitrogen atmosphere. The slurry was

stirred with a Heidolph MR2002 at 750 rpm for 1 min. When stirring was stopped, sedimentation of the filler particles was followed by measuring the difference in height between the front of the filler suspension and the bottom of the flask. The time dependence of this value was plotted and compared to the curves reported for the addition of 3 10<sup>-4</sup> and 1 10<sup>-3</sup> mol TEA, respectively.

Powdery samples were pretreated with gold and observed with a JEOL scanning electron microscope.

## RESULTS AND DISCUSSION

Figure 2 schematizes how a Al/Ti/Mg catalyst is attached onto a solid surface functionalized with hydroxyl groups.

As will be detailed later, titration of the surface hydroxyl groups strongly supports that the kaolin treatment with the alkyl aluminum (TEA) triggers the filler deagglomeration to the point where all the interparticle hydrogen bonds have disappeared.<sup>41</sup> For this reason, the filler is first dried and then treated with TEA. Indeed, the better the filler is deagglomerated and, thus, the catalyst is dispersed, the more homogeneous the PFC is.

The amount of alkyl compounds (TEA, BOMAG, and EADC) and transition metal alkoxide (TBT) has been calculated on the basis of the hydroxyl content of the previously dried filler. In order to avoid the undesirable formation of free catalyst, only 25% (or 50%) of the surface OH groups have been taken into account. Thus, TEA and BOMAG have been first added to the filler in such an amount that 25% (or 50%) of the OH groups have been consumed in a supposedly quantitative reaction (Fig. 2).

It is worth pointing out that ethylaluminum dichloride (EADC) is used as a chlorinating agent

**Table IV** Dependence of the Catalyst Efficiency on the Catalyst Composition and the Percentage of the Surface Hydroxyl Groups Used in the Catalyst Anchoring

No.	Composition Al/Ti/Mg	mmol Ti (10 <sup>-2</sup> )	OH <sup>b</sup> (%)	tp <sup>c</sup> (min)	Catalyst Efficiency (C.E.)	
					(kgPE/gTi × h)	(kgPE/molTi × h)
1	120/2/10	13.12	50	30	13.7	655.9
2	120/2/10	6.16	25	27	31.4	1503.4
3	120/1/10	3.28	25	55	43.0	2058.8
4	120/2/0	6.16	25	62	2.2	102.9

Polymerization conditions: 20 g, Satintone W/W, PC<sub>2</sub>H<sub>4</sub> = 4 bar<sup>a</sup> and PH<sub>2</sub> = 2 bar.

<sup>a</sup> Ethylene was used as received.

<sup>b</sup> Percentage of the surface OH groups used in the catalyst preparation.

<sup>c</sup> tp = polymerization time.

for Mg and Ti compounds and as a reducing agent for the Ti atoms, i.e., from Ti<sup>+4</sup> to Ti<sup>+3</sup>.

### Effect of the Catalyst Al/Ti/Mg Composition

In a first series of experiments, polymerization-filled composites have been prepared from ethylene and hydrogen used as received. Even under these conditions of partial gas purity, the catalyst efficiency can be quite high and very encouraging, as shown in Table IV in comparison with Table I. These preliminary results indicate the importance of the catalyst composition, for example, the relative content of Ti (entries 2 and 3) and the presence of Mg (entries 2 and 4).

Furthermore, the percentage of the filler hydroxyl groups used in the catalyst preparation is also of a prime importance, because the reaction of 25 rather than 50% of the surface OH groups has promoted a twofold increase in the catalyst efficiency (entries 1 and 2, Table IV). This is the main reason why 25% OH groups have been systematically used afterwards. On the basis of the 120/z/10 Al/Ti/Mg composition, the Ti amount (z) has been changed in order to optimize the catalyst efficiency. Table V shows that the best value for z is 0.75 in the range from 0.5 to 2, which corresponds to the 120/0.75/10 catalyst composition. The catalyst efficiency is then as high as 148 kgPE/gTi × h, which is quite remarkable compared to data reported in the scientific literature (see Table I, for insoluble catalyst). This very high efficiency is actually associated with a very low amount of transition metal attached onto the filler, i.e., 1.22 10<sup>-6</sup> mol Ti/g Satintone W/W.

The Mg/Ti ratio has then been varied from 0 to 15, while keeping constant all the other experimental conditions optimized so far, i.e., ethylene

polymerization as promoted by a catalyst with a Al/Ti ratio of 120/0.75 and anchored on the filler surface through 25% of the total OH groups.

Figure 3 shows that the original catalyst efficiency of 2 kgPE/gTi × h in the absence of BOMAG rapidly increases upon increasing amounts of the Mg compound until reaching a Mg/Ti ratio of ca. 13, so that the best catalyst efficiency actually fits and confirms the previously proposed Al/Ti/Mg composition, i.e., 120/0.75/10. It is clear from these experiments that there is a lower quantity of BOMAG, below which the catalyst is not as efficient as it might be. This constitutive component, which is partly transformed into MgCl<sub>2</sub> by reaction with EADC, acts effectively as a support for the Ti atoms and consequently increases the number of efficient catalytic sites. Some analogy with the classical MgCl<sub>2</sub>/TiCl<sub>3</sub> Ziegler–Natta catalyst might be found in the dependence of the catalyst efficiency on the Mg/Ti ratio.<sup>42</sup>

The effect of the catalyst composition on the thermal properties and melt viscosity of the final polyethylene composites has also been investigated (Table V). Whatever the investigated Al/Ti/Mg composition, the melting temperature (*T<sub>m</sub>*) of the polyethylene matrix, as measured after a first heating run and quenching in liquid nitrogen, is ca. 137°C, except for one sample (*T<sub>m</sub>* = 133°C) the filler content of which is higher than all the other PFCs (entry 4). Similarly, the crystallinity degree is basically independent of the catalyst composition, although slightly lower in the presence of 42 wt % of filler.

Melt viscosities are expectedly high in relation to a high filler content (32 wt %). Indeed, kaolin used in this study is an anisotropic flake-like filler known for a drastic increase in the melt viscos-

**Table V** Effect of the Ti Content (z) on the Catalyst Efficiency and the Thermal Properties and Melt Viscosity of the Final PE Composites

No.	Filler wt %	Al/Ti/Mg 120/Z/10	C.E. kgPE(gTi × h)	$T_m$ °C	$X_c$ %	MI <sub>2</sub>	MI <sub>10</sub>	MI <sub>21</sub>
						g/10 min		
1	28	2.00	111	137	59	0.0	0.3	1.1
2	32	1.50	92	137	58	0.0	0.1	0.2
3	32	0.75	148	138	59	0.1	0.5	1.1
4 <sup>a</sup>	42	0.50	30	133	53	—	—	—

Polymerization conditions PC<sub>2</sub>H<sub>4</sub> = 4 bar, PH<sub>2</sub> = 2 bar, 20 g Satintone W/W (25% OH).

<sup>a</sup> Ethylene used as received.

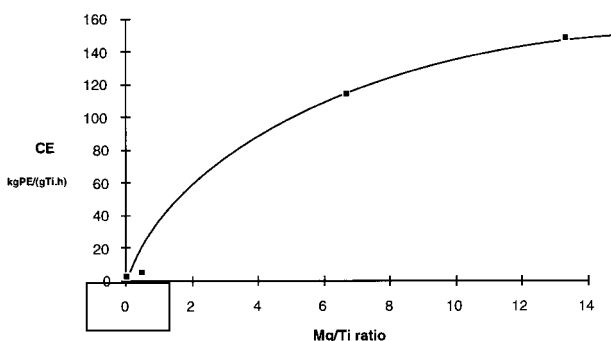
ity.<sup>43</sup> The experimental data (Table V) show that optimization of the catalyst composition is not reflected in the melt flow index.

### Effect of Hydrogen as Transfer Agent

As previously mentioned, it is very important to control the molecular weight of the polyethylene matrix, which has a decisive effect on the mechanical properties and the processability of the final PFC. Chain length currently depends on the catalyst and the addition of a transfer agent, whereas the molecular weight distribution is dependent on a possible nonequivalence of the catalytic sites and their associated distribution. Actually, supported catalysts are known for some distribution in the activity of the catalytic sites.

In order to make this distribution narrower, internal and/or external Lewis bases have been added to the catalyst composition, for instance, in isotactic polypropylene polymerization.<sup>44</sup>

The nonstereospecific catalytic sites are located



**Figure 3** Effect of the Mg/Ti molar ratio on the Al/Ti/Mg catalyst efficiency. PH<sub>2</sub> = 1.5 bar and PC<sub>2</sub>H<sub>4</sub> = 4 bar, 20 g Satintone W/W, and Al/Ti/Mg composition: 120/0.75/Mg.

on the (110) plane of MgCl<sub>2</sub>. The addition of an internal base such as ethyl benzoate is able to form specifically strong chelating complexes with tetracoordinated Mg atoms located on the (110) plane of MgCl<sub>2</sub> and prevents the subsequent reaction with titanium species. As a result, dimeric titanium species are favorably formed onto the (100) face and lead to stereospecific propylene polymerization. The role of the external Lewis bases, for example, methyl-para-toluate, is to reduce the displacement of the internal base by the cocatalyst, AlR<sub>3</sub>, which is a strong Lewis acid and consequently prevent the formation of nonstereospecific catalytic sites.<sup>45</sup>

Typical transfer agents are hydrogen<sup>46</sup> and  $\alpha$ -olefins,<sup>47</sup> for example, 1-hexene or 1-octene. Hydrogen has been indeed widely reported as a very active transfer agent in ethylene polymerization initiated with MgCl<sub>2</sub>-supported catalysts. In line with this effect and the very low melt flow indices, the effect of H<sub>2</sub> on the efficiency of the kaolin-anchored catalyst and the molecular characteristics of polyethylene has been studied. An increase in the partial hydrogen pressure increases the PFC melt index and the catalyst efficiency (Table VI). In the absence of hydrogen, the catalyst efficiency is as low as 37.5 kgPE/gTi × h and MI is so small that it cannot be measured. Upon addition of hydrogen at a partial pressure of 1.5 bar (entry 2, Table VI), a sharp increase in catalyst efficiency and melt index is observed. Although this effect seems to level off until a partial pressure of 4 bar, a further remarkable increase is reported at a partial pressure of 6 bar.

Although up to the present time, there is no comprehensive agreement on the exact influence of hydrogen on the polymerization kinetics,<sup>48</sup> similar observations were reported by Chien et al.<sup>49</sup>

Although hydrogen has been reported to have a



**Table VI Effect of Hydrogen Partial Pressure on Both the Catalyst Efficiency C.E. and the Melt Index (MI) and Molecular Weight of PE**

No.	$P_{H_2}$ bar	C.E. kgPE/(gTi $\times$ h)	MI <sub>2</sub>	MI <sub>10</sub>	MI <sub>21</sub>	$M_p^a$ 10 <sup>-3</sup>
			g/10 min			
1	0.0	38	/	/	/	246
2	1.5	110	0.0	0.3	1.5	109
3	2.0	148	0.1	0.5	1.1	95
4	4.0	157	0.0	0.3	1.7	85
5	6.0	295	0.1	1.0	4.0	87
6	2.0 <sup>b</sup>	92	0.0	0.1	0.2	226
7	4.0 <sup>b</sup>	114	0.1	0.5	1.1	171

Al/Ti/Mg:120/0.75/10; Pethylene = 4 bar, 20 g Satintone W/W and filler content: 32 wt %.

<sup>a</sup> Molecular weight at the maximum of the SEC elution peak.

<sup>b</sup> Al/Ti/Mg composition = 120/1.50/10.

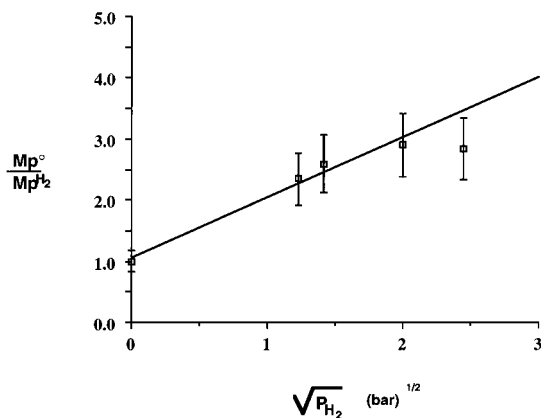
beneficial effect on the propylene polymerization, this conclusion does not hold when ethylene is concerned. It is worth pointing out that substitution of organic alcohols for the silanol groups on the filler surface significantly changes the course of the ethylene polymerization, all the other experimental conditions being the same. We have indeed reported<sup>35</sup> that the addition of H<sub>2</sub> onto Al/Ti/Mg-*n*-propanol catalysts results in the expected decrease in chain length but in combination with a drastic decrease of the catalyst efficiency. Thus, although the catalyst preparation and composition are comparable, the anchoring of the catalyst onto a silanol-type filler surface is responsible for a change in the activity of the alcohol-based catalyst analogue. Some explanation might be found in a monomer diffusion limitation towards the supported catalyst. Ethylene polymerization is, indeed, known to be diffusion controlled.

Furthermore, and now similarly to the alcohol-based catalysts,<sup>35</sup> the hydrogen effect on the efficiency of the kaolin-based catalyst depends on the catalyst composition. Indeed, when the relative amount of Ti is increased by a factor of 2, i.e., 120/1.5/10, the effect of H<sub>2</sub> is less pronounced on both the catalyst efficiency and the melt index (entries 6 and 7 compared to entries 3 and 4 in Table VI).

In addition to the melt indices (MI) of the final PFCs, molecular weight of the PE matrix has also been estimated by size exclusion chromatography (SEC) (see Experimental section). For this purpose, PE has been separated from the filler particles by dissolution in hot 1,2,4-trichlorobenzene and filtration.

Because the ethylene polymerization is initi-

ated from catalyst attached to the filler surface and/or pores, the growing chains ends are localized in this position and rapidly immobilized by the polymer precipitation and partial crystallization. This situation is thus comparable to chains tethered on a solid surface,<sup>50</sup> which is a particular case of adsorption through one chain extremity rather than a multisegment adsorption (loop and train conformation). As a rule and whatever the intimate mechanism, adsorption of polymer chains on a solid surface is known to form tightly bound and loosely bound polymer chains around the filler particles.<sup>51</sup> This effect explains why polyethylene is not quantitatively solubilized in hot aromatic solvents prior to SEC analysis. It is also at the origin of an apparent increase in the particle sizes. Furthermore, upon increasing the filler content, the regions of loosely bound polymer overlap each other and their mobility becomes increasingly restricted, which results in the high melt viscosity observed. Average molecular weights ( $\bar{M}_n$ ,  $\bar{M}_w$ ,  $M_p$ ) and polymolecularity (MWD) of the HDPE chains extracted of the PFCs have been analyzed by SEC. In order to estimate the accuracy of these experimental data, five samples of the same PFC (entry 2 in Table III) have been separately dissolved in hot trichlorobenzene and analyzed. For the sake of comparison, a commercially available HDPE has also been analyzed. It appears that deviations from the average values are systematically larger for the PFC compared to the nonfilled HDPE. Deviations reported for  $\bar{M}_n$  are, however, comparable in contrast to  $\bar{M}_w$  and above all MWD. This observation is consistent with the stronger adsorption of the longest chains onto the filler particles and the problem



**Figure 4** Dependence of the polyethylene molecular weight ( $M_p$ ) on the square root of the hydrogen partial pressure (polymerization conditions: Table VI).

met in their complete (and reproducible) dissolution.

Nevertheless, it appears that  $M_p$  parameter is the most accurate for both HDPE and PFC samples. Table VI shows a qualitative agreement between the decrease in molecular weight and the increase in MI upon increasing  $H_2$  partial pressure, which confirms the chain-transfer activity of hydrogen.

Figure 4 confirms the validity of the Keii's equation<sup>46</sup> [eq. (3)], which is a relationship between the polymer molecular weight and the hydrogen pressure.

$$\frac{M_p^0}{M_p^{H_2}} = 1 + K(P_{H_2})^{1/2} \quad (3)$$

The agreement is good except for the PFC prepared under hydrogen pressure of 6 bar. It must be noted that in this experiment, the hydrogen partial pressure (6 bar) is higher than the ethylene partial pressure (4 bar).

### Effect of 1-Octene as Transfer Agent

Addition of an  $\alpha$ -olefin to ethylene may result into distinct effects, i.e., copolymerization or chain transfer reaction. It is known that there is a sharp decrease in the opportunity for the comonomer to be copolymerized as the size of the  $\alpha$ -olefin increases.<sup>52</sup> For instance, 1-hexene has been reported as an effective comonomer,<sup>53–57</sup> in contrast to 1-octene, which has proved to be a transfer agent for the growing polyethylene chains.<sup>58–61</sup> This chain transfer activity of 1-octene has been recently observed in the ethylene polymerization

initiated by the *n*-propanol-based catalysts of well-defined Al/Ti/Mg compositions.<sup>35</sup> Indeed, no 1-octene comonomer unit has been detected by <sup>13</sup>C-NMR spectroscopy in the final polyolefin chains. Because this research aims at the one-step production of HDPE “homogeneous” composites of a not exceedingly high melt viscosity, it is worthwhile checking the potential of 1-octene as a transfer agent, which would keep the polymer unmodified excepted for molecular weight.

Table VII shows that 1-octene can significantly improve the melt processability of the PFC when it is combined with hydrogen.

Melt indices, however, depend on the octene–ethylene molar ratio in such a complex way that no reliable relationship emerges. The effect of 1-octene on the PE melt viscosity is remarkably higher than that of hydrogen. Indeed, at a constant catalyst composition and  $H_2$  partial pressure,  $MI_{21}$  increases from 1.1 g/10 min in the absence of 1-octene (entry 7, Table VI) up to possibly 70 g/10 min when 1-octene is added (entry 3, Table VII). In a parallel way,  $M_p$  has decreased from 171,000 down to 45,000.

Although the increase in MI is the expected effect when 1-octene is added to ethylene, it is not understood why the melt index start to decrease when the relative amount of 1-octene goes on increasing. The <sup>13</sup>C-NMR spectroscopy showed no experimental evidence for a copolymerization effect that would counterbalance an initially observed chain-transfer reaction. Furthermore, a qualitative parallel between the change in melt viscosity of the final composite and modification in the catalyst efficiency is observed. The catalytic system is clearly sensitive to 1-octene but in a complex manner. Compared to MI, some modifications observed in the melting temperature ( $T_m$ ) and crystallinity degree ( $X_c$ ) are still more puzzling (Table VII).

### Effect of Size and Nature of the Filler

For Satintone W/W, and the Al/Ti/Mg catalyst (120/0.75/10), PFCs have been produced with two additional inorganic fillers, i.e., kaolin of a smaller mean particle size (Satintone 5; 0.8  $\mu\text{m}$ ) than Satintone W/W (1.4  $\mu\text{m}$ ), and a surface treated basic filler, i.e., barite (Table VIII). Characteristics of these fillers are given in Table VIII. Barite was surface treated (see Experimental) in order to create acidic —OH groups and to anchor the catalyst successfully. Even though the catalytic efficiency is much lower compared to Sat-

**Table VII Effect of 1-Octene on the Ethylene Polymerization Initiated by the Kaolin-Based Al/Ti/Mg Catalyst**

No.	1-Octene	CE	$T_m$ (°C)	$X_c$ (%)	MI <sub>10</sub>	MI <sub>21</sub>	MI <sub>21</sub>
	(mol) 10 <sup>-3</sup>	(kgPE/gTi × h)			g/10 min		
1	0.0	92	140	55	0.00	0.00	0.32
2	4.0	164	136	60	0.57	3.20	13.75
3	8.0	118	132	73	2.10	14.50	70.00
4	12.0	—	138	68	0.00	0.06	0.37
5	40.0	64	132	54	0.00	0.00	0.00

PC<sub>2</sub>H<sub>4</sub> = 4 bar, PH<sub>2</sub> = 4 bar, 20 g Satintone W/W, filler content: 32 wt %, catalyst Al/Ti/Mg composition = 120/1.5/10.

intone W/W and should be optimized, Table VIII shows that the catalyst used in this study may be used to produce a range of PFCs containing various types of filler, for example, with acidic, neutral, and even basic surface groups and of different size and shape. Enhanced mechanical properties are expected on the basis of a smaller particle size (Satintone 5) and a more regular shape of the barite particles as it will be reported elsewhere.<sup>39</sup>

#### Deagglomeration of the Filler

Deagglomeration of the mineral particles is of prime importance in order to have a finer and more homogeneous filler dispersion within the final composite together with a larger surface area for the catalyst deposition. As previously mentioned, the interparticular hydrogen bonding is expected to be disrupted by reaction of the filler with the organometallics used in the catalyst preparation, i.e., TEA and BOMAG (Fig. 2). This preliminary reaction should make the filler sur-

face more hydrophobic and accordingly prevent the particles from reagglomerating.

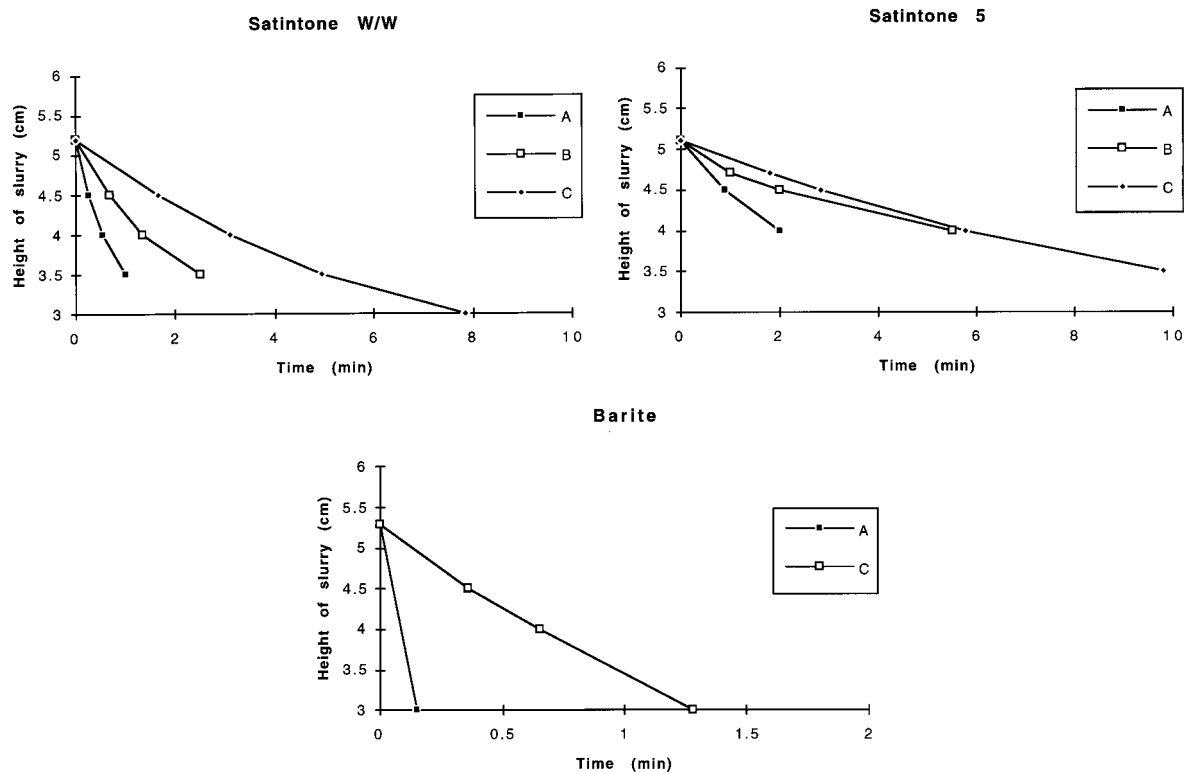
In order to estimate the effect of this surface reaction onto the particles deagglomeration, increasing amounts of TEA have been added to the filler dispersion in heptane, i.e., (a) no TEA addition; which corresponds to the filler slurry prior to the catalyst preparation; (b) addition of as much TEA as the total amount of TEA and BOMAG used in the first step of the catalyst preparation (Fig. 2); (c) addition of an amount of TEA equal to the total amount of organometallics used in the whole reaction of catalyst preparation.

The sedimentation time, i.e., the time required to settle down a given amount of the filler slurry in heptane after the stirring is stopped, has been proposed as a measurement of the filler deagglomeration. These measurements have been carried out for the three investigated fillers, i.e., Satintone W/W, Satintone 5, and Blanc Fixe N. Figures 5(a)–(c) show that the filler is actually deagglomerated by reaction with TEA because the sedimentation time is accordingly increased, which is evidence of a more homogeneous, finer, and stable particles dispersion. Whatever the filler, the same qualitative effect is observed. Of course, when kaolin particles are concerned, the sedimentation time depends on the average particle size [Fig. 5(a)–(b)]; it is longer for the smaller Satintone 5 particles (0.8 μm), compared to Satintone W/W (1.4 μm). Furthermore, density of the mineral particles also influences the sedimentation time: the higher the density is (i.e., barite > kaolin), and the shorter the sedimentation time [Fig. 5(c)]. Undoubtedly, the procedure used for the catalyst preparation triggers deagglomera-

**Table VIII Effect of the Mean Particle Size and Nature of the Filler on the Catalyst Efficiency**

No.	Filler	Filler Content (wt %)	C.E. (kgPE/gTi × h)
1	Satintone 5	65	2
2	Satintone 5	63	3
3	Barite	55	39
4	Barite	32	24

PC<sub>2</sub>H<sub>4</sub> = 4 bar, PH<sub>2</sub> = 2 bar, 20 g filler catalyst; Al/Ti/Mg = 120/0.75/10.



**Figure 5** (a) Effect of TEA on the filler deagglomeration, as measured by sedimentation of the Satintone W/W dispersion in heptane. A: untreated filler particles; B: filler particles added with  $3 \cdot 10^{-4}$  mol TEA; and C: filler particles added with  $10^{-3}$  mol TEA. (b) Effect of TEA on the filler deagglomeration, as measured by sedimentation of the Satintone 5 dispersion in heptane. A: untreated filler particles; B: filler particles added with  $3 \cdot 10^{-4}$  mol TEA; and C: filler particles added with  $10^{-3}$  mol TEA. (c) Effect of TEA on the filler deagglomeration, as measured by sedimentation of the Barite dispersion in heptane. A: untreated filler particles; and C: filler particles added with  $10^{-3}$  mol TEA.

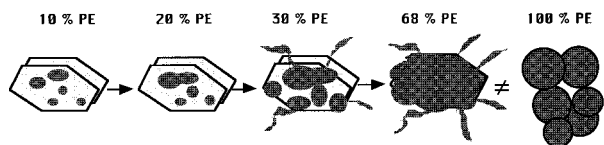
tion of the mineral particles from the surface where the polyethylene chains will be growing to form homogeneous composites, as discussed in the next section.

### Polyethylene Growth onto Particle Surface

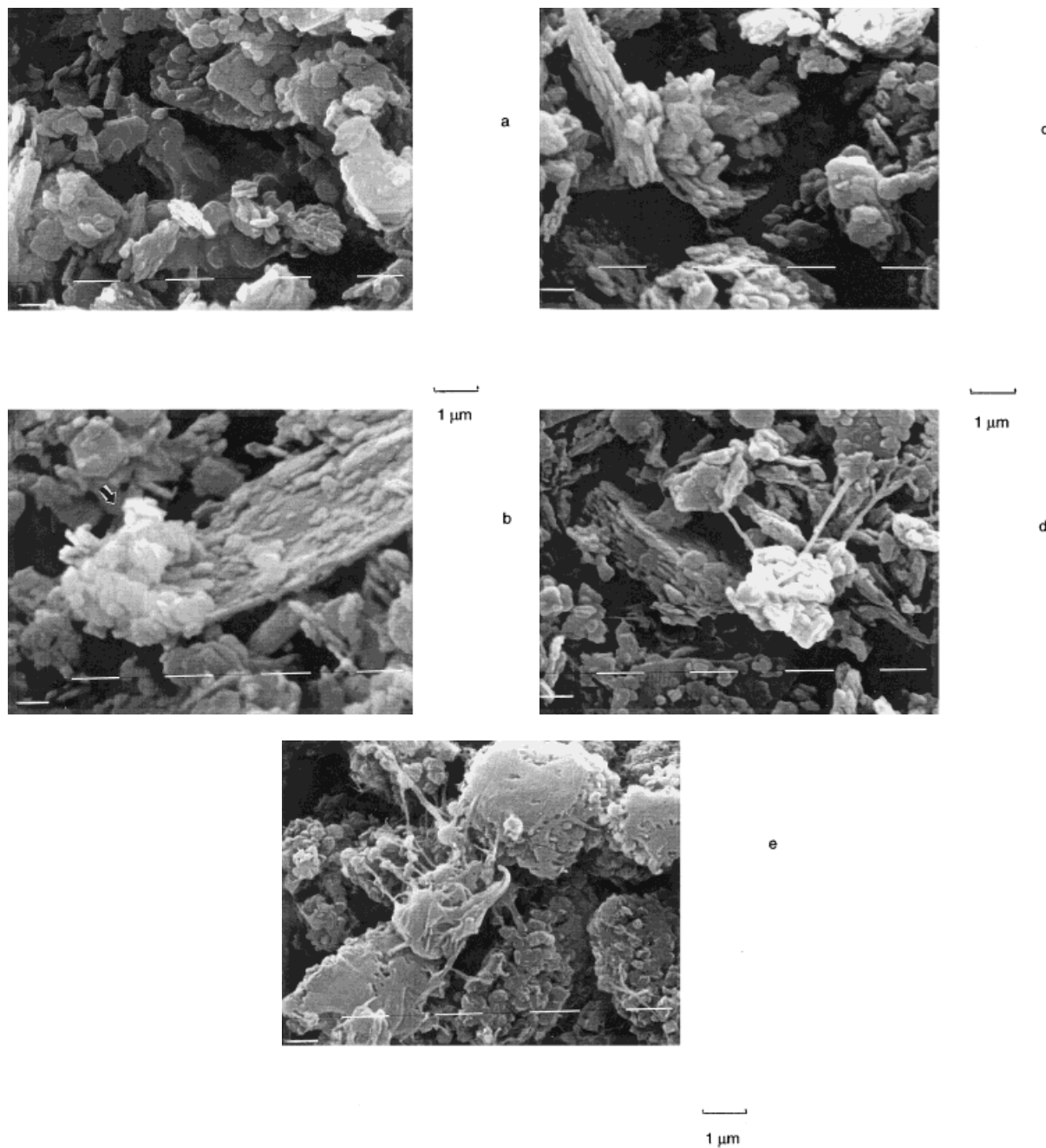
A homogeneous coating of the filler surface by the catalyst and ultimately by the polymer is thought to be essential for the production of high mechanical performances of PFCs. Thus, polymerization in bulk rather than from the particle surface and particles agglomeration must be avoided. Sedimentation of the filler dispersions in heptane has already proved that the filler was deagglomerated before the catalyst deposition. Scanning electron microscopy (SEM) is a very useful technique to observe the progress in the filler coating by the growing polymer chains. Figure 6 schematizes growth of polyethylene on the surface of kaolin

plates. Initially, heaps of polyethylene are formed, that grow with increasing polymerization time and finally overlap each other to completely cover the particle surface.

At still increasing polyethylene contents, fibrils are budding from the surface and growing away. They ultimately interconnect the near neighbor particles to each other. The structure of nascent polyethylene during the polymerization filling process



**Figure 6** Sketch of the polyethylene growth on the surface of a kaolin plate. PE content = 10 wt %, 20 wt %, 30 wt %, and 68 wt %. Globular PE particles are observed with a traditional Mg-based catalyst (100% HDPE).

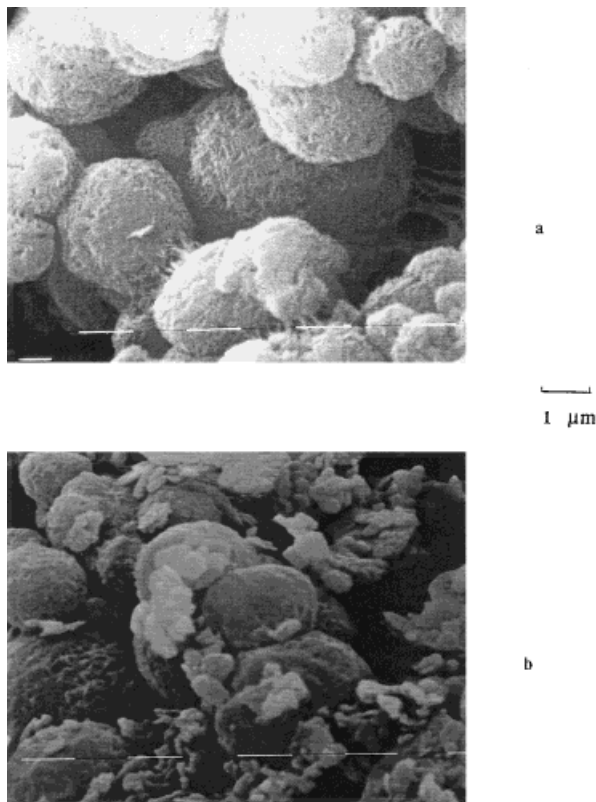


**Figure 7** (a–e) SEM observation of HDPE growing on the surface of kaolin Satintone W/W. HDPE content = a: 0 wt %; b: 10 wt %; c: 20 wt %; d: 30 wt %; and e: 68 wt %.

has been described by many authors,<sup>22–25,62–64</sup> but scientists are still puzzled with the fibril formation. Actually, the observation of polyethylene threads depends on the filler, i.e., shape, size, and specific surface, the catalyst composition (V- or Ti-based catalyst<sup>62</sup>), and the filler content.<sup>25</sup>

Figures 7(a)–(e) clearly illustrates the ex-

pected steps schematized in Figure 6, in case of growth of PE from the kaolin Satintone W/W surfaces. SEM observations are completely different when the ethylene polymerization is initiated by a traditional Mg-supported Ti catalyst<sup>35</sup> as such [Fig. 8(a)] and added with untreated kaolin particles [Fig. 8(b)]. In the vicinity of the uncoated



**Figure 8** (a–b) HDPE polymerization initiated by a *n*-PrOH-based Al/Ti/Mg catalyst as such (a) and added with untreated Satintone W/W particles (b).

filler particles, the characteristic spheres of PE can be observed [Fig. 8(b)], although PE threads interconnecting particles are visible in Figure 8(a).

These comparative experiments clearly demonstrate the selective formation of PE chains from the treated surface of the kaolin particles used in this study.

## CONCLUSIONS

The polymerization filling technique has proved to be successful in the production of kaolin and barite containing polyethylene composites.

Using a magnesium based catalyst, very high catalyst efficiencies have been reached with an optimum value of 300 kgPE/(gTi × h) (14,650 kgPE/(mol Ti × h)) for kaolin filler (Satintone W/W). Although the activity of catalyst attached onto surface-treated barite particles is much smaller, i.e., ca. 39 kgPE/gTi (2300 kgPE/mol Ti), it is competitive compared to data reported in the scientific literature (Table I). The catalyst compo-

sition is of a prime importance and the optimal Al/Ti/Mg composition has been found as 120/0.75/10. The amount of Ti accordingly requested is as low as  $1.2 \cdot 10^{-6}$  mol/g of filler.

Hydrogen is not only a convenient molecular weight regulator, but also an efficient activator, as shown by the increase in the catalyst efficiency, for example, from 38 to 295 kgPE/(gTi × h) as the molecular hydrogen pressure ( $P_{H_2}$ ) is increased from 0 to 6 bar. Similarly, an  $\alpha$ -olefin such as 1-octene also behaves as an active transfer agent, although in a complex relationship with the 1-octene/ethylene molar ratio. The anchoring of the Al/Ti/Mg catalyst onto a filler surface changes the catalyst efficiency and dependence of the chain growth on the addition of hydrogen and/or  $\alpha$ -olefins. Structure and activity of the polymerization sites are far from being known, so that our understanding is still essentially empirical and needs further fundamental research effort. Sedimentation of filler in heptane has convincingly shown that the mineral particles are deagglomerated by preliminary reaction with the organometallic constitutive components of the catalyst. Furthermore, SEM observations have confirmed that the filler particles are firstly coated by the growing PE chains, followed by the interconnection of the near neighbor particles through PE threads. A completely different morphology is observed when the Al/Ti/Mg catalyst is not previously anchored onto the filler particles. In addition to the very high catalyst efficiency, the polymerization filling technique herein reported allows “homogeneous” composites to be prepared with valuable mechanical properties, as will be discussed in the next paper.<sup>39</sup>

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