

## **Polyolefin-Based Composites by Polymerization-Filling Technique**

PH. DUBOIS, M. ALEXANDRE, F. HINDRYCKX, and R. JERÔME

Center for Education and Research on Macromolecules (CERM) University of Liège B6,  
4000 Liège, Belgium

### **Contents**

1. INTRODUCTION
  2. POLYMER COMPOSITES BY MELT BLENDING
  3. SURFACE MODIFICATION OF MINERAL FILLERS BY COUPLING AGENTS
  4. POLYMER COATING OF FILLER PARTICLES
    - 4.1. Preencapsulation of the Filler
    - 4.2. Ziegler-Natta Polymerization from the Filler Surface
  5. CONCLUSIONS
- REFERENCES

### **1. INTRODUCTION**

Dispersions of inorganic fillers within polymers are commonly designated as polymer-based composites. The properties of these materials are isotropic or anisotropic, depending on the geometry of the filler particles and the effect of the processing conditions on their orientation. Fillers are used to improve some physicomechanical properties of the polymer, the material processability, or decrease the final cost [1]. As a typical example, highly filled composites in which the filler concentration approaches the maximum packing fraction are known for their use in the shaping of ceramic articles [2].

The history of filled polymers began at the turn of this century with the filling of thermosetting plastics based on phenol- and urea-formaldehyde resins with such things as paper, asbestos, and wood flour. Later, this technology was extended to rubbers to increase tensile strength, modulus, and hardness by the incorporation of large amounts of reinforcing fillers such as carbon black.

The addition of large amounts of fillers to thermoplastics was also considered, but was less encouraging. Indeed, although mineral fillers can improve rigidity and dimensional stability, they can also increase brittleness and melt viscosity. These drawbacks mainly originate from incompatibility between the hydrophilic surface of the minerals and the hydrophobicity of the most currently used thermoplastics. This is the reason why different surface treatments have been designed to improve the filler-polymer interfacial adhesion and to create an interphase layer that significantly improves the properties of the composite [3]. This paper reviews the main strategies that have been proposed to produce valuable polyolefin-based composites.

### **2. POLYMER COMPOSITES BY MELT BLENDING**

The formation of polymer composites by melt blending is most straightforward since the particulate filler is mixed with the powdered or granulated polymer in a high-speed dry mixer, and this premixture is then processed in the melt under shear deformation conditions by two-roll mills or screw mixers, for instance. The rheology of polymer melts filled with rigid particles depends on shape and orientation of the dispersed particles and on the filler-polymer

interactions. It is characteristic of solid particles dispersed in viscoelastic liquids to migrate toward the center of the flow and to form a "nut-in-a-shell" structure. This causes the depletion of the surface layer [4] and, accordingly, often causes brittleness. Table 1 shows that, in the absence of any specific interfacial interactions, the mineral fillers increase the modulus of polyethylene (PE), although the ultimate elongation and the impact strength are drastically reduced [5].

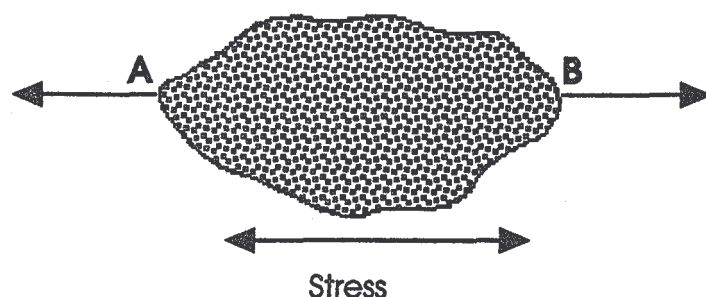
**TABLE 1** Physical Properties of Polyethylene/Mineral Mixtures

	Initial modulus, GPa	Izod 25 <sup>0</sup> C, J/m	Ultimate elongation, %
HDPE <sup>a</sup>	0.7	80	900.0
+40% kaolin <sup>b</sup>	3.1	17	1.6
Calcinated kaolin	3.1	20	2.7
CaSO <sub>4</sub>	2.8	15	1.3
Mica	6.5	20	0.3
CaCO <sub>3</sub>	2.7	21	3.0

Reprinted with permission from Ref. 5. <sup>a</sup>High-density polyethylene ( $M_w \sim 90,000$ ). <sup>b</sup>All percentages are by weight.

This dramatic brittleness is usually attributed to stress concentrations because of either a nonhomogeneous mineral dispersion or a poor mineral-polymer adhesion. Polyethylene is, however, expected to wet a clean mineral surface and to promote a decrease in the surface free energy. Fowkes has calculated that PE in close contact with an iron surface (0.4-nm separation) would have an interfacial tensile strength of over 100,000 psi (689 MPa). Low interfacial strength might actually result from the preferential adsorption of moisture or low molecular weight fractions at the interface or from a slow adsorption process [6].

The mechanical strength of dispersion-filled composites depends on the effect of the normal stresses applied to each particle (Fig. 1). When these stresses are the highest (Points A and B), separation of the filler from the matrix is expected to take place with formation of voids. Growth and mutual interactions of these voids can initiate cracks and failure of the specimen [1]. This explains that mechanical strength is as high as the resistance to the filler-matrix separation.



**FIG. 1.** Diagram of normal stresses applied to a particle. A and B are the points at which normal stresses are maximum.

The void size is controlled by the size and size distribution of the filler particles. As a rule, smaller voids are initiated by smaller particles, and a smaller void content (in volume) is

observed at a constant volume fraction of filler. At high filler loadings, the voids initiated by the near-neighbor particles have the opportunity to interact with and to merge into each other, which, causes rapid specimen failure. As an example, Table 2 gives the experimental results for a high-density polyethylene (HDPE) matrix filled with tufa of various particle sizes [1].

**TABLE 2** Effect of Mean Particle Size on the Elongation at Break Value  $\epsilon$  for HDPE-Tufa Composites<sup>3</sup>

Particle size, $\mu\text{m}$	$\epsilon$ , %
2	200
10	120
30	15

Reprinted by permission from Ref. 1. Volume fraction of filler,  $\phi = 0.22$ .

Even though brittleness is commonly increased with filler particle size, some data show that very fine fillers (about 2  $\mu\text{m}$ ) may increase the composite brittle-ness as a result of the agglomeration of the filler particles. For instance, the content of the filler particles and their agglomerates has been estimated in polypropylene-calcium carbonate composites [7, 8], and the tensile impact strength has been found to decrease rapidly with increasing values of  $A_v$ , that is, the area occupied by the filler particles on a molded surface per surface unit of composite (Fig. 2).

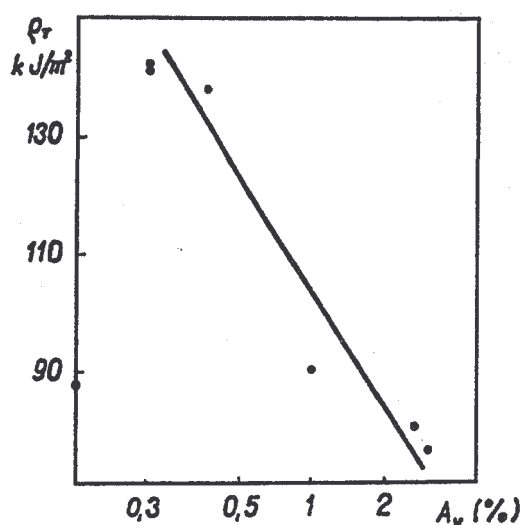


FIG. 2. Dependence of the tensile impact strength (without notch)  $p_7$  on surface content of filler particles and/or their aggregates  $A_v$  for polypropylene- $\text{CaCO}_3$  composites. (Reprinted by permission from Ref. 8.)

Actually, increasing the content of filler particles has a detrimental effect on the tensile impact strength when these particles and/or their agglomerates are larger than about 10  $\mu\text{m}$ . Thus, when their size is large enough, fillers have the same effect as notches or cracks, which act as stress concentrators and decrease the impact strength [9].

The spatial distribution of the mineral particles within the composites has a decisive effect on the structure-property relationships. This distribution must be as uniform as possible to avoid domains in which a filler content that is higher than average is a source of brittleness.

Efforts have been devoted to the modification of the filler surface in order to toughen filled polyolefins (PE or polypropylene). In this regard, it is generally accepted that a good interfacial adhesion between filler and polymer is a decisive factor. A well-known example is the compounding of some fillers with a polar polymer such as polyvinyl chloride (PVC) [1],

for which the adhesion is promoted by interactions of the acid-base type, as shown by infrared (IR) spectroscopy [10] and by inverse gas chromatography (IGC) [H]. In the case of polyolefins such as linear low-density polyethylene (LLDPE), IGC studies show that adhesion can be promoted by minimizing the acid-base properties of the fillers used [12].

In conclusion, although the filler content and size and the chemical nature of each component significantly influence the rheology and the mechanical properties of polymer composites, any modification of the polymer-filler interactions also has a considerable effect on these properties. These interactions can be improved by the surface treatment of the filler, either by agents able to bridge the filler to the matrix (coupling agents) or by the preliminary coating of the filler particles. These two general strategies are discussed in the two sections, with a special emphasis on the so-called polymerization-filling process in Section 4.

### **3. SURFACE MODIFICATION OF MINERAL FILLERS BY COUPLING AGENTS**

In 1964, Plummer and Neumeyer [13] showed that vinyltriethoxysilane was effective in reinforcing many polymer-filler systems. This led to the extensive study of numerous silane coupling agents [14].

Hawthorne and Solomon published on the reinforcement of PE by surface-modified kaolins [15]. They treated the kaolin surface with different alkylamines, silanes, and aluminum carboxylates. The filler surface contains active sites able to form strong donor, acceptor, or saltlike bonds with organic amines and metal cations. In addition, the filler contains reactive surface hydroxyl groups that either are part of the crystal lattice or result from the spontaneous surface hydrolysis. These groups can form strongly bonded condensation products with reactive silanes or metal alkoxides and thus provide the complete surface coverage with molecules favorably oriented. Table 3 shows that the treatment of kaolin with saturated reagents results in increased impact strength and elongation at break for composites containing 20 wt% filler (equivalent to 8.2 vol%) and also results in a reduction in tensile strength compared to the untreated composite. A 40 wt% filler decreases the elongation at break and tensile strength. These results confirm those predicted by Nielsen [16] for systems in which adhesion between the filler and the matrix is reduced or absent. They suggest that, while treatment with short-chain saturated reagents improves the kaolin-PE compatibility and the filler dispersion, it weakens the interaction between the filler and the matrix.

**TABLE 3** Effect of Kaolin Modification with Saturated Reagents on the Mechanical Properties of HDPE/Kaolin Melt Blends

Filler or coating composition	Filler loading, % wt/wt	Yield stress, kg cm <sup>-2</sup>	Stress at break, kg cm <sup>-2</sup>	Elongation at break, %	Impact strength, kgm/m
Reference materials					
Unfilled HDPE	0	289	274	1045	2.77
+ Kaolinite	20	280	178	218	1.24
	40	292	281	13	0.65
Kaolin derivatives					
Saturated coating					
0.6 n-Hexylamine	20	276	168	291	1.38
	40	276	276	36	0.74
5.0 Triethoxysilane	20	279	182	162	1.92
5.0 Octadecyltriethoxy-silane	20	272	193	668	1.38
2.5 Oxyaluminum-2-ethylbutyrate	20	269	174	300	1.91
2.5 Oxyaluminum-laurate	20	274	171	16	1.73
	40	245	241	5	1.38
Unsaturated coating					
2.0 3-(Trimethoxysilyl)propyl methacrylate	20	301	202	277	1.96
2.0 Vinyltriethoxylane +3,0 amyl-triethoxysilane	20	313	20.3	71	1.58
1.5 Oxyaluminum-methacrylate	20	296	191	420	2.79
	40	325	298	14	2.34
1.5 Oxyaluminum-methacrylate +2.5-bis-(?-butylperoxy)-2,5-dimethylhexane <sup>a</sup>	20	301	187	430	3.04
	40	318	310	12	2.51

Reprinted by permission from Ref. 15. <sup>a</sup>Peroxide contents were 0.05% wt/wt kaolin.

Adhesion between the matrix and the filler can be improved by grafting the resin matrix with compounds strongly adsorbed onto the mineral, such as vinyl and methacryloxy silanes or aluminum methacrylates. Kaolin has been coated with an (unsaturated) oxyaluminum methacrylate by treatment with diisopropoxyaluminum methacrylate. This coating results from the partial hydrolysis of the aluminum alkoxide by residual surface-adsorbed water molecules or hydroxyl groups. Free radicals can be readily generated in molten PE either by thermomechanical chain scission during compounding or by a peroxide added on purpose. Radical grafting of the methacrylate units onto PE occurs, as proved by the PE melt viscosity, which does not change deeply, although it usually decreases as a result of the thermomechanical degradation during mixing. Then, the final composites show an increased tensile strength compared to both the unfilled PE and the untreated kaolin composites. In the best systems, there is a small decrease in the elongation at break, which is parallel to the increased toughness.

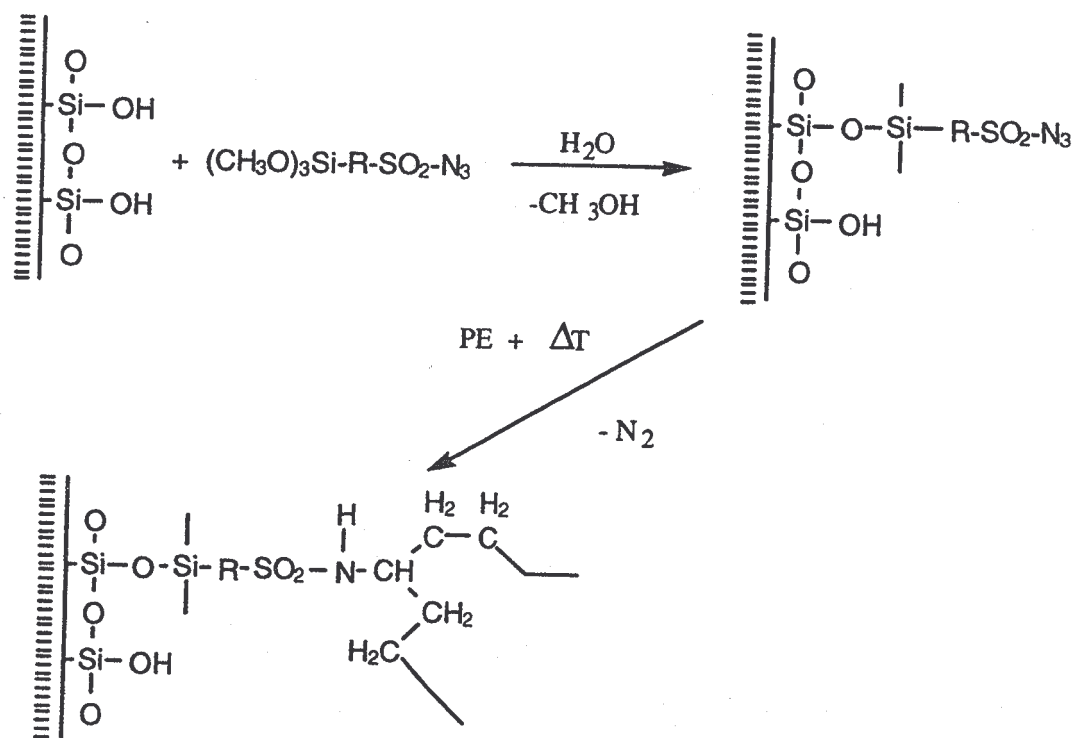
Later, the surface of fillers was treated with other coupling agents, such as organic titanates [1, 17-23], phosphates [24, 25] and borates [22], stearic acids [26-31], lauric acid [22, 32],

chlorinated paraffins [1], and functional silanes [18, 33-35]. Silane derivatives and organic titanates are known to be the most universal coupling agents. In 1981, major U.S. producers of dispersed fillers were selling products treated with one of these coupling agents [1]. In conclusion, the surface treatment of fillers by coupling agents has improved the filler dispersion in many polymers. However, in the case of polyolefins, a good dispersion of the filler is not sufficient to avoid brittleness. It is the reason why the direct bonding (grafting) of the filler to polyolefin has been proposed and accomplished using a difunctional coupling agent, namely, an azidosilane derivative [37-39]. This compound can be attached on the filler surface and then grafted onto the polyolefin matrix. An azidosilane coupling agent is added to inorganic fillers such as glass, mica, clay, and metal oxides. The methoxysilane hydrolysis by moisture forms a silanol, which then reacts or condensates with the active groups at the filler surface. The treated filler is dispersed in the polymer and reacts with it during the melt compounding. Heat activation of the sulfonyl azide groups forms a nitrene, which is the actual species reactive toward polyethylene (Eq. 1).

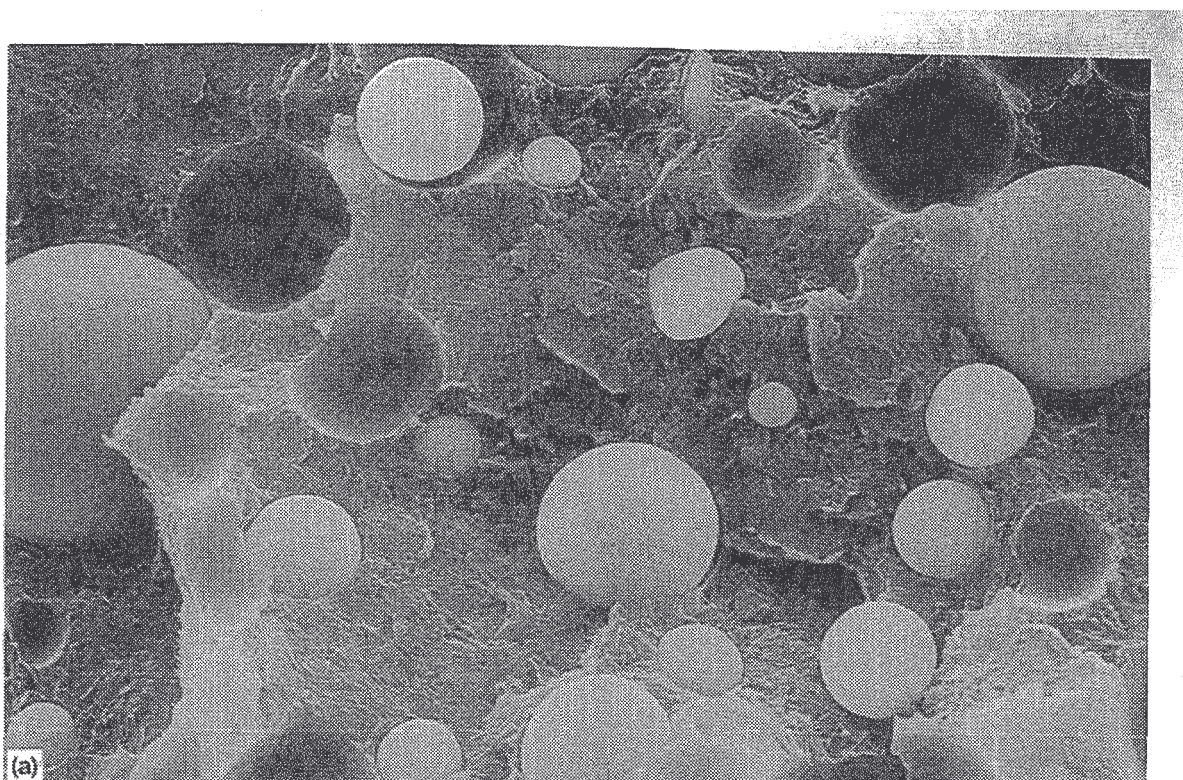
Very substantial improvement in tensile, flexural, and heat distortion properties is observed with little loss in impact strength. The fracture surfaces of glass-sphere-filled PE composites with various degrees of interfacial modification have been examined by scanning electron microscopy (SEM). It appears that the failure is adhesive for the unmodified composites (Fig. 3a) and for the composites with nearly monolayer modification. If the interfacial modification is such that a thicker layer of bound matrix is formed around the glass surface the failure is cohesive (Figs. 3b, 3c). Figure 3a shows that the glass surface remains clean when no azidosilane coupling agent is used. The fracture is initiated at the sphere equator, and the PE failure is relatively brittle, as expected, at  $-196^{\circ}\text{C}$ . At the most important surface modification examined (100 equivalent molecular layers), Fig. 3c shows that the fracture is now initiated at the poles of the glass spheres and occurs completely through the matrix. The surface loading is referred to as the number of equivalent molecular layers, based on the assumption that each azidofunctional silane molecule occupies a  $1.5\text{ nm}^2$  area [38]. Figure 3b shows an intermediate micrograph in which the failure is classified as cohesive. The plane of fracture has moved away from the sphere equator. Polyethylene is observed to cover the entire glass surface, with large domains bound to the surface. The polymer bonding to the filler and the structure of the interfacial region can be chemically controlled with important effects on the initiation and mechanism of fracture.

Very recently, Wang, Lu, and Wang [40] have reported on the toughening and reinforcement of HDPE/ $\text{CaCO}_3$  blends by the concomitant use of carboxyl-ated PE and  $\text{CaCO}_3$  fillers grafted with acrylamide. The improvement of the mechanical properties has been attributed to a series of chemical and physico-chemical interactions taking place between the two components during the blending process, which were confirmed by Fourier transform infrared (FTIR) and extraction experiments.





(1)





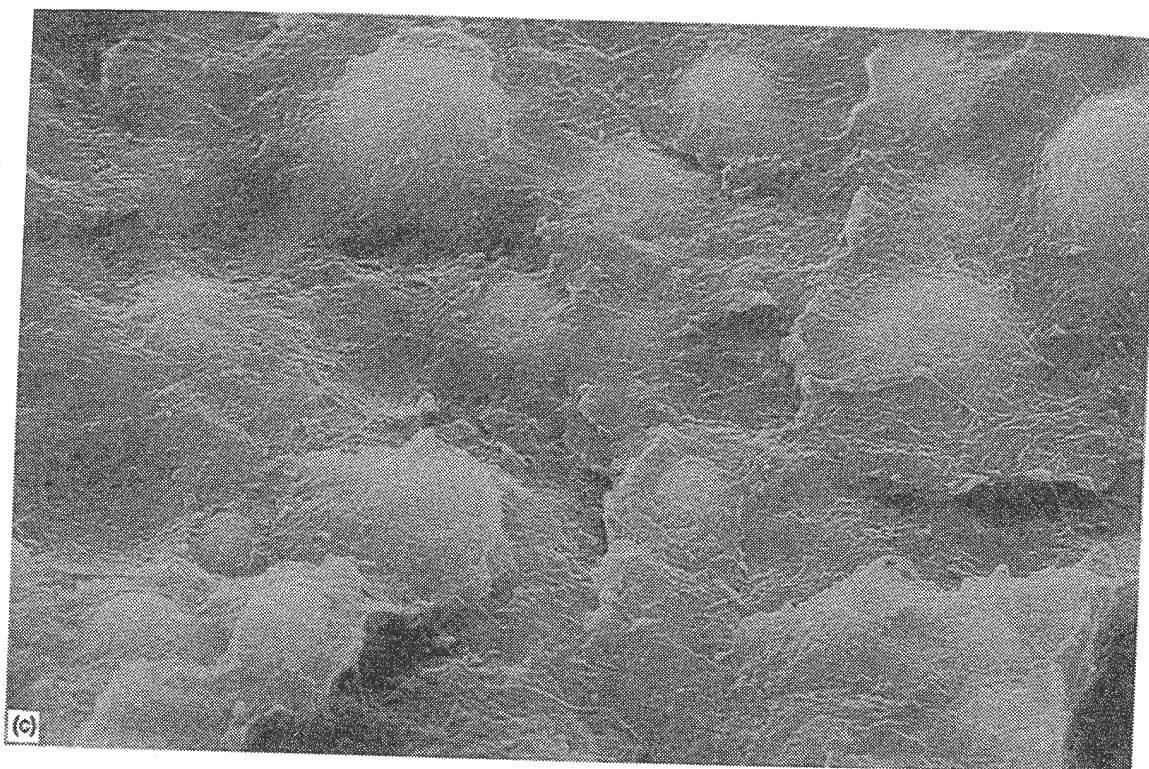
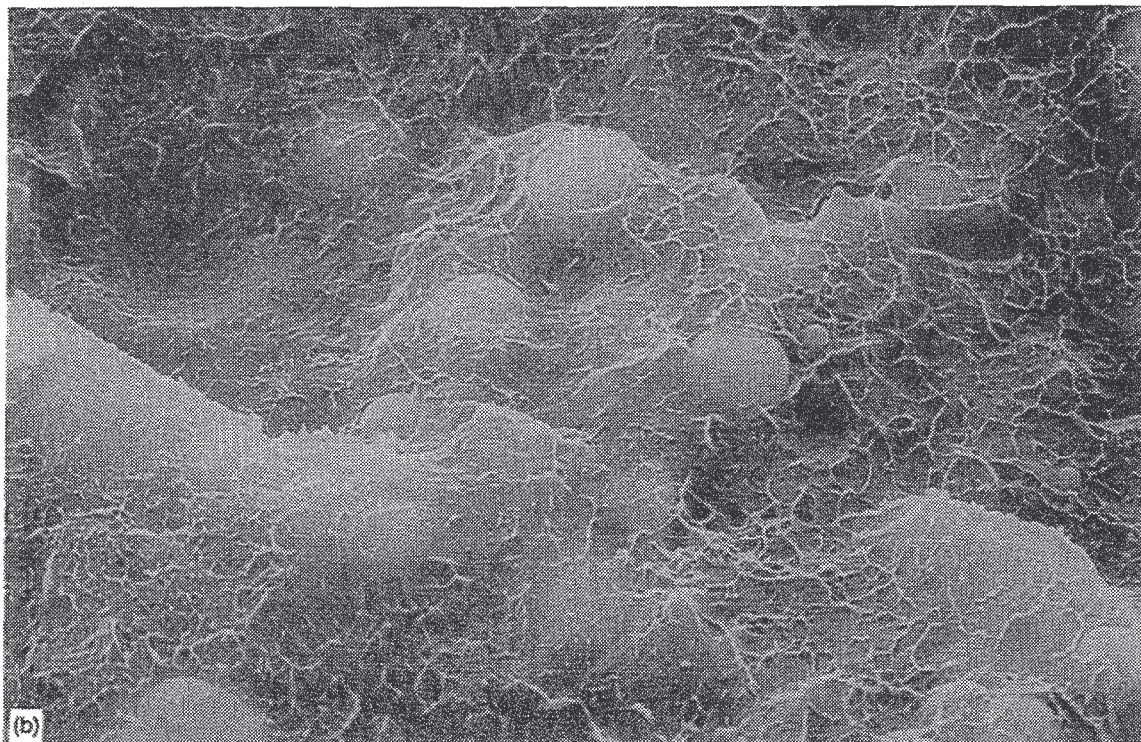


FIG. 3. Scanning electron microscopy of fraction surfaces of glass spherical particles (average particle size, 10-13  $\mu\text{m}$ )/polyethylene ( $M_w \sim 6.10^4$ ): (a) composite without interfacial modification; (b) composite with glass beads modified by 5 equivalent molecular layers of azidofunctional silane; (c) composite with glass beads modified by 100 equivalent molecular layers of azidofunctional silane. (Reprinted by permission from Ref. 38.)



## 4. POLYMER COATING OF FILLER PARTICLES

The second strategy efficient in controlling the filler-polymer interactions is based on the coating of the filler particles with a polymer. There are two possible approaches: (1) preencapsulation of the filler, immobilizing a polymer coating on the surface; and (2) monomer polymerization on a preactivated filler-surface. The first approach has been successful only in few cases, such as "in situ" polymerization of the polymeric shell, polymer precipitation from solution, or suspension and blending of the filler with a viscous polymer [41]. Polymerization on active sites anchored onto the solid surface offers, in our opinion, much better opportunities and is more extensively discussed.

### 4.1. Preencapsulation of the Filler

In spite of the improvement of the interfacial adhesion by coupling agents (Section 3), the interface between a ductile matrix and a nonductile filler remains a source of mechanical weakness since deformation results in local stress concentrations responsible for the matrix-filler debonding and dramatic crack propagation. Moreover, restriction of the mobility of the chain segments in direct contact with the particle surface results in a local zone of increased modulus and a sharp interface between the "coated" filler and the ductile matrix.

A zone of an intermediate modulus can, however, be formed by encapsulating the particles with a suitable polymer. In 1969, Amicon Corporation developed a technique for the reinforcement of thermoplastics using specially treated fillers such as kaolin or colloidal asbestos. Each particle is actually encapsulated in a layer of a relatively high modulus polymer that links the matrix to the mineral surface and accordingly reduces the formation of deleterious stress concentrations at the matrix-filler interface [42-44].

These modified fillers are claimed to yield tough and strongly reinforced composites of PE known as Ceraplasts.

The encapsulating layer is formed, for instance, during the polymer-clay melt compounding by the addition of reactants that concentrate at the polymer-clay interface and form a cross-linked resin layer around the mineral particles. This layer, schematically shown in Fig. 4, is covalently bonded to the PE and ionic-ally or covalently bonded to the mineral.

Typically, the mixture of reactants may be

- A compound bearing a polymerizable unsaturation and adherent to the mineral surface. In the case of kaolin, amino groups are known to be strongly bonded to the mineral surface.
- A compound with two or more polymerizable unsaturations to form the tightly cross-linked layer.
- A thermally activated free-radical initiator for the polymerization of the unsaturated compounds and the grafting of the PE matrix to the encapsulating layer.

The stress transfer requires a diffuse interface between the PE matrix and the cross-linked layer around the particles. As shown by the exhaustive extraction of Ceraplast samples by hot xylene, the weight of the insoluble cross-linked resin and bonded PE is such that a layer about 120 Å thick completely encapsulates the kaolin platelets. The mechanical properties of such a layer must contribute to those of the final composite. This layer coating is quite thick compared to the conventional organosilanolate or titanate layers, which are believed to be of the order of several molecules (5-20 Å) thick.

The Ceraplast technology improves the HDPE properties as shown in Table 4.

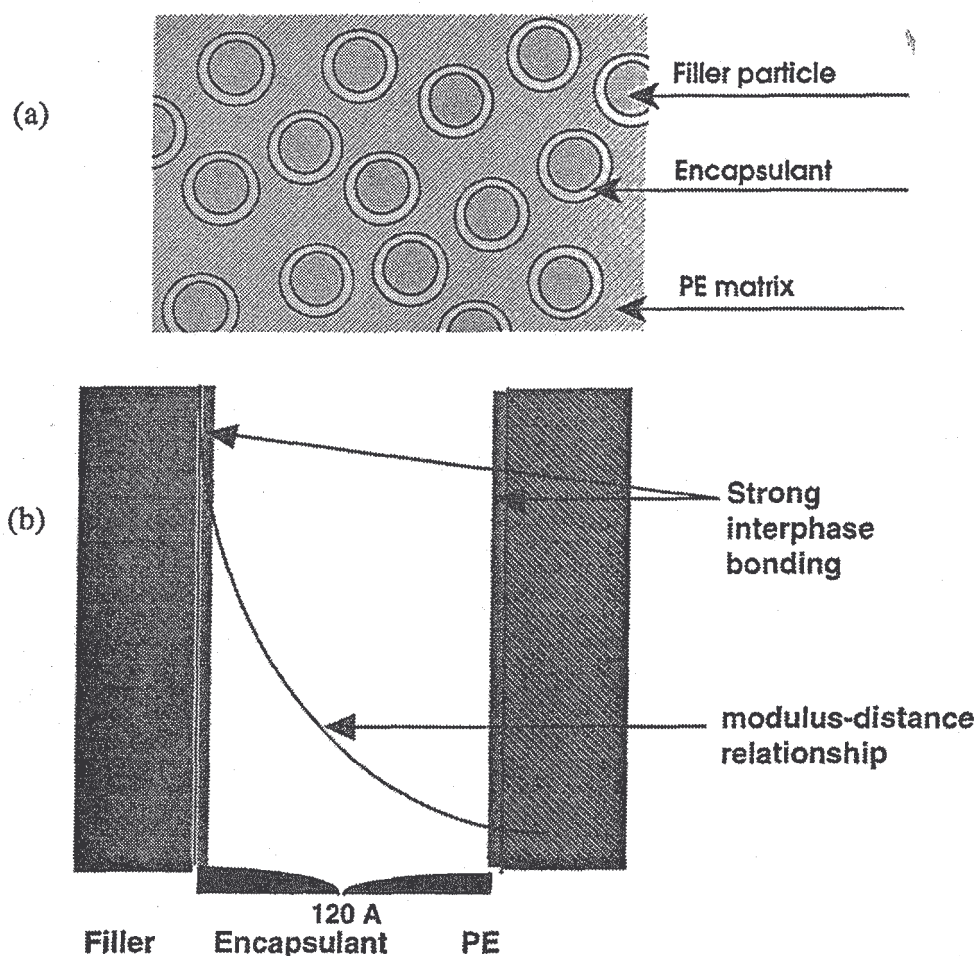


FIG. 4. Ceraplast technology: (a) a Ceraplast; (b) a "graded seal."

TABLE 4 Comparison of Mineral Treatments for the Filling of Polyethylene

Filler type	None	Raw kaolin	Organophilic kaolin	Kaolin Ceraplast
Filler level, wt%	0	40	40	40
Tensile modulus, E, GPa	0.67	1.58	1.44	1.34
Yield elongation, $\epsilon_y$ , %	13	None	None	10
Break elongation, $\epsilon_b$ , %	600	5	7	60
Yield strength, $\sigma_y$ , MPa	22.7	25.2	26.2	20.7
Izod impact, E, J/m	121.9	15.9	26.5	450.5
Hardness (Rockwell-R)	31	—	—	52
Deflec. temperature, 455 MPa, $^{\circ}\text{C}$	75.5	—	—	96.1

Reprinted by permission from Ref. 43.

Toughness is markedly improved; the Izod value of 450 J/m is largely in excess to that of the base resin. Moreover, Ceraplast composites exhibit a ductile failure rather than the brittle failure characteristic of composites prepared from kaolin untreated or treated with coupling agents. The other improvements (e.g., in hardness and heat distortion temperature) are benefits of the higher modulus.

The improved quality and performances of Ceraplasts are unquestionable, but the cost of this technology is more than four times that using unmodified clay [1]. Less-complex processes also exist that are economically more attractive.

As an example, Hawthorne et al. [15, 45] have reported a method for making the mineral surface "acidic" by simple coating procedures with inorganic oxides, particularly alumina/silica combinations [46]. The acidic surface is then used to initiate the cationic polymerization of vinyl, or preferably divinyl, monomers such as divinyl benzene, divinyl ether, isoprene, and piperylene (Table 5, entries 4-6). The residual acidic sites are then neutralized with ammonia or an organic base. During compounding, grafting occurs between the encapsulating polymer layer and the matrix polymer via radical precursors previously attached to this layer. An alternative method reported by these authors is the radical copolymerization of strongly basic monomer, such as vinyl pyridine, and a divinyllic monomer, such as 1,3-butylene dimethylacrylate, on the kaolin particle.

Various polymer-encapsulated kaolins (Table 5, entries 7-12) have been prepared from monomer compositions to yield moduli that range from those of hard, highly cross-linked polymers to those of soft, rubbery, and lightly cross-linked polymers.

**TABLE 5** Mechanical Properties of Preencapsulated Kaolin-Polyethylene Composites<sup>a</sup>

Entry	Filler used <sup>b</sup>	Filler, wt%	$\sigma_y$ MPa	$E_b$ , %	Impact energy, kgm/m
1	HDPE	0	28.9	1045	2.8
2	+ Untreated kaolin	20	28.0	218	1.2
3	+ Untreated kaolin	40	29.2	13	0.7
4	+ 4% Isoprene <sup>c</sup>	20	30.0	90	—
5	+ 4% Piperylene <sup>c</sup>	20	30.0	140	1.3
6	+ 4% styrene <sup>d</sup>	20	29.9	45	1.6
7	+ 1.5 BAEMA, 1.5 BDMA, 1.5 MMA, BP, DBP	20	26.9	545	2.2
8	+ 1.5 BAEMA, 1.5 BDMA, 1.5 MMA, BP, DBP	40	25.2	9	1.6
9	+ 1.0 MVP, 5.0BDMA <sub>5</sub> BP	20	28.0	67	2.8
10	+ 1.0 MVP, 5.0 BDMA, DICUP <sup>6</sup>	20	30.3	359	2.1
11	+ 0.5 MVP, 3.0 DEGA, BP, LIOI	20	30.8	222	1.9
12	+ 0.5 MVP, 3.0 DEGA, BP, LIOI	40	33.0	24	2.3

<sup>a</sup>After Réfs. 15 and 45.

<sup>b</sup>The abbreviations for ingredients used in the surface treatment are as follows: BAEMA = *t*-butylaminoethylmethacrylate; BDMA = 1,3-butylene difnethylacrylate; MMA = methylmeth-acrylate; BP = benzoyl peroxide; DBP = di-*f*-butyl peroxide; MVP = 2-methyl-5-vinyl pyridine; DICUP = dicumylperoxide; DEGA = diethylene glycol diacrylate; LIOI = "Lupersol 101" 2,5-bis-(*t*-butyl-peroxy)-2,5-dimethylhexane.

<sup>c</sup>Polymerization NH<sub>3</sub> terminated; polymer oxidized before use (by oxygen atmosphere at room temperature). Polymerization NH<sub>3</sub> terminated; polymer ozonized before use (exposure to ozonized oxygen 2.5 mg/100g of kaolin).

<sup>d</sup>Monomers polymerized during compounding process; DICUP content 0.1% wt/wt kaolin.

Dispersion of these modified fillers in polyethylene of various grades results in improved processability and tensile and impact strengths compared to composites containing untreated fillers. Nevertheless, the process remains expensive, and, in many cases, price overbalances usefulness.

In addition to preencapsulation of the filler by in situ polymerization, fillers can be modified



by a liquid layer [47-49], which is able to wet both the polymer and the filler particles. Thus, an interface of liquid oligomeric ethylene oxide between the filler, such as chalk, and low-density polyethylene (LDPE) completely changes the mechanical properties of the composite. Chalk was suspended in water and the required amount of oligomers (0.5-20% by weight) was added; the thick pulp was dried in an oven at 85 °C until of a constant weight. The unmodified and modified chalks were thoroughly mixed with PE granules and extruded at 150 °C. Compositions containing up to 50% chalk modified with oligomers exhibit a typical thermoplastic behavior (i.e., neck formation and plastic deformation). The effect of filling on the relative elongation at break, ultimate stress, elastic modulus, and impact strength is illustrated in Fig. 5. The ethylene oxide oligomers could have a twofold effect on the material failure: the liquid modifier could increase the fracture surface and/or absorb energy [50]. Similar results have been obtained for chalk-, talc-, and kaolin-filled HDPE [48]. The ethylene oxide oligomer ( $M_w = 300$ ) was used as 0-20 wt% of the filler. The filled HDPE samples have quite high ultimate elongation and impact strength, whereas the elastic modulus and tensile strength are very close to neat HDPE.

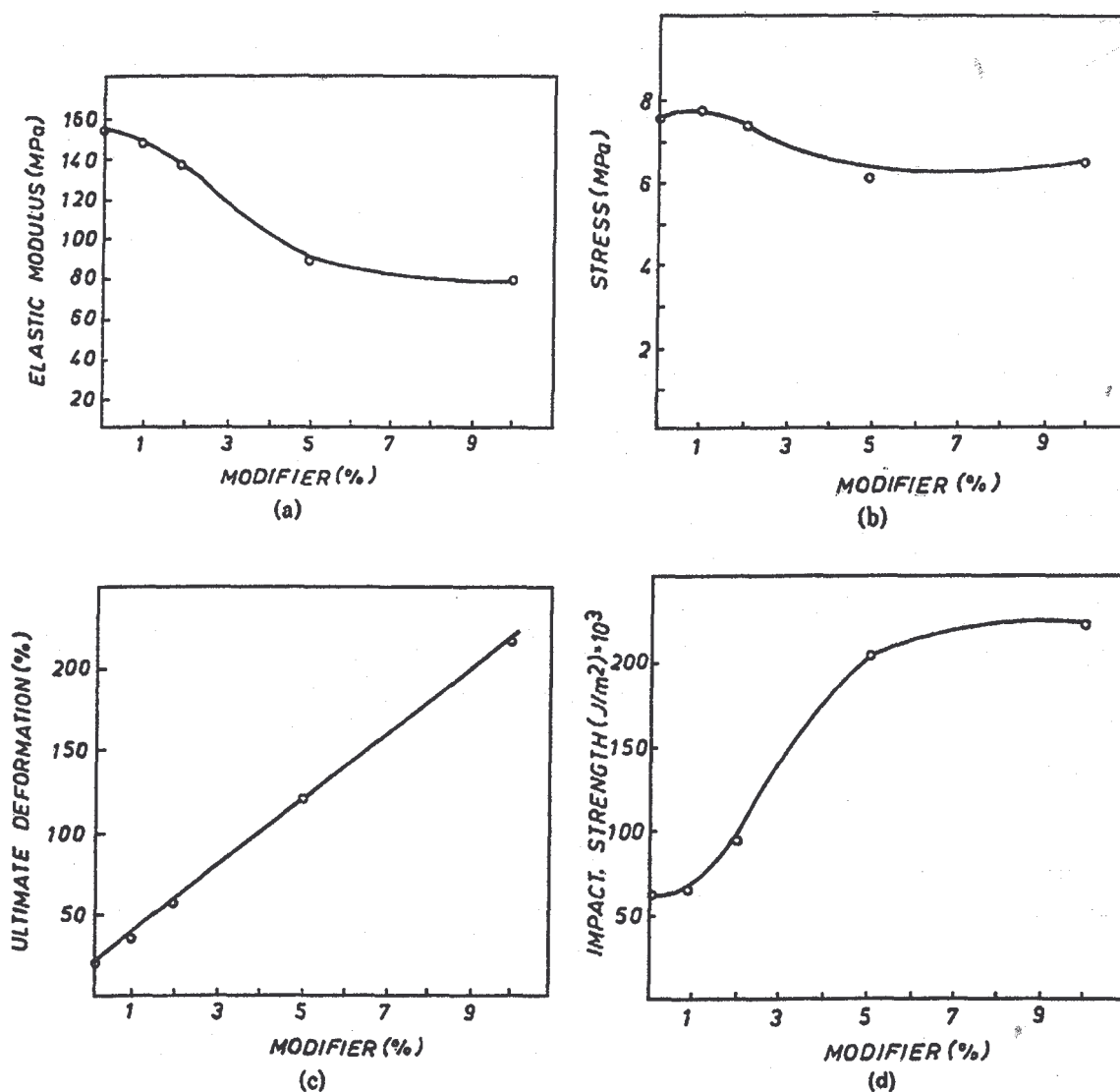


FIG. 5. Mechanical properties of low-density polyethylene filled with chalk (50% wt/wt) modified with various amounts of an ethylene oxide oligomer: (a) elastic modulus; (b) stress; (c) ultimate deformation; (d) impact strength. (Reprinted by permission from Ref. 49.)

Similarly, Fridman et al. [51] grafted 5% to 20% ultrahigh molecular weight PE (UHMWPE) onto tufa, calcite, kaolin, and perlite particles. The coated filler was compounded with HDPE and LDPE (Fig. 6), and the impact strength was observed as maximum at 50-60% filler. The ultimate tensile strength varied similarly. The UHMWPE seemed to be responsible for the high strength of the composite.

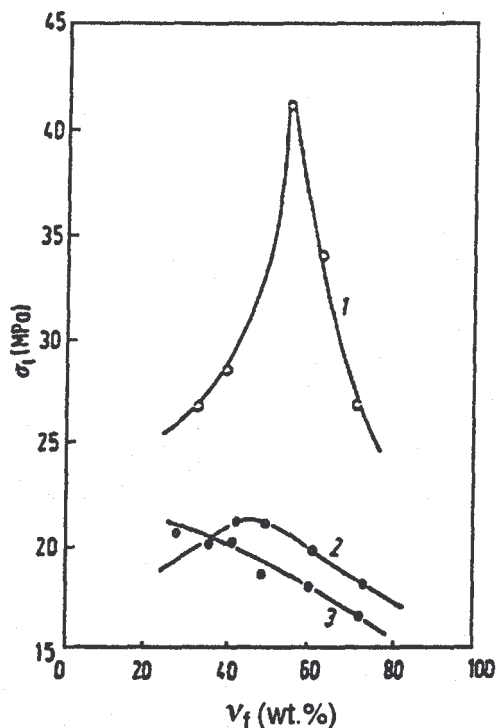


FIG. 6. Dependence of tensile strength  $\sigma_1$  of composites HDPE-tufa on the weight fraction of filler  $v_f$ . The particle size is 8  $\mu\text{m}$ . (1) 20% UHMWPE grafted onto tufa and blended with HDPE; (2) tufa, UHMWPE (20 wt% to filler) blended with HDPE; (3) tufa blended with HDPE. (Reprinted by permission from Ref. 1.)

As an alternative to the classical blend technology, it has been proposed to polymerize the monomer on the filler surface, with formation of highly mineral-filled PE that shows high elongation and ductility. These composites result from the ethylene or propylene polymerization initiated with catalytically activated minerals. Accordingly, chains of molecular weight greater than  $10^6$  are formed from the mineral surface and lead to the production of materials designed as "homogeneous composites" [5].

#### 4.2. Ziegler-Natta Polymerization from the Filler Surface

The emergence of coordinative catalytic polymerization has led to a new generation of catalysts supported on organic or inorganic fillers [52]. The first type of supported organometallic catalysts was prepared [53, 54] by deposition of molybdenum, tungsten, and chromium hexacarbonyls over  $\text{Al}_2\text{O}_3$ . Catalysts containing molybdenum and tungsten were used in the metathesis of olefins, whereas chromium-containing ones were active in ethylene polymerization. The use of Ziegler-Natta catalysts in the production of polymerization-filled PE was suggested simultaneously and independently in the United States [55-57] and the former Soviet Union [58, 59].

These new catalysts have such high activity that they are used in very small amounts, and their residues may be left in the polymer. Moreover, polymerization on the surface

- favors a uniform distribution of the filler throughout the polymer
- provides optimum opportunity for the polymer to wet and to be adsorbed on the mineral

surface

- is the only process for the preparation of composites based on very high molecular weight polymers.

#### 4.2.1. Types of Filler

Olefins can be polymerized from the surface of a very wide range of fillers, including minerals [5], metals and their oxides [60], carbon black [61], and organic materials such as lignin [62]. Composites containing fibrous fillers such as glass [63] and carbon fibers [64, 65], asbestos [66, 67], cellulose [68], wood flour, or plasma-treated UHMWPE [69] are not discussed here since they are extensively reviewed elsewhere [70-72].

Any finely divided mineral or synthetic compound can be used as a support. These can include alumina and its hydrates, metal phosphates and sulfates, silicas ( $\text{SiO}_2$ ) such as sand, pumice, metal carbonates, metal oxides such as titania (e.g., rutile and anatase), zinc oxide, antimony oxide, and iron oxide (e.g., magnetite:  $\text{FeO-Fe}_2\text{O}_3$ ), water-insoluble silicates, and natural /mixtures of these compounds such as slate.

The term *alumina hydrates* refers to aluminas of the general formula  $\text{Al}_2\text{O}_3\text{-}n\text{H}_2\text{O}$ , where  $x$  ranges from 1.5 to 3.0. Typical water-insoluble silicates include calcium silicates ( $\text{CaSiO}_3$ ) such as wollastonite; magnesium silicates such as talc and asbestos; magnesium calcium aluminum silicates [ $(\text{Mg}_5\text{Ca})\text{O}^* \text{Al}_2\text{O}_3\text{-}5\text{SiO}_2\text{-}n\text{H}_2\text{O}$ ] such as montmorillonite and serpentine; lithium aluminum silicates such as spodumene [ $(\text{Li}_5\text{Na})_2\text{Al}_2\text{Si}_4\text{O}_{12}$ ]; potassium aluminum silicates such as feldspar ( $\text{K}_2\text{O-Al}_2\text{O}_3\text{-OSiO}_2$ ) and mica ( $\text{K}_2\text{O-}3\text{Al}_2\text{O}_3\text{-}6\text{SiO}_2\text{-}2\text{H}_2\text{O}$ ); magnesium ion silicates such as olivine [ $(\text{Mg}_5\text{Fe})_2\text{SiO}_4$ ]; aluminum silicates ( $\text{Al}_2\text{O}_3\text{-SiO}_2$ ) such as sillimanite and kyanite; and aluminum silicate clays of the formula  $\text{Al}_2\text{O}_3\text{-}x\text{SiO}_2\text{-}z\text{H}_2\text{O}$ , where  $x$  is 1 to 5 and  $n$  is 0 to 4, such as kaolin, attapulgite, Guller's earth, and bentonite.

These fillers have various shapes, including acicular and platelike particles. They must first be conditioned to remove all the polymerization inhibitors from the surface [1] (e.g.,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{O}_2$ , etc.). The influence of the filler shape and conditioning on polymerization and properties of composites is discussed in the next section.

#### 4.2.2. Polymerization-Filled Composites

The first experiments with  $\text{TiCl}_4$  plus  $\text{AlR}_3$  catalyst for ethylene polymerization onto cellulose fibers and carbon black particles were carried out in 1964 and 1965 [73, 74], but the final dispersions were not very homogeneous. Today, physical adsorption and chemical reaction methods to attach a transition metal compound onto a filler surface have been developed. Physical adsorption methods consist of depositing a layer of transition metal compounds on the surface and pores of the filler. The presence of functional groups on the surface is not required [75].

Chemical reaction methods are based on the reaction of transition metal or organometallic compounds ( $\text{MR}_n$ ) with the reactive groups (e.g., hydroxyls) available on the filler surface:



The occurrence of this reaction has been proved by IR, electron spin resonance (ESR), and nuclear magnetic resonance (NMR) spectroscopy, by the volumetric measurement of the released alkane ( $\text{KH}$ ), and by gas-liquid chromatography (GLC) and chemical analysis of the decomposition products of the activated surface [52, 76, 77].

Some catalytic systems used to initiate the polymerization filling of polyole-fins are listed in



Table 6. The activity of the supported catalysts depends on the conditions for their preparation: type and structure of the oxide support, temperature for preliminary dehydration of the carrier, specific reaction between the filler and the organometallic compound, and distribution of the active sites on the carrier surface and pores.

#### 4.2.2.1. Preparation of the Active Sites.

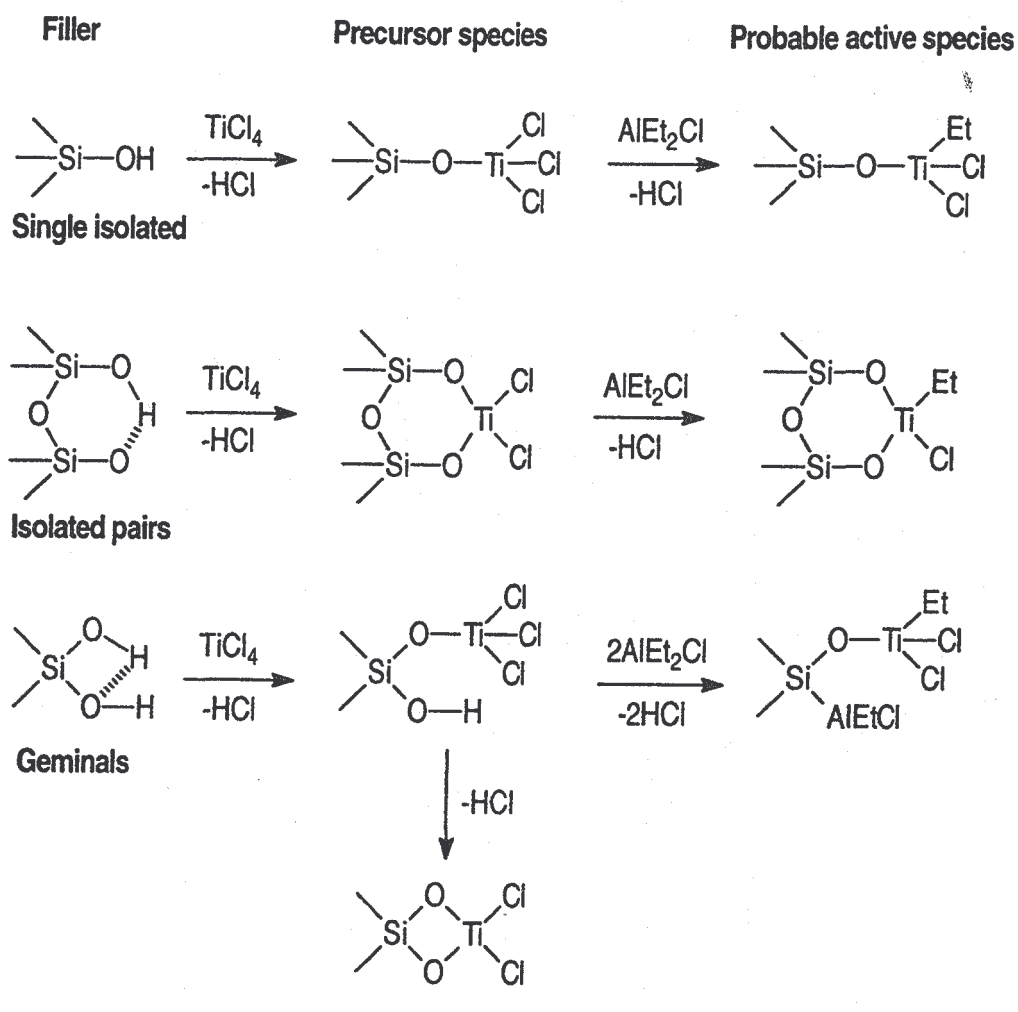
Two techniques were developed to attach the coordination catalyst onto the mineral filler in an irreversible manner. In the first process, the catalyst is intrinsically active, whereas in the second one, the transition metal is only active when attached to the mineral filler [5]. In a third technique, the supported catalyst is activated by the selective removal of the ligands. *Active Catalyst Attached to the Surface:* While virgin kaolin is inert to olefins, calcinated kaolin is a rather active ethylene polymerization catalyst [92, 104-107]. The clay must be calcinated above 400°C. Water is irreversibly lost in the process, and the clay particles are no longer crystalline, even though the appearance of the stacked platelike structure is unchanged (Eq. 2).

The genuine catalytic activity of the calcinated clay is undoubtedly due to the presence of 0.6-2.0% titanium dioxide, known as a coordination polymerization catalyst. Polymerization of ethylene onto this calcinated kaolin, however, results in a heterogeneous composite.

TABLE6 Catalytic Systems Currently Used in Polymerization-Filled Composites

Catalyst types	Reference no.
<b>Titanium:</b>	
TiCl <sub>4</sub> + AlR <sub>3</sub> ; TiCl <sub>4</sub> + AlR <sub>n</sub> Cl <sub>3-n</sub>	1, 5, 78-82
Ti(OR) <sub>4</sub> + AlR <sub>n</sub> Cl <sub>3-n</sub>	1, 83
AlR <sub>n</sub> Cl <sub>3-n</sub> + Mg(OR) <sub>2</sub> + Ti(OR) <sub>4</sub>	84, 85
TiO <sub>2</sub>	5
Ti(BH <sub>4</sub> ) <sub>3</sub>	86, 87
TiCl <sub>4</sub> + AlR <sub>2</sub> Cl; TiCl <sub>4</sub> + Mg(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	88-91
Ti(CH <sub>2</sub> -C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	92
Bis(arene); bis (toluene)Ti; bis(mesitylene)Ti	93, 94
TiCl <sub>4</sub> + AlR <sub>3</sub> + Mg(OR) <sub>2</sub>	82
<b>Zirconium:</b>	
Zr(CH <sub>2</sub> -C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	5, 95-98
Zr(BH <sub>4</sub> ) <sub>4</sub>	79-86, 99, 100
Zr(C <sub>3</sub> H <sub>5</sub> ) <sub>4</sub>	76, 87
<b>Vanadium:</b>	
VCl <sub>4</sub> + AlR <sub>3</sub> ; VCl <sub>4</sub> + AlR <sub>n</sub> Cl <sub>3-n</sub>	1
VCl <sub>3</sub> + AlR <sub>n</sub> Cl <sub>3-n</sub>	1, 101
(VCl <sub>4</sub> + VO(OEt) <sub>3</sub> )/AlEt <sub>2</sub> Cl	102
<b>Chromium:</b>	
CrRCl <sub>4</sub> ; Cr(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ; Cr(O <sub>2</sub> CR) <sub>3</sub>	1, 55
Cr(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	80, 87, 99
<b>Hafnium:</b>	
Hf(CH <sub>2</sub> -C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	103
Bis(arene)Hf	93
Hf(BH <sub>4</sub> ) <sub>4</sub>	86

In order to avoid the heterogeneous filler dispersion, titanium oxide can be attached onto the surfaces by reaction of  $\text{TiCl}_4$  or an alkyl titanate with many minerals [108, 109] (Eq. 3). The mechanism for the reaction of  $\text{TiCl}_4$  vapor with OH groups of amorphous  $\text{SiO}_2$  has been studied by Damyanov et al., who have observed a higher reactivity when the OH groups are hydrogen bonded [HO]. It is essential to remove the unreacted titanium reagent before the catalyst is formed by hydrolysis, drying, and addition of aluminum alkyl (Eq. 4). This active coordination catalyst yields homogeneous PE composites [5].



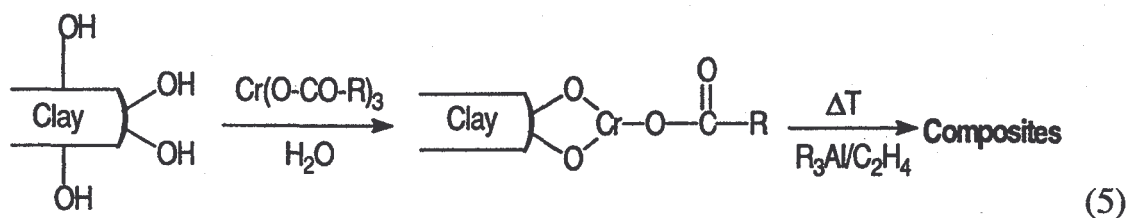
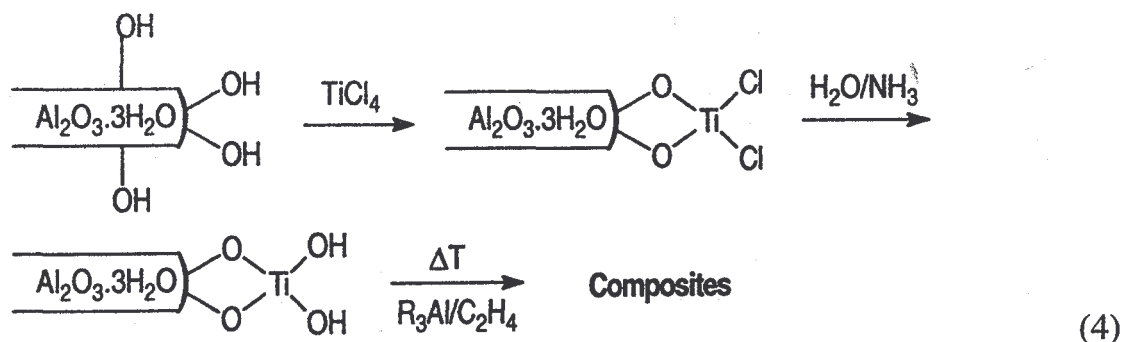
(3)

Typical properties of these composites are listed in Table 7. Even at an  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  content as high as 70%, the impact strength stays high [98].

Transition metals other than titanium can also be used. Chromium chelates and esters are strongly adsorbed onto many mineral surfaces to form chromium esters with the surface silanol groups (Eq. 5).

After hydrolysis and heat treatment, the chromium is activated by aluminum alkyls and used in ethylene polymerization [55]. The chromium catalysts complement the titania systems because they are more active on silica-containing minerals (e.g., clay,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , talc,  $\text{MgOSiO}_2 \cdot 2\text{H}_2\text{O}$ , etc.) than on aluminas. They also give lower molecular weight polymers

than titanium catalysts. Both types of catalysts allow composites to be prepared from uncalcinated clays.



**TABLE 7** Properties of Composites Prepared from Anchored Catalysts

Mineral	Al <sub>2</sub> O <sub>3</sub> - 3H <sub>2</sub> O <sup>a</sup>	Clay <sup>b</sup>	Clay <sup>b</sup>	Clay <sup>b</sup>	Talc <sup>c</sup>
Catalyst	Ti <sup>d</sup>	Ti <sup>ii</sup>	Cr <sup>e</sup>	Cr <sup>f</sup>	Cr <sup>g</sup>
% Filler	69	66	69	49	59
Notched Izod impact, J/m (-18°C)	390	280	318	795 <sup>h</sup>	186
Modulus, GPa	2.5	4.0	4.1	3.0	4.4
Tensile, MPa	19	20	17	23	18
Elongation ε <sub>n</sub> %	160	230	110	500	150

Reprinted by permission from Ref. 5.

<sup>a</sup>C-33 Alumina hydrate, Alcoa Company.

<sup>b</sup>"Harwick" GK clay (Al<sub>2</sub>O<sub>3</sub>-2SiO<sub>2</sub>-2H<sub>2</sub>O).

<sup>c</sup>Hydrated magnesium silicate [Mg<sub>3</sub>Si<sub>4</sub>O]<sub>0</sub>(OH)<sub>3</sub>.

<sup>d</sup>Hydrolyzed TiCl<sub>4</sub>.

<sup>e</sup>Hydrolyzed Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>.

<sup>f</sup>Cr(OAc)<sub>3</sub>.

<sup>g</sup>Methacryloylchromium chloride.

<sup>h</sup>Izod impact at 20°C.

Compared to the calcinated clays, the reinforcement is lower, but a higher loading is possible and ductility is retained [111].

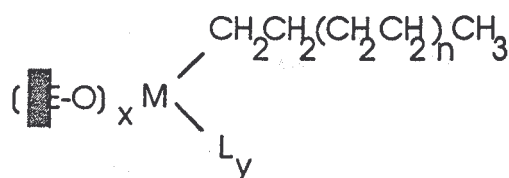
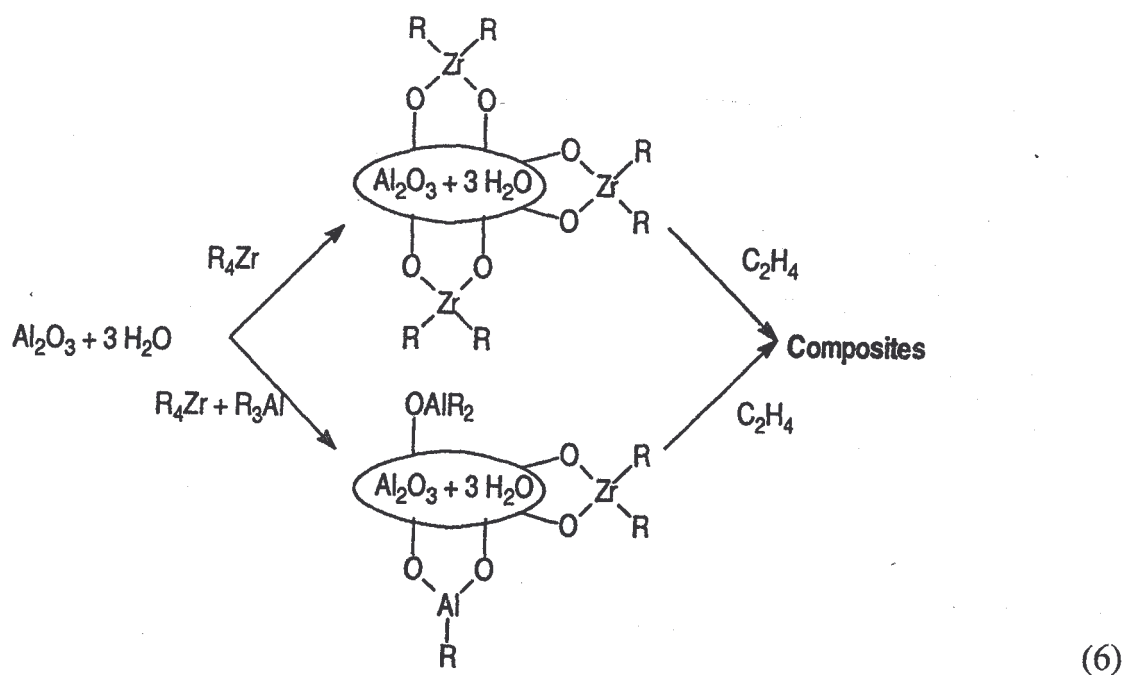
*Catalysts Only Active on the Filler Surface:* A major deficiency of the previous procedure is that all the mineral must be chemically treated and dried prior to polymerization. A simpler



and more practical route involves alkyl transition metals, which are active catalysts only when adsorbed onto the mineral surface. Ethylene polymerization was initiated with an extremely active  $(\text{PhCH}_2)_4\text{Zr}$  attached onto colloidal silica or alumina [111, 112]. Later, Howard et al. found that these transition metal alkyls could be used alone or, better, in combination with an aluminum alkyl (Eq. 6) [5].

The combination of  $\text{tBu}_3\text{Al}$  and  $(\text{PhCH}_2)_4\text{Zr}$  in solution is not active in ethylene polymerization, but it becomes extremely active when a mineral substrate is added. At a constant zirconium concentration, the polymerization activity increases with the added alkyl aluminum up to an aluminum/zirconium ratio of 20 to 30, and then it rapidly decreases at higher ratios. This may reflect either competition for the surface sites or the inhibition of the active sites by complex-ation with the aluminum alkyl in excess. The zirconium catalyst is about 100-200 times more active than a titanium catalyst prepared by hydrolysis of  $\text{TiCl}_4$  or  $\text{Ti}(\text{OR})_4$  on the same substrate.

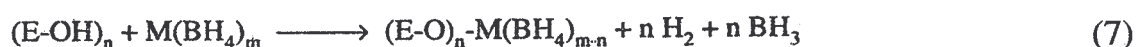
*Activation of the Supported Catalysts by Removal of the Ligands:* Preparation of polymerization catalysts by the anchoring of organometallic compounds onto the filler surface allows the composition of the active sites, and thus their reactivity, to be controlled. The active center of such systems agrees with Formula 1.



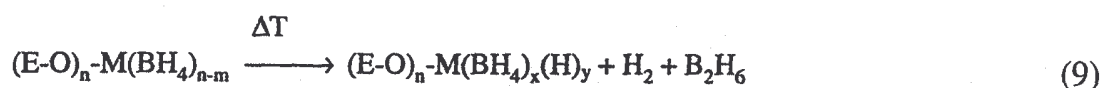
**FORMULA 1.**

It is possible to change the transition metal  $M$  and its oxidation state; the element  $E$ , which forms the carrier; and the ligand  $L$ . The active centers are usually a small fraction of the supported metal. Formation of the active centers requires coordination vacancy on the

supported ion. Heating of catalysts, treatment with hydrogen, or ultraviolet (UV) irradiation may be efficient in removing the organic ligand from the anchored complex and usually result in increased activity. Under optimal treatment conditions, the number of active polymerization centers may be as high as 20-40% of the supported metal [87]. Samples prepared by anchoring hydroborate complexes of titanium, zirconium, hafnium, and uranium onto oxide supports have been studied [86, 87, 99, 100]. The tetrahydroborate complexes were obtained by milling metal chlorides with  $\text{LiBH}_4$  and were purified by sublimation. When supported on silica and alumina, tetrahydroborate compounds interact with the surface hydroxyl groups according to the reaction in Eq. 7. This reaction was confirmed by IR and NMR spectroscopy and analysis of the reaction products [75]. The same conclusion was drawn from the study of the reaction of  $\text{Zr}(\text{BH}_4)_4$  with hydroxyl groups [113]. The released  $\text{BH}_3$  can either recombine to form diborane or interact with surface hydroxyl groups as in Eq. 8.



Surface hydroborate complexes do not polymerize ethylene. The heating of the anchored hydroborate complexes leads to the formation of M-H bonds, which is the necessary step for promoting the catalytic activity (Fig. 7). Based on IR, NMR, and chemical analyses, decomposition of the surface tetrahydroborate complexes can be described by Eq. 9.



The surface hydrides produced by decomposition of surface tetrahydroborate complexes are stable up to  $300^\circ\text{C}$ . The high thermal stability of the surface hydrides seems to be due to their firm attachment to the surface, which precludes their decomposition via bimolecular reactions. As shown by IR spectroscopy, polymerization is a multistep process. Among the studied catalysts, zirconium-containing catalysts on alumina are the most active ones (Table 8).

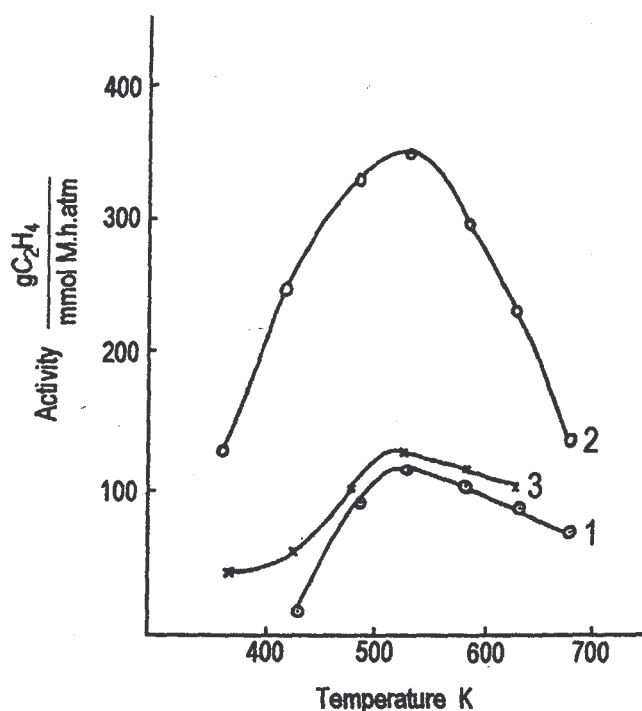


FIG. 7. Activity of (1)  $Zr(BH_4)VSiO_2$ , (2)  $Zr(BH_4)VAI_2O_3$ , and (3)  $Ti(BH_4)VAI_2O_3$  catalysts versus the heating temperature in vacuo (the supports were dehydroxylated at  $400^\circ C$ , except for Sample 3, which was at  $700^\circ C$ ). Polymerization of  $C_2H_4$  at  $80^\circ C$  and 6 atm. (Reprinted by permission from Ref. 86.)

TABLE 8 Polymerization of Ethylene by Supported Tetrahydroborate Catalysts<sup>3</sup>

Experiment no.	Catalyst	Content of Tm, mmolZg	g PEZ(g cat	Activity g PEZ • h) (mmol Tm'h'atm)
1	$Ti(BH_4)VSiO_2$	0.34	80	45
2	$Ti(BH_4)VAI_2O_3$	0.24	300	230
3	$Zr(BH_4)_4/SiO_2$	0.38	630	300
4	$Zr(BH_4)VAI_2O_3$	0.28	1200	800
5	$Hf(BHt)_4ZSiO_2$	0.38	200	100
6	$Hf(BHt)_4ZAI_2O_3$	0.28	430	280
7 <sup>b</sup>	$Ti(CH_2C_6H_5)VSiO_2ZH_2$	0.31	100	55
8 <sup>b</sup>	$Ti(CH_2C_6H_5)_4ZAI_2O_3$	0.27	400	280
9 <sup>b</sup>	$Zr(C_3H_5)_4ZSiO_2/H_2$	0.56	200	60
10 <sup>b</sup>	$Zr(C_3H_5)_4ZAI_2O_3$	0.41	440	190
11 <sup>b</sup>	$Zr(CH_2C_6H_5)_4ZAI_2O_3$	0.17	1100	1200
12 <sup>b</sup>	$Hf(C_3H_5)_4ZSiO_2$	0.50	75	25
13 <sup>b</sup>	$Cr(C_3H_5)_2ZSiO_2^0$	0.38	500	260

Reprinted by permission from Ref. 86.

<sup>a</sup>Support is dehydroxylated in Experiments 1 and 2 at 723 K, Experiments 3-7 at 923 K; catalysts are activated by heating at 423 K for Experiments 1 and 2 and 523 K for Experiments 3-7; polymerization conditions: 353 K, pressure of ethylene 5.5 atm.

<sup>b</sup>Data are given for comparison. <sup>c</sup>Polymerization temperature, 333 K.

#### 4.2.2.2. Pretreatment of the Mineral Fillers.

*Filler Thermal Conditioning:* Filler drying at high temperature, in vacuo, or in a flow of an inert gas is a traditional procedure in powder technology. For some fillers (mainly minerals such as perlite, kaolin, glass beads), the conditioning may include open firing [5]. For fillers containing physically sorbed water or crystalline hydrate water, the heat treatment can cause only partial desorption of moisture. Complete removal of water from aluminum hydroxide, kaolin, per-lite, and other water-containing minerals is economically impossible. Successful surface polymerization needs the control of the OH groups' concentration on the surface. At room temperature, the hydroxyl groups on the surface of many inorganic oxides are covered by several layers of hydrogen-bonded water, which may be partly removed by heating in vacuo or by a stream of dry gas. In the case of silica, refluxing in xylene and removing the azeotropic mixture of water/ xylene is also effective. Higher drying temperatures for silica alter the concentration of the surface hydroxyl groups.

Candlin and Thomas [76] studied this effect for silica slurred in toluene (Fig. 8). The hydroxyl content of the filler was determined by volumetric titration of the gas released by reaction of the hydroxyl groups with  $\text{CH}_3\text{MgCl}$  or  $\text{Zr}(\pi\text{-allyl})_4$ . On heating, the hydroxyl groups are progressively lost, and at  $500^\circ\text{C}$ , virtually all geminate hydroxyl sites are eliminated to form surface siloxane bridges,  $\text{Si}-\text{O}-\text{Si}$ . Nevertheless, the isolated OH sites remain up to about  $600^\circ\text{C}$ . The thermal behavior of alumina is more complex, but residual surface Al-OH groups are believed to persist up to  $800^\circ\text{C}$ .

Thus, the drying temperature of the filler affects the activity of the catalyst. Damyanov, Velikova, and Petkov have shown that the activity of a supported catalyst, prepared by reaction of  $\text{SiO}_2$  particles with titanium tetrachloride vapor, is increased with the temperature of drying (Fig. 9) [82].

Similarly, Nesterov has studied the ethylene polymerization (Eqs. 10-12) initiated by modified tetrahydroborate compounds of chromium, titanium, and zirconium attached onto natural aluminosilicates [86]. Table 9 shows the effect of the temperature of the carrier dehydroxylation on the catalyst-filler activity. As the temperature for the filler dehydroxylation is increased, a sharp decrease in the zirconium content and an increase in activity (more than one order of magnitude) are observed (Table 9, entries 1, 3-6). The concentration in zirconium is directly proportional to the concentration of the surface hydroxyl groups, which decreases as the dehydroxylation temperature of the carrier is increased. Simultaneously, the stoichiometry of the reaction between the complex and the surface hydroxyl groups changes according to Eq. 6, leading to increased catalytic activity. The atomic activity of the supported catalyst considerably increases when the content of zirconium is decreased at a constant dehydroxylation temperature of the carrier (Table 9, entries 1, 2, 7, 8).

When natural aluminosilicates with small specific surface area (tufa, pumice, kaolin) are used, the decrease in the zirconium content does not modify the uniformity of the coating of the filler particles.



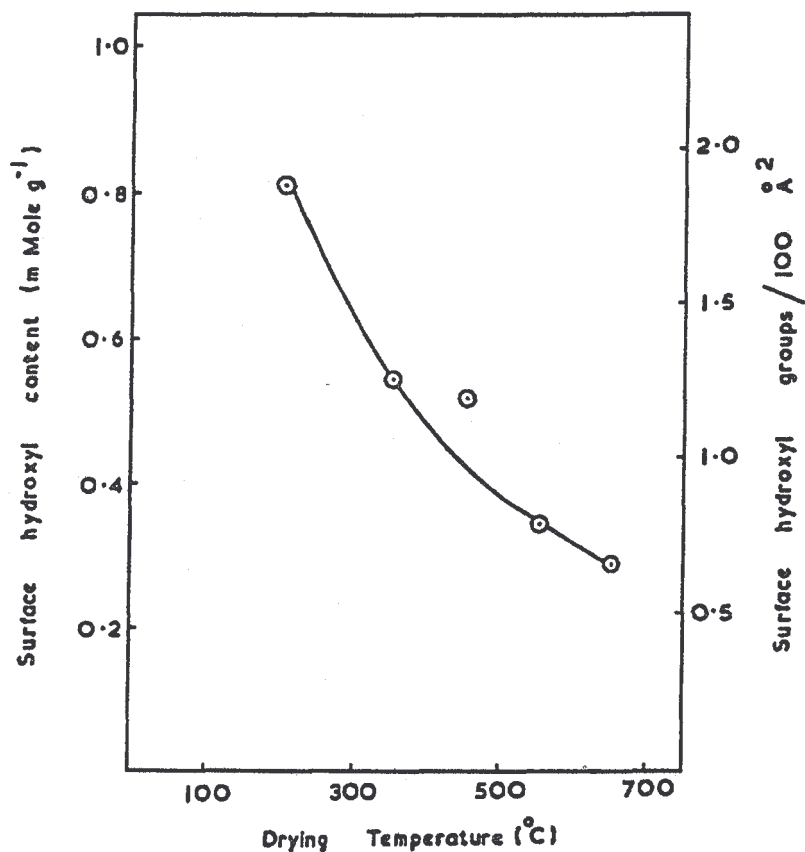


FIG. 8. Dependence of the available hydroxyl groups on the drying temperature for 4% wt/vol slurry of silica in toluene. (Reprinted by permission from Ref. 76.)

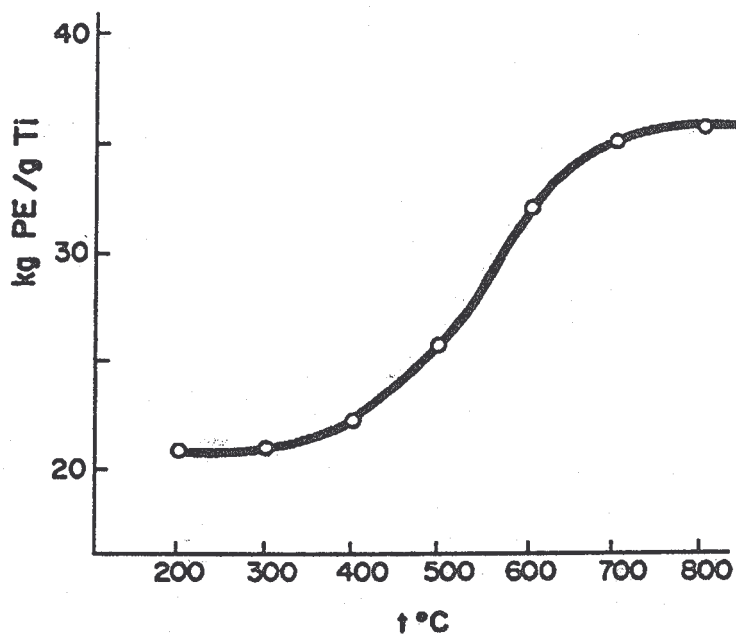
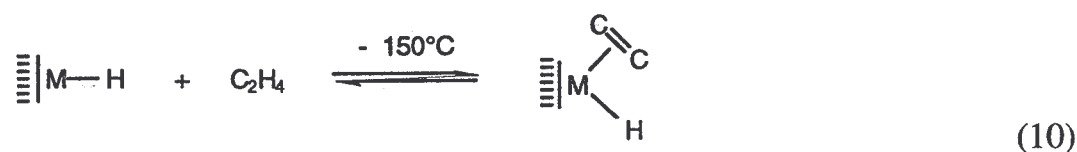
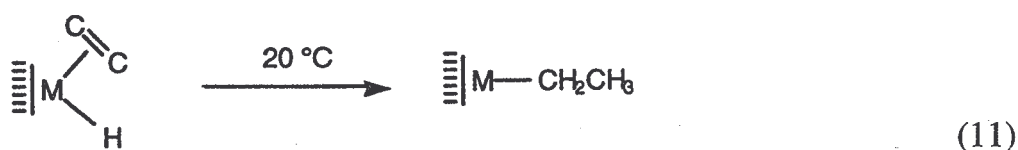


FIG. 9. Dependence of the catalyst activity on the temperature of precalcination of the Vulcasil ( $\text{SiO}_2$ ) support ( $AV_{\text{Ti}} = 25$ ,  $Mg/\text{Ti} = 30$ ,  $P = 10 \text{ kg/cm}^2$ ,  $T = 60^\circ\text{C}$ ,  $t = 20 \text{ min}$ ). (Reprinted by permission from Ref. 82.)

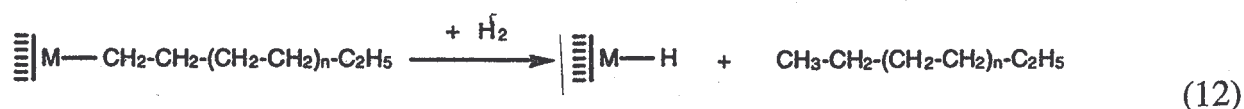
• Coordination of ethylene :



• Ethylene insertion into the M-H bond :



• Transfer onto hydrogen :



**TABLE 9** Dependence of Catalytic Activity on the Zirconium Content for Supported  $\text{Zr}(\text{BH}_4)_4$  Catalysts in Ethylene Polymerization

Entry	Catalyst $\text{Zr}(\text{BH}_4)_4$ on	Temperature of dehydroxylation, $^\circ\text{C}$	Content of <b>Zr</b> , wt%	Effi gPE/ (g cat h atm)	ciency gPE/ (mmol Zr h atm)
1	Tufa	350	0.100	0.3	28
2	Tufa	350	0.014	0.2	130
3	Tufa	600	0.004	0.1	340
4	Pumice	200	0.200	0.3	15
5	Pumice	350	0.100	0.4	34
6	Pumice	600	0.003	0.1	270
7	Kaolin	350	0.250	0.3	11
8	Kaolin	350	0.020	0.1	57

Reprinted by permission from Ref. 100.

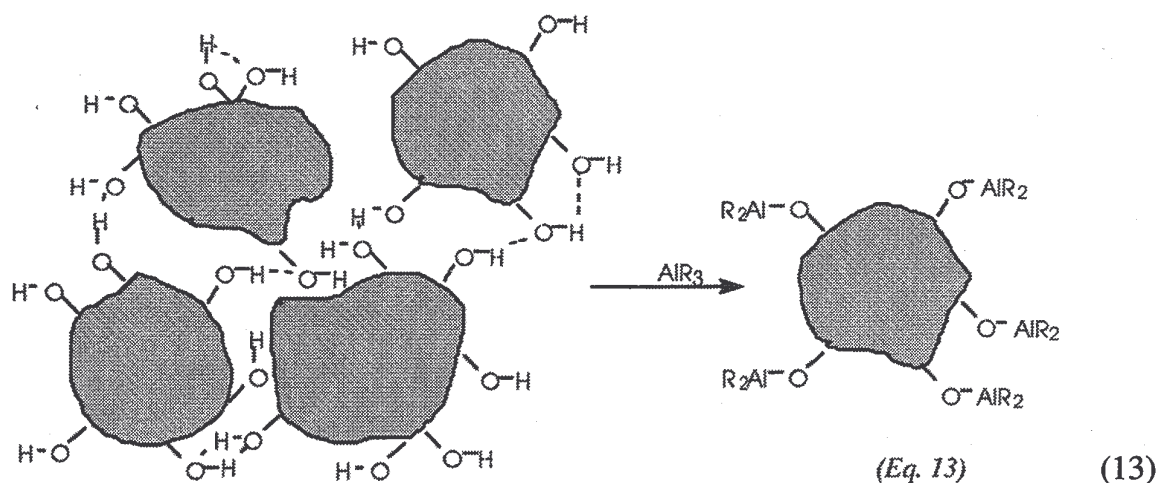
Finally, the optimal dehydration temperature  $T_d$  for the highest catalytic activity depends on the supported organometallic compounds. For example,  $T_d$  is about  $100^\circ\text{C}$  for  $\text{Zr}(\text{C}_3\text{H}_5\text{VSiO}_2)$  and about  $800^\circ\text{C}$  for  $\text{Cr}(\text{C}_3\text{H}_5\text{VSiO}_2)$  systems [45]. As  $r_d$  rises, the molecular mass of the polymer formed tends to decrease.

*Chemical Conditioning of the Filler:* The filler surface may be dehydroxy-lated by chemical methods such as reaction with alkylaluminums [5]. Clays, especially freshly calcinated ones,

are extensively aggregated, which is apparent when they are slurried in a hydrocarbon. Thus, 10% (g/mL) of calcinated kaolin in hexane forms a mayonnaiselike suspension, presumably as a result of inter-particle hydrogen bonding. Deaggregation of the particles must be complete prior to the ethylene polymerization to avoid heterogeneity of the coating. This can be accomplished by reaction of the surface hydroxyl groups with an organo-philic reagent such as an alkyl aluminum [49].

In addition to the alkylation of surface OH groups, alkylation of siloxane, alumoxane, and Si—O—Al groups also takes place in clays [1] (Eq. 13).

The effect of alkyl aluminum on clay dispersion is illustrated in Fig. 10. The viscosity of a 15% clay/hexane dispersion, which is very high (2000 to 3000 cps), drastically drops to less than 100 cps on addition of an alkyl aluminum.  ${}^i\text{Bu}_3\text{Al}$  and  ${}^i\text{Bu}_2\text{AlCl}$  are the most effective alkylating agents; thus, 100 g of clay free from adsorbed water (surface OH concentration  $\sim 4$  meq/100 g) requires only 400 mg (2.0 meq) of  ${}^i\text{Bu}_3\text{Al}$  to reduce the viscosity to that of the solvent. Larger (hexyl) or smaller (methyl) alkyl groups are not as effective as the isobutyl groups.



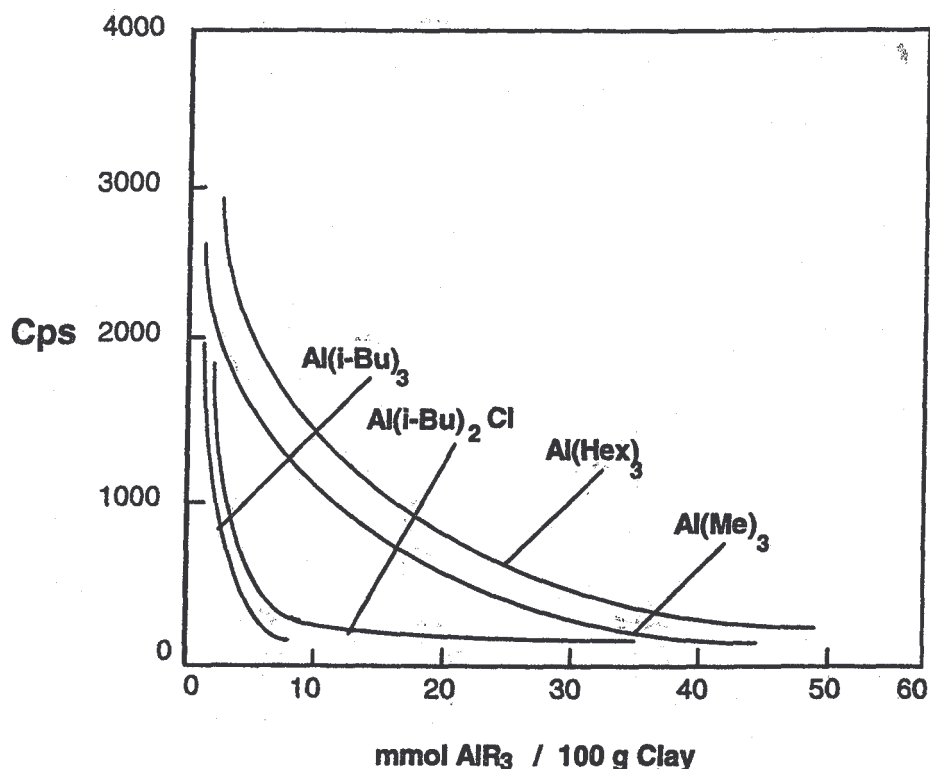


FIG. 10. Effect of trialkylaluminum on the viscosity of clay-hexane dispersions.

**Conditioning Minerals:** The filler used in polymerization-filled composites (PFCs) should have a neutral-to-acidic surface. Many fillers (such as alumina hydrates, silicas, water-insoluble silicates, insoluble calcium phosphates, titania, zinc oxide, iron oxide, etc., and mixtures thereof) naturally have neutral-to-acidic surfaces. Other fillers (such as calcium sulfate, calcium carbonate, barium sulfate, etc.; see Table 10) are basic in nature and thereby inhibit polymerization. Other minerals, such as mica and silicas that contain alkali metals or alkaline earth metals, show variable polymerization behavior [49].

When the filler is not neutral to acidic, polymerization can occur provided that the filler particles are previously treated with an acidic oxide such as silica, alumina, or hydrogenophosphate.

Actually, the filler is treated with a compound that is then hydrolyzed to an acidic oxide. For instance, carbonate fillers are merely coated by mixing an aqueous suspension containing about 10-50 wt% of the solid filler with an aqueous solution of 1-10 wt % of an aluminum salt. Other minerals can be coated by an aqueous salt solution in the presence of ammonia. Hydrogenophosphate coatings are obtained by treating the filler with phosphoric acid. Silica coating results from treatment of calcium carbonate with silicon tetrachloride. The reactions involved in the formation of these coatings may be schematized as in Eqs. 14-17.

TABLE 10 Mineral Oxides Requiring an Acid Coating

CaCO<sub>3</sub>, CaSO<sub>4</sub>, CaF<sub>2</sub>, CaSiO<sub>3</sub>  
BaCO<sub>3</sub>, BaSO<sub>4</sub>  
ZnCO<sub>3</sub>  
Dawsonite (Na<sub>2</sub>O·2CO<sub>2</sub>·2H<sub>2</sub>O)  
Basic silicas, micas, feldspar, and the like

Reprinted by permission from Ref. 5.



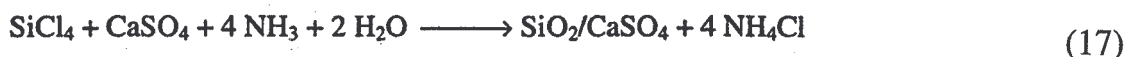
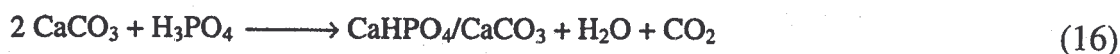
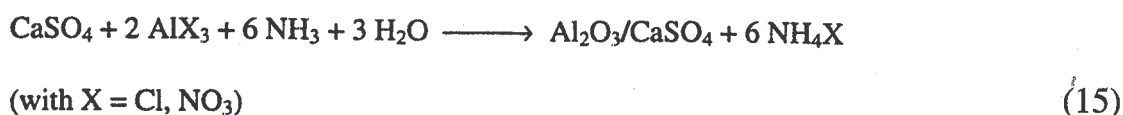
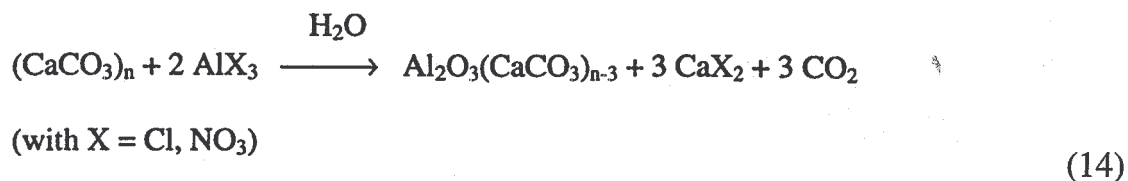


TABLE 11 Polymerization on Basic Minerals

	Zr, mmol/100g	Product, % mineral	Activity, g PE/(g filler h)
CaCO <sub>3</sub>	0.1	90 <sup>a</sup>	0.1
CaCO <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>	0.1	50	2.5
CaCO <sub>3</sub> -H <sub>3</sub> PO <sub>4</sub>	0.3	70	2.7
CaCO <sub>3</sub> -SiO <sub>2</sub>	0.3	72	1.1
CaSO <sub>4</sub>	0.1	Trace polymer	—
CaSO <sub>4</sub> -Al <sub>2</sub> O <sub>3</sub>	0.1	50	0.6

Reprinted by permission from Ref. 5. <sup>a</sup>Reaction stopped after 10% polymer formed.

#### 4.2.3. Homogeneity of the Polymerization-Filled Composites

Table 11 shows the effect on the ethylene polymerization rate of the coating of CaCO<sub>3</sub> or CaSO<sub>4</sub> with an acidic oxide [5].

One of the main targets of the polymerization-filling method is homogeneity of the final composites. This homogeneity may be merely estimated by molding the powdery composite into a film observed by transmitted light. Mineral-rich areas are very dark, and mineral-poor areas are more translucent.

Howard et al. [5] have developed a method based on the centrifugal force and grinding action of an air micronizer. This method is applicable to composite powders resulting from the polymerization.

The sample is introduced into the airstream of the micronizer, and the particles are ground by high-speed impacts and fractionated according to their size and density. Collection of these fractions provides a measure of the particle composition range. So, the blend of PE and mineral is completely separated. The early fractions are virtually pure mineral, and the later fractions are pure polymer. The change in composition throughout the fractionation is shown in Fig. 11. In contrast, a composite prepared by surface polymerization of ethylene onto clays gives fractions of a comparable mineral content.

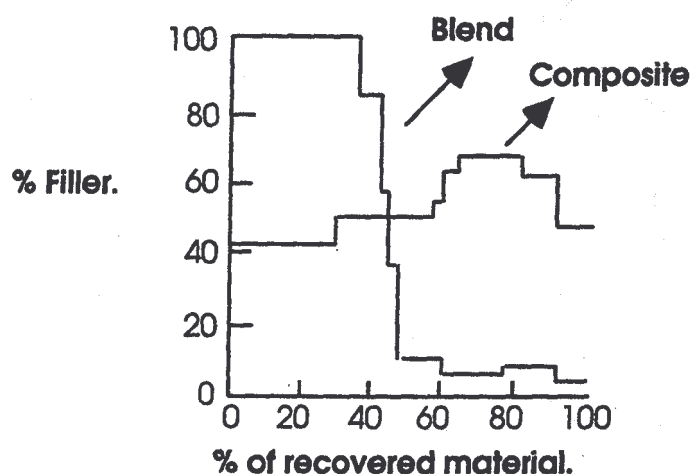


FIG. 11. Fractionation by micronization.

The degree of heterogeneity in clay-based composites prepared with various catalysts is illustrated in Table 12 [5]. Composition of the first fraction and dispersity  $\Delta$  or breadth of the distribution are measured. With a blend of PE and mineral, the first fraction is nearly pure mineral, the last one pure polymer, hence, the dispersity is very large. With  $TiCl_4$  as a catalyst, free mineral is present, and  $\Delta$  is still very large because polymerization preferably occurs on catalyst particles in solution rather than on the mineral surface. The final example is a homogeneous composite that shows no free mineral or polymer and has the narrowest composition distribution.

The major advantage of a homogeneous distribution of the filler within the matrix is that a higher filler loading is possible before the composite becomes brittle [5].

TABLE 12 Fractionation of Polyethylene/Clay Composites by Micronization

	Original sample	First fraction	Clay Maximum fraction	Minimum fraction	Dispersity $\Delta$
Blend	50	99	99	6	93
Clay- $TiCl_4$ /BusAl	40	16	51	16	35
Calcinated clay/' $Bu_3Al$	48	42	61	42	19

Reprinted by permission from Ref. 5.

#### 4.2.4. Properties of the Polymerization-Filled Composites

Added minerals provide polymers with increased stiffness or modulus. Howard, Glazar, and CoUette [111] used the Einstein-Guth-Gold equation (EGG) (Eq. 18) to compare composites prepared by polymerization-filling and melt blending and to investigate the effect of the mineral shape and content on the composite modulus;  $E_c$  and  $E_p$  are the composite and matrix modulus, respectively, and  $\phi$  is the volume fraction of filler.

$$E_c = E_p (1 + 2.5 \phi + 14.1 \phi^2) \quad (18)$$

As predicted by the EGG equation, the modulus of composites sharply increases with the filler content. For composites with clays, this equation underestimates  $E_c$  due to a filler shape effect [111].

The most desirable property of composites is toughness or impact resistance at high filler loadings. Polymerization-filled composites are substantially tougher than melt-blended analogues. The impact properties of PFCs, especially of clay composites, are very sensitive to molecular weight. Izod impact rises sharply as the inherent viscosity  $\eta_{inh}$  increases from about 12 to 20 (corresponding to an increase in  $M_w$  from  $2.1 \cdot 10^6$  to  $5.1 \cdot 10^6$ ; Fig. 12). A similar increase in impact strength is observed for unfilled PE as the molecular weight increases from  $10^5$  to  $10^6$ . This effect has been attributed to a decrease in crystallinity of the unfilled polymer.

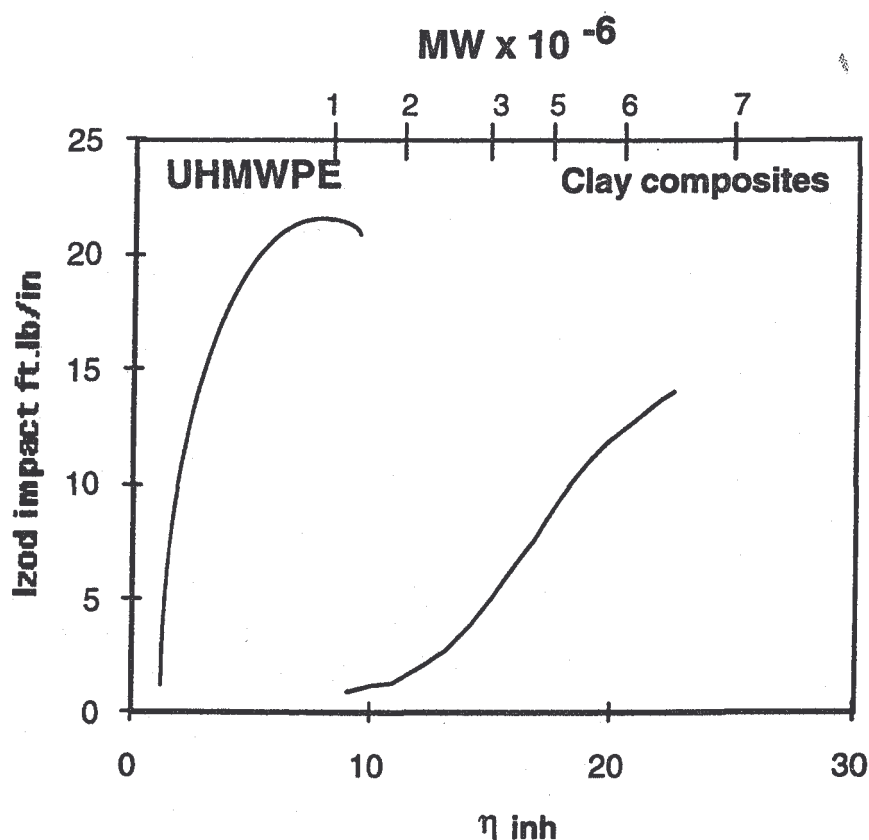


FIG. 12. Effect of molecular weight on the impact strength of clay composites (50 wt%).

The combination of high impact strength, ductile fracture, and high modulus that can be achieved by the polymerization-filling technique has been sought for a long time. Composites derived from clay and gibbsite ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) offer a particularly attractive balance of stiffness and toughness. They offer a high toughness at the same modulus or an increased stiffness at the same impact strength compared with some commercial plastics and with glass-reinforced resins (Fig. 13) [111].

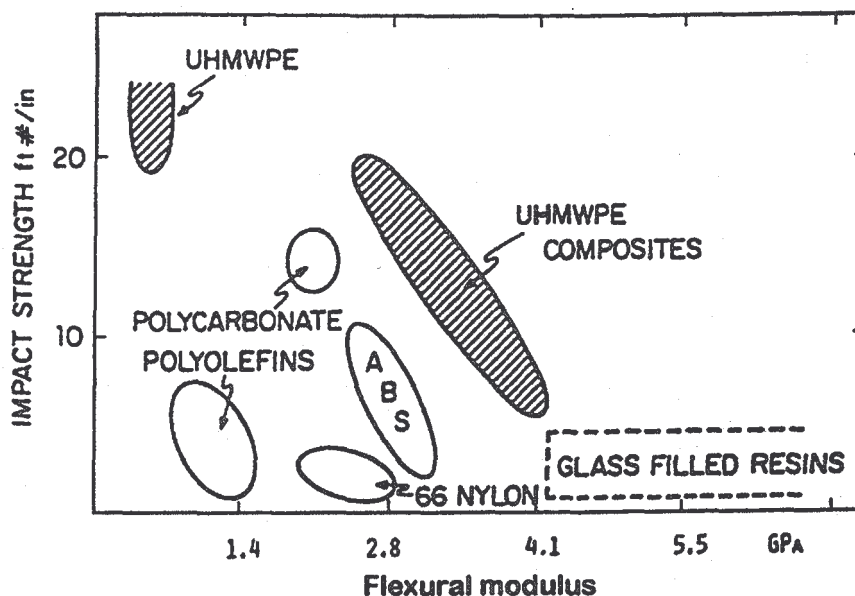


FIG. 13. Izod impact versus flexural modulus. (Reprinted with permission from Ref. 111.)

The weight fraction of the filler also influences the mechanical properties of composites prepared by the polymerization-filling process. The dependence of tensile strength  $\sigma$ , and relative elongation  $\epsilon$  on the filler content for the PFC is compared to melt-blended composites for which the matrix is a blend of UHM-WPE and PE (Fig. 14). Polymerization-filled composites (with tufa, kaolin, calcite,  $\text{Al}_2\text{O}_3$ , milled perlite, etc. as fillers) loaded up to 50-60 wt% have a relative elongation of about 200% at fracture [1].



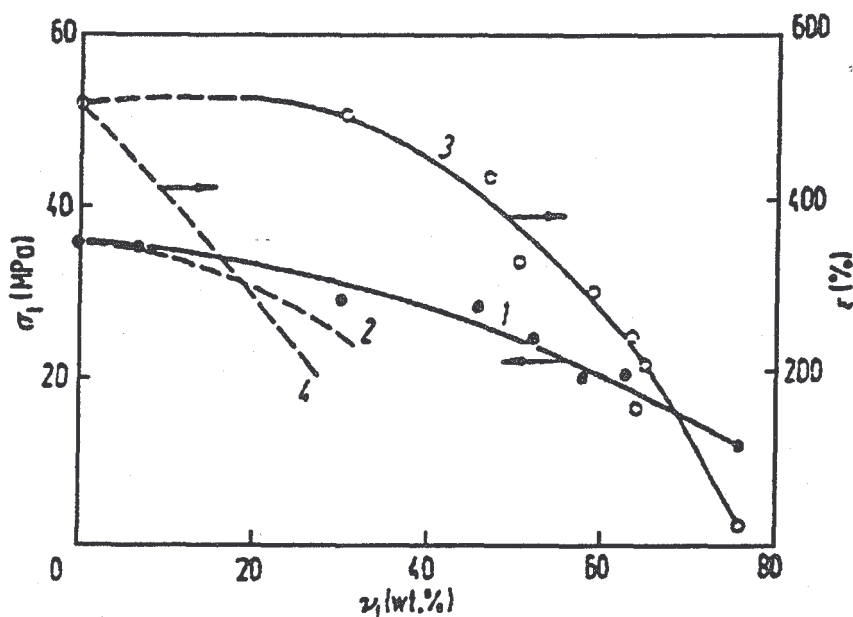


FIG. 14. Dependence of tensile strength  $\sigma$ , and elongation at break  $\epsilon$  for composites (5- $\mu\text{m}$  calcite particles) on the filler weight fraction. (1) and (3) are polymerization-filled UHMWPE composite; (2) and (4) are blended UHMWPE-PE composite. (Reprinted by permission from Ref. 1.)

The filler size may have an effect since kaolin particles of a small size (2  $\mu\text{m}$  instead of 9  $\mu\text{m}$ ) increase the Izod impact strength, the rupture strength, and the relative elongation, whereas the Young modulus and the heat distortion are slightly decreased [112].

It is essential that composites, whatever their production technique, can be molded and extruded. The UHMWPE that results from surface polymerization is a unique material since it is not transformed into a viscoelastic fluid when melted. Therefore, it cannot be processed by extrusion and injection molding. When heated and deformed by high shear forces, it is severely degraded and yields a material of a very broad molecular weight distribution. The mechanical properties of degraded UHMWPE are quite inferior to those of HDPEs of the same average molecular weight. Although UHMWPE cannot compete with commercial-grade HDPE in their traditional range of applications, it has some unique properties, such as high wear resistance, excellent chemical resistance, and impact strength, which may warrant an ever-increasing demand for it. Furthermore, UHMWPE-based composites have additional interesting properties, such as thermal stability [1], electric conductivity (using carbon black as filler) [114], and good fire resistance with a low smoke-generator factor (based on gibbsite fillers) [112, 115]. Moreover, the pressing, sintering, compression, and heat-molding techniques suitable for pure UHMWPE are also well suited to the filled material.

It proved to be quite a problem to decrease the molecular weight of polymerization-filled PE. An attempt was reported for ethylene polymerization in heptane in the presence of dispersed fillers (kaolin, talc, aluminum hydroxide) activated with the  $\text{VOCl}_3\text{-AlEt}_2\text{Cl}$  catalytic system [115]. The PE molecular mass was controlled by transfer to hydrogen, and the molecular weight was decreased from  $(1.8\text{-}2.5) \times 10^6$  to  $(1.2\text{-}1.6) \times 10^5$ , resulting in materials with melt flow indices close to the extrusion grades. Figures 15 and 16 show some physico-mechanical properties of such composites as a function of the molecular weight. A decrease in molecular weight can have a detrimental effect on some mechanical properties.

Very recently, some of us reported on the possibility of controlling the molecular weight of the growing PE chains over a wide molecular weight range corresponding to HDPE [85].

Composites were produced by ethylene polymerization promoted by an original aluminum/titanium/magnesium catalyst attached onto the filler surface (Eq. 19). The catalyst was fixed in such a way that either 50% or 25% of the kaolin hydroxyl groups were consumed in order to avoid the undesirable formation of free catalyst. When a basic filler such as barite was used, it had to be first coated with alumina in order to form an acidic surface (see Eqs. 14 and 15).

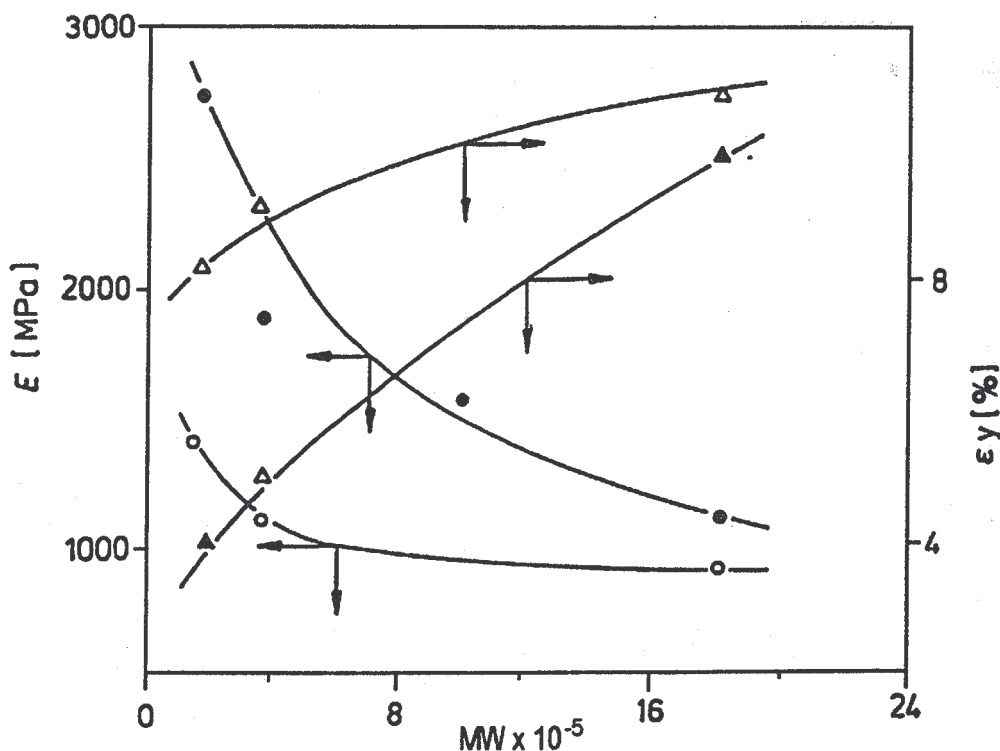


FIG. 15. Dependence of modulus  $E$  and yield strain  $\epsilon_y$  of the polymer matrix (unfilled symbols) and polyethylene-based composites polymerization filled with kaolin (filled symbols) on function of polymer molecular weight. Kaolin content: 30 wt%.

In this system, the catalyst composition is of prime importance, and the optimal Al/Ti/Mg composition has been found to be 120/0.75/10. At this constant catalytic composition, hydrogen is a convenient regulator of the molecular weight, which has been found to decrease as the square root of the hydrogen partial pressure (Keii's law; Fig. 17). Moreover, hydrogen also behaves as an efficient activator, which leads to a catalyst efficiency as high as 295 kg PE/g Ti-h (Table 13).

It has to be noted that  $\alpha$  olefins such as 1-octene also behave as active transfer agents, although in a rather complex way. Using a suitable combination of hydrogen and octene, the melt index ( $MI_2$ ) of a 32 wt% kaolin-containing composite is increased from 0.01 g/10 min (when 6 bar of hydrogen and no octene are used) up to 2.1 g/10 min (with 6 bar of hydrogen and  $8 \cdot 10^{-3}$  mole of 1-octene). Even though the melt index is still low, these PFCs can be processed and shaped into articles by standard processing techniques.

The superiority of these PFCs over melt-blended composites emerges from a comparison of the impact energy (IE) and the elongation at break  $\epsilon$ , (Table 14). It is, however, worth noting that a straightforward comparison of PFCs with melt-blended composites is quite a problem because of the difficulty of matching molecular weight and molecular weight distribution of the PE in each of between kaolin particles and the polymer. In contrast, Fig. 19a shows filler particles still attached to the polymeric matrix through PE fibrils.

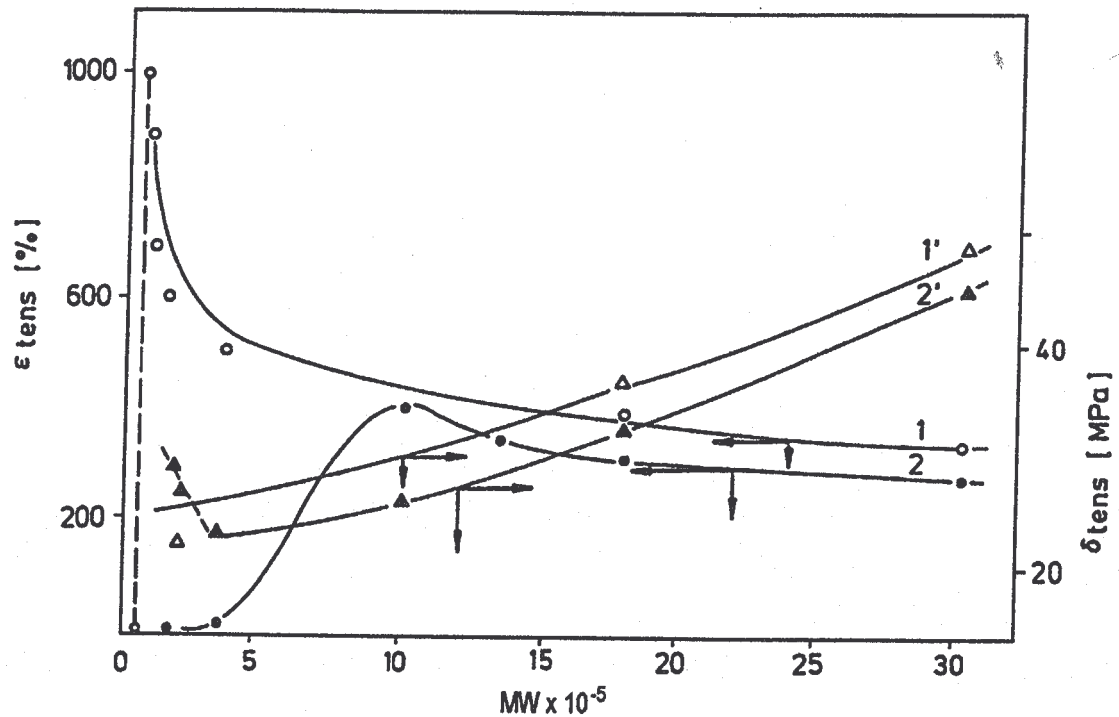
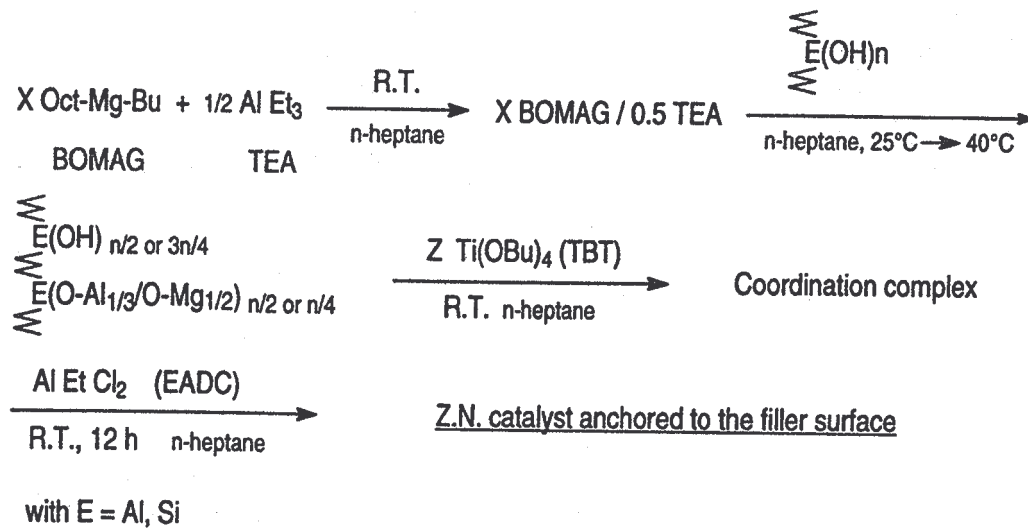
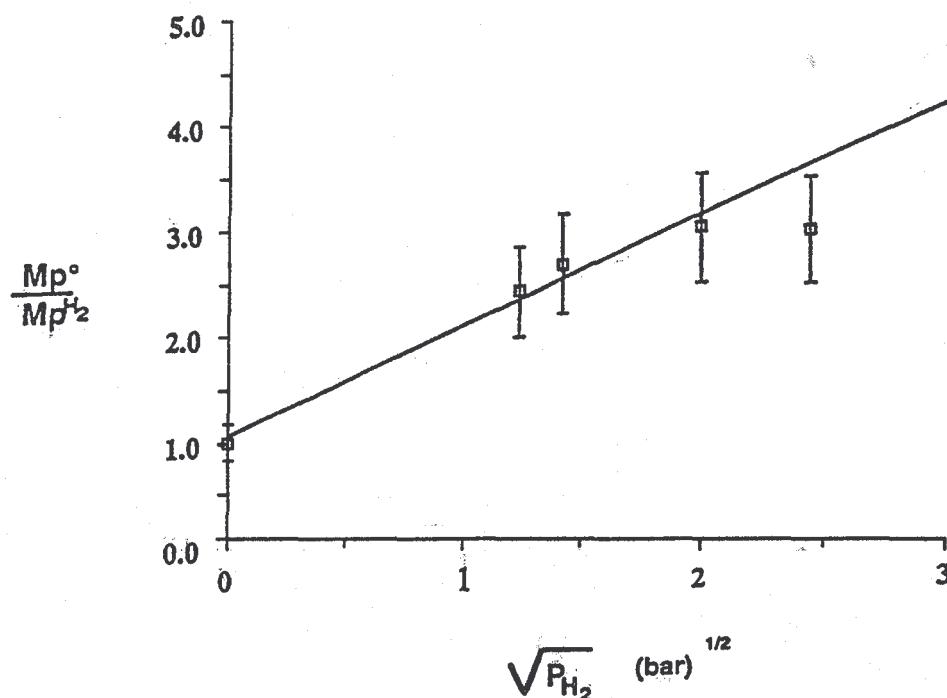


FIG. 16. Variation of relative elongation at rupture  $\epsilon_{tem}$  and ultimate tensile strength  $\epsilon_{tens}$  on molecular weight for polyethylene matrix (1, 1') and polymerization-filled composites (2, 2'). Kaolin content: 30 wt%.





**FIG. 17.** Dependence of the polyethylene molecular weight  $M_p$  on the square root of the hydrogen partial pressure. Polymerization conditions: Al/Ti/Mg = 120/0.75/10;  $-P_{C_2H_4} = 4$  bar; temperature = 60°C. (Reprinted by permission from Ref. 85a.)

**TABLE 13** Effect of Hydrogen Partial Pressure on Polyethylene

bar	CE, kg FEJ(E TvV)	MI <sub>2</sub>	MI <sub>10</sub> g/10 min	MI <sub>21</sub>	Mp <sup>a</sup> 10 <sup>-3</sup>
0.0	38	—	—	—	246
1.5	110	0.0	0.3	1.5	109
2.0	148	0.1	0.5	1.1	95
4.0	157	0.1	0.3	1.7	85
6.0	295	0.1	1.0	4.0	87

Reprinted by permission from Ref. 85a.

CE = catalyst efficiency; MI = melt flow index.

$P_{C_2H_4} = 4$  bar; kaolin content = 32 wt%; Al/Ti/Mg catalyst = 120/0J5/10. <sup>a</sup>Molecular weight at the maximum of the SEC elution peak.



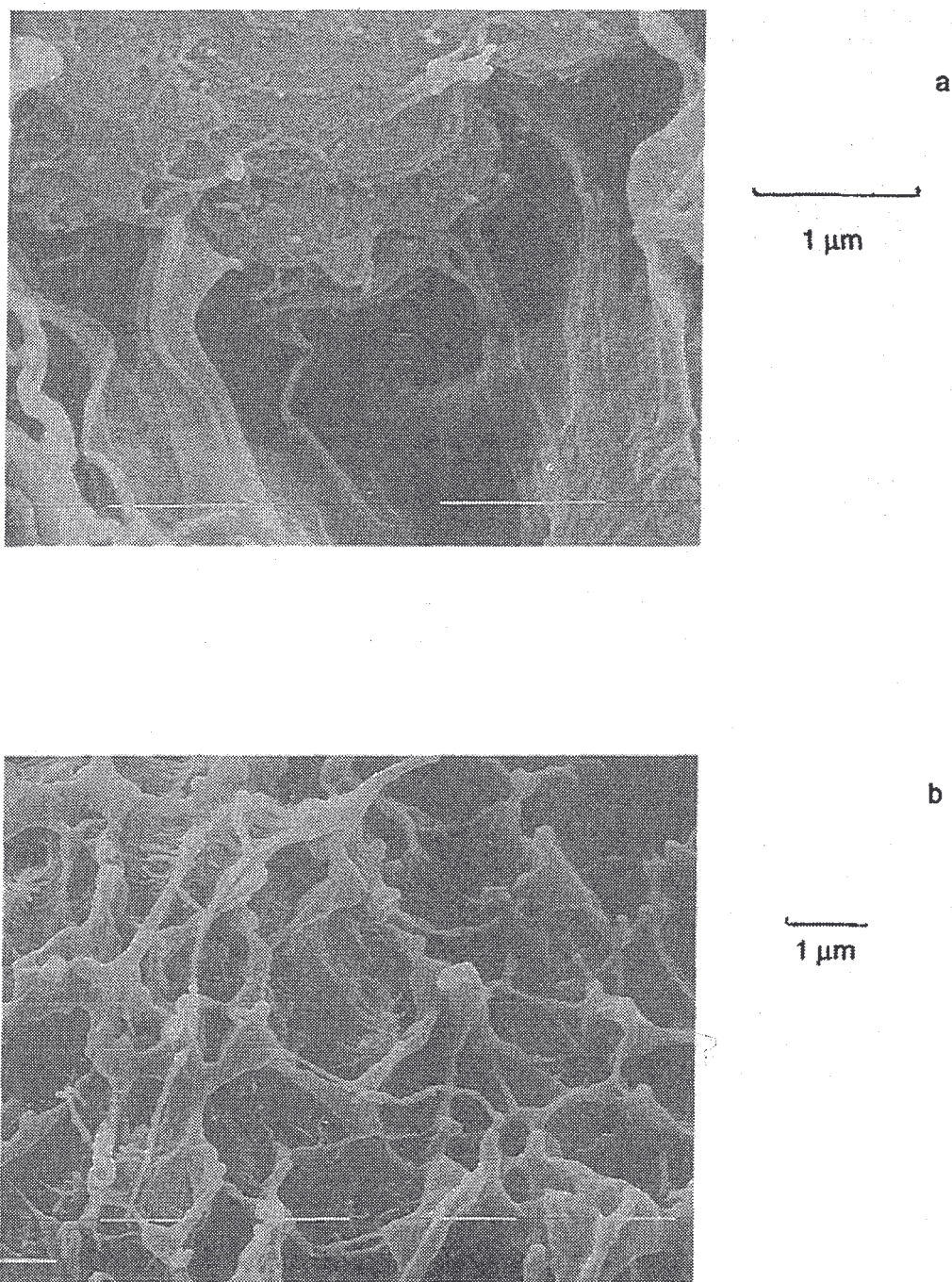


FIG. 19. SEM of fracture surfaces resulting from impact testing: (a) polymerization-filled composite; (b) melt-blended composite. (Reprinted by permission from Ref. 85b.)

These observations illustrate the improvement in adhesion promoted by the polymerization-filling technique. This is further highlighted by the study of PE growth from the kaolin surface. PFCs of increasing PE weight content have been synthesized and observed by SEM (Figs. 20a-20e).

Based on these observations, Fig. 21 is a sketch of the PE growth from the kaolin surface. Heaps of PE initially formed on the surface of kaolin plates grow with increasing polymerization time and finally overlap each other to cover the particle surface completely. At still increasing PE contents, fibrils bud from the surface and grow away. They ultimately interconnect the near-neighbor particles to each other.

The structures observed at high PE contents are completely different from those observed for PE produced by a traditional magnesium-supported titanium catalyst that gives globular PE particles (Fig. 22).

It must be noted that, for supported organometallic catalysts, the morphology of the formed polymer strongly depends on structural characteristics of the support, such as particle size, shape, and pore structure. Semikolenova et al. [80] studied the growth of PE as initiated by  $\text{Cr}(\text{C}_5\text{H}_5)_2$  and  $\text{Zr}(\text{BH}_4)_4$  anchored on aluminosilicate minerals such as tufa (irregular polyhedrons) and kaolin (plates). The polyolefinic chains produced by the catalyst supported on the nonporous aluminosilicate (tufa) first cover the filler with a uniform polymer film, so that the particle size increases until reaching a gain of 2-3  $\mu\text{m}$  in diameter. Then, these "primary" particles start to crack, with formation of "secondary" particles and ultimately wormlike particles (Fig. 23).

If the original size of the tufa particle is smaller than 2  $\mu\text{m}$ , wormlike particles are directly formed without the intermediate cracking of primary particles (Fig. 24). In the case of kaolin plates, the polymer growth on planes A would be responsible for the formation of wormlike particles (Fig. 25).

In conclusion, mechanical properties of PFCs strongly depend on the properties of the matrix, particularly when UHMWPE is formed. Other parameters that contribute to the improved properties of PFCs compared to the melt-blended analogues are a better dispersion of the filler combined with an enhanced inter-facial adhesion, as confirmed by SEM (Figs. 18a and 19a). Moreover, polyolefinic chains grow from the filler surface and/or pores and are thus in intimate contact with the particles. Polymer growth is strongly dependent on size and shape of the filler, leading to morphologies that completely differ from PE produced by traditional  $\text{MgCl}_2$ -supported catalysts.



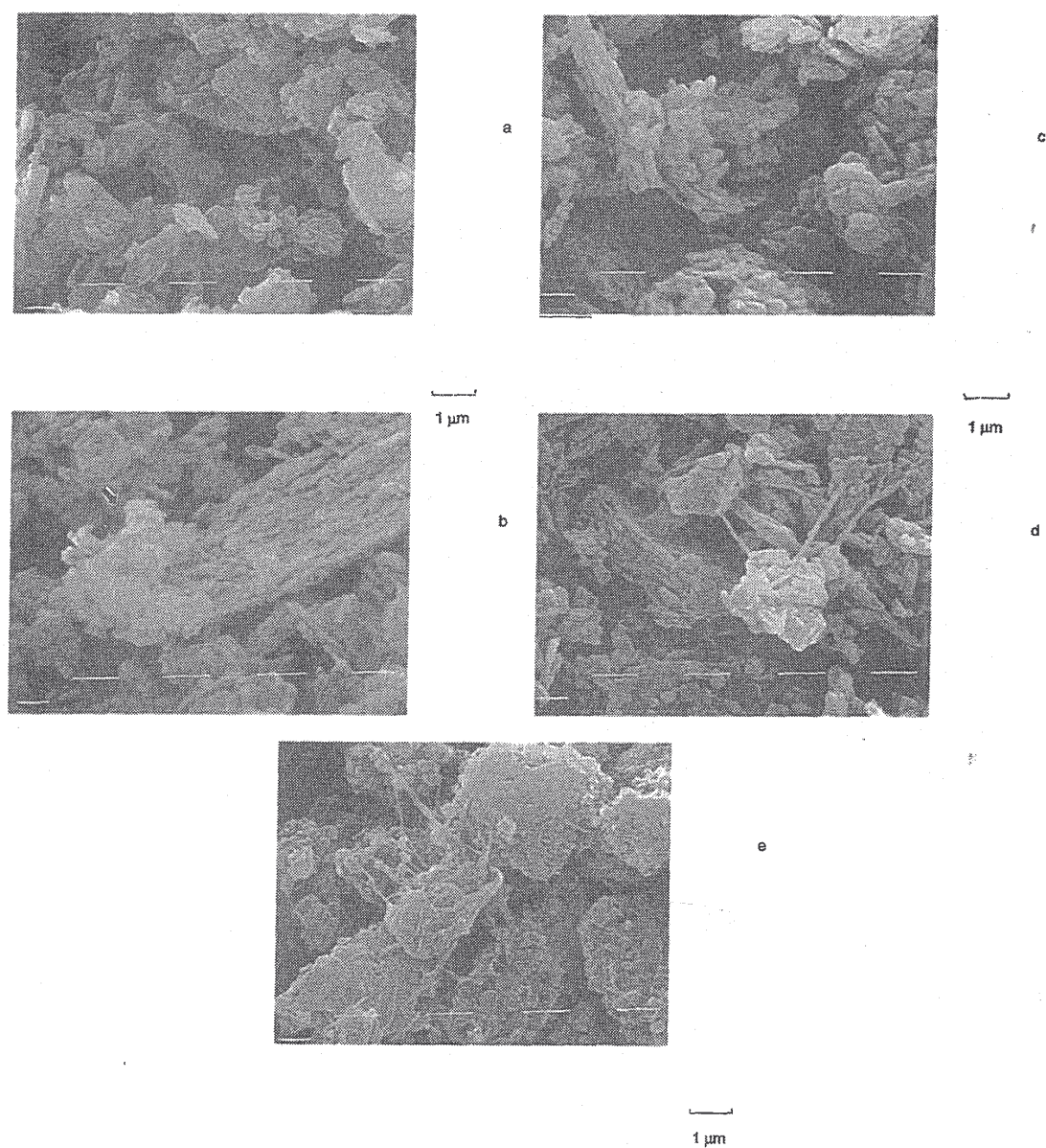


FIG. 20. SEM observations of HDPE growing on the surface of kaolin Satintone W/W. HDPE content: a, 0 wt%; b, 10 wt%; c, 20 wt%; d, 30 wt%; and e, 68 wt%. (Reprinted by permission from Ref. 85a.)

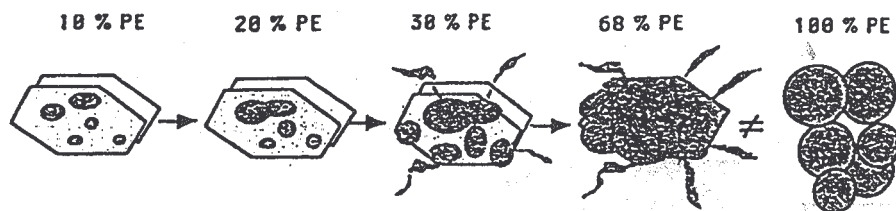
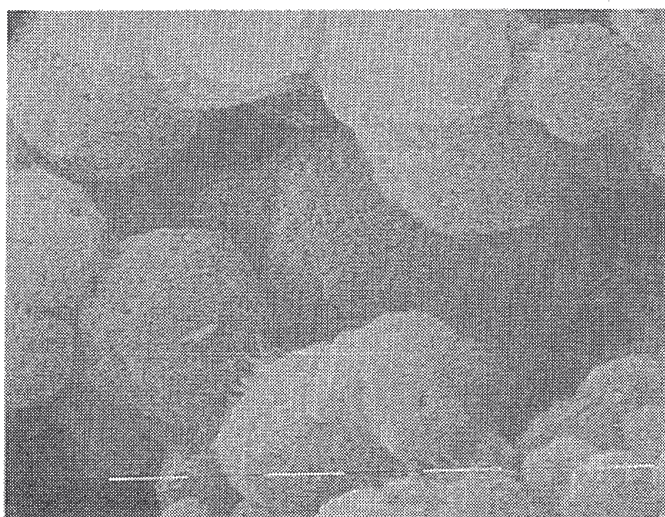


FIG. 21. Sketch of polyethylene growth on the surface of a kaolin plate. (Reprinted by permission from Ref. 85a.)



1  $\mu\text{m}$

FIG. 22. SEM observation of globular HDPE particles produced by a magnesium-supported titanium catalyst. (Reprinted by permission from Ref. 85a.)

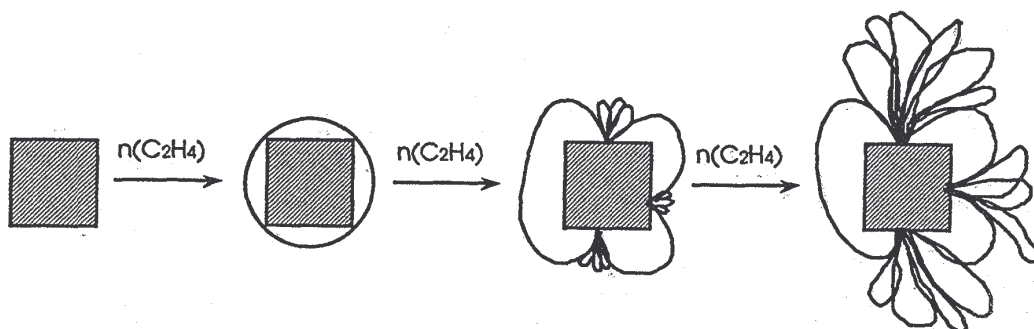


FIG. 23. Polyethylene growth on a large tufa support ( $>3 \mu\text{m}$ ).

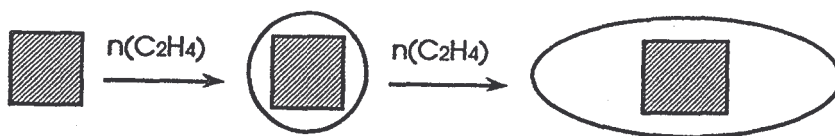


FIG. 24. Polyethylene growth on small tufa support ( $<2 \mu\text{m}$ ).

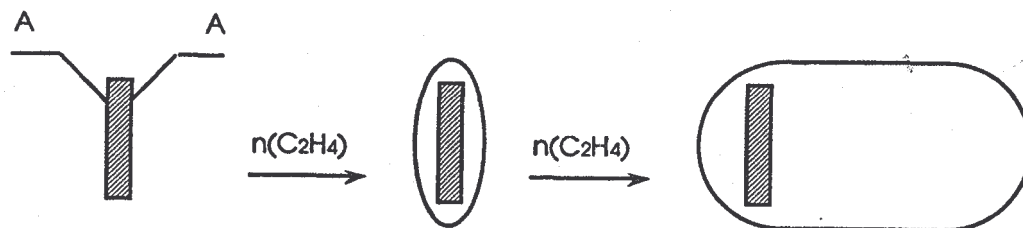


FIG. 25. Polyethylene growth on kaolin plates.

#### 4.2.5. Crystallization of the Growing of High-Density Polyethylene Chains

Dependence of the physicomechanical properties of PE on crystallinity is well known and is still valid for the filled materials [116]. The crystallization mechanism in polymers is usually complex [117]. In the presence of filler particles, crystallinity of a semicrystalline matrix is commonly increased, depending on the filler nature [118]. For instance, the crystallinity degree increases more rapidly in the presence of clay than in the presence of glass fiber or CaCO<sub>3</sub> (Table 15) [119]. In their study on glass-bead and mineral-filled PE, Dolakova and Hudecek [118] analyzed impact fracture surfaces by SEM and observed fibrils linking the particles and the matrix. Gähde et al. [120] observed a lamellar growth perpendicular to the interface in silane-modified, kaolin-filled PE. Chacko et al. [121] came to the same conclusion, particularly for Dupont-CaCO<sub>3</sub>/UHMWPE PFCs. The lamellae, indeed, nucleate on the filler surface and grow normal to the surface over about 300-400 nm [121].

Minkova and Magagnini [122] studied crystallization of PE prepared from a TiO<sub>4</sub>ZEt<sub>2</sub>AlCl-ClAlk or -marble-supported catalyst. The average size of spherulites is isothermally crystallized filled composites is lower than that of unfilled PE by 27-40% (Table 16). This indicates that the polymer nucleation density increases in the presence of chalk or marble fillers, which behave as efficient nucleating agents. When samples are crystallized at a cooling rate of 5°C/miri, the dimension of spherulites is slightly decreased by the filler compared to the case for isothermal crystallization. None of these fillers has a nucleating ability at a high cooling rate (20°C/min) [123].

According to Minkova, Velikova, and Damyanov [123], a supramolecular structure is formed around the filler particles. The active polymerization is located on the particle surface, from which the polymerization starts. At a finite distance from the active sites, the polymer chains begin to crystallize by folding, and lamellae are formed normal to the filler surface. The lamellae form a radial envelope around the filler particles. Recently, Howard [124] has claimed the formation of a bimodal crystalline structure of folded lamellae and highly extended chains observed by DSC analysis. Such a supramolecular structure is thought to contribute favorably to the mechanical properties of the PFCs.

**TABLE 15** Crystallinity Degree of High-Density Polyethylene Filled with Various Fillers

Incorporated filler	wt%	Crystallimty degree
Unfilled HDPE	0	71.2
CaCO <sub>3</sub>	15	71.7
Clay	15	74.6
Clay	30	76.5
Glass fiber	15	73.1

Reprinted by permission from Ref. 119.



**TABLE 16** Dependence of Spherulite Radius on Filler Concentration

Degree of filling, wt%	R, ( $\mu\text{m}$ ), <sup>a</sup> isothermal crystallization <sup>1</sup>	R, ( $\mu\text{m}$ ), <sup>a</sup> nonisothermal crystallization, 5°C/min <sup>c</sup>	R ( $\mu\text{m}$ ), <sup>a</sup> nonisothermal crystallization, 20°C/min <sup>c</sup>
0.0	5.2	3.9	3.5
Chalk			
7.3	3.5	3.7	3.3
11.8	3.8	3.5	3.4
23.5	3.8	3.3	3.5
Marble			
5.2	3.2	3.0	3.5
12.1	3.1	2.6	3.4
21.7	3.1	2.4	3.4

Reprinted by permission from Ref. 122.

The average size of the spherulites was determined using  $H_v$  diffraction patterns of low-angle light scattering. Isotherm at 122°C. <sup>c</sup>DSC measurements: same cooling and heating rates.

## 5. CONCLUSIONS

Originally, polymers were filled with inert filler to cut prices of expensive polymers. The discovery of rubber reinforcement provided filler with a completely new role. However, the production of highly filled composites based on semicrystalline polymers, such as HDPE, was not very encouraging. Most efforts aimed to improve the interfacial adhesion using compounds not only reactive toward the filler surface, but also compatible with the polymer matrix, such as aminosilanes and titanate esters. Encapsulation of the filler with special polymers was also investigated.

The polymerization-filling technique is a new way to produce composites with remarkably improved performances. Composites are produced in one step as the olefin is polymerized by a coordination catalyst anchored on the surface of mineral particles. This provides the filler with a polymer coating and finally results in homogeneous composites. Indeed, the fine filler dispersion that results from the catalyst preparation is preserved during the ethylene polymerization.

These composites consist of UHMWPE, and the filler content may be as high as 85 wt% of minerals. A remarkable combination of advantageous mechanical properties in terms of stiffness, creep, heat deflection, and flame resistance is observed, while the impact resistance is preserved.

The polymerization-filling technique has been successfully extended to clays such as kaolin, calcinated kaolin, gibbsite alumina trihydrate, mica, and so on, but also to calcium carbonate, calcium silicate, calcium sulfate, silica, calcium fluoride, calcium phosphates, titanium dioxides, zinc oxide, and various mixtures of these minerals. The composite properties are dependent on the mineral content, shape, and size. Table 17 illustrates some mechanical properties of PE composites prepared by polymerization from the surface of various fillers. It shows the marked improvement in the properties of mineral-PE composites even when the mineral content is as high as 70% and more.

The impact resistance is remarkably high even at low temperatures (Fig. 26) in comparison

with polycarbonate and flame-resistant acrylonitrile-butadiene-styrene (ABS) plastics. The composites containing alumina trihydrate are also flame resistant, and when they do burn under forced conditions, they develop very little smoke. Figure 27 shows the extremely low smoke generation of PE/  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  composites over wood and selected commercial polyolefins.

**TABLE 17** Mechanical Properties of UHMWPE-Mineral Composites Prepared by the Polymerization-Filling Technique

Filler <sup>3</sup>	Catalyst system	Filler content %	Izod impact, j/m, -18°C	Elastic modulus $E$ , GPa	Ultimate tensile strength $\sigma_b$ , MPa	Ultimate elongation $\epsilon_b$ , %
Kaolin (1)	Ti <sup>b</sup>	66 <sup>e</sup>	280	4.0	20	230
	Ti <sup>c</sup>	69 <sup>f</sup>	318	4.1	17	110
	Zr <sup>d</sup>	73 <sup>e</sup>	223	1.6	19	80
	Zr <sup>d</sup>	73 <sup>f</sup>	80	6.2	17	23
Talc (2)	Cr <sup>e</sup>	59	186	4.4	18	150
Gibbsite (3)	Ti <sup>b</sup>	69	390	2.5	14	160
Mica (2)	Zr <sup>d</sup>	44	80	6.2	—	—
CaCO <sub>3</sub>	Zr <sup>d</sup>	61	477	4.1	22	330
		75	191	5.2	17	100
Fe <sub>2</sub> O <sub>3</sub>	Zr <sup>d</sup>	67	>800	3.9	23	85
		78	201	6.5	22	1
Glass (4)	Zr <sup>d</sup>	81	1.33	21.3	68	1
PAN (4)	Zr <sup>d</sup>	72	345	3.2	63	45
		91	376	4.2	48	26
		0	79	0.7	—	900
HDPE, $M_w = 90\text{K}$		0	79	0.7	—	900
UHMWPE, $M_w \geq 10^6\text{K}$		0	1060	0.6	—	1000

<sup>a</sup>Mineral shape: (1) rupture stack plates; (2) thin plates; (3) irregularly spherical; (4) continuous fibrous.

<sup>b</sup>Hydrolyzed  $\text{TiCl}_4$ . <sup>c</sup>Hydrolyzed  $\text{Ti}(\text{O}^i\text{Pr})_4$ . <sup>d</sup> $\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)/\text{Bu}_3\text{Al}$ . <sup>e</sup>Average particle size = 2  $\mu\text{m}$ , <sup>f</sup>Average size = 9  $\mu\text{m}$ .

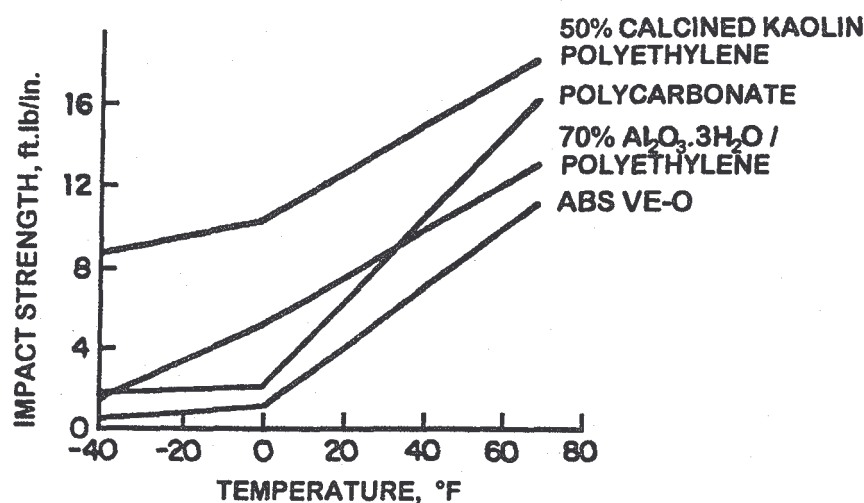


FIG. 26. Dependence of notched Izod impact strength on the temperature for different composites. (Reprinted by permission from Ref. 125.)

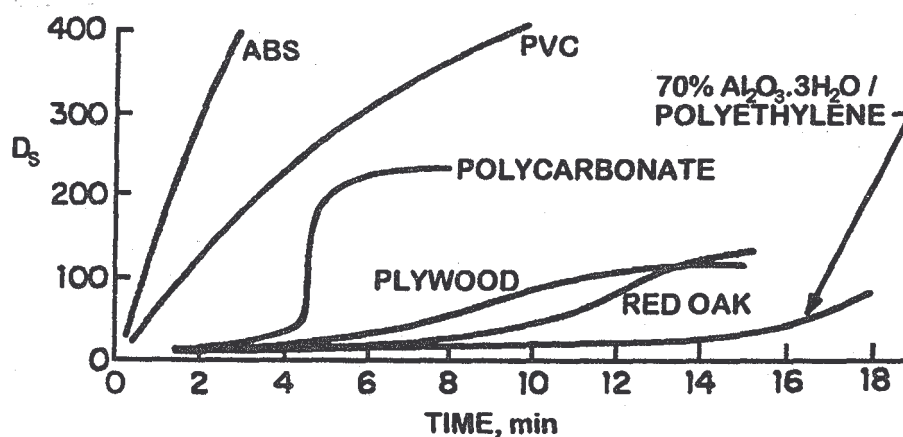


FIG. 27. Measurement of smoke generation in the NBS flaming mode for different materials. (Reprinted by permission from Ref. 125.)

Almost no smoke is formed in the flaming mode within 14 min. The same composites, in spite of the high mineral loading, still have electrical properties suitable for low-voltage insulation applications, although they are not as good as UHMWPE [125].

A new trend for particulate-filled polyolefin is to use filler bearing intrinsic properties. Metallic fillers seem particularly interesting since they can produce materials with original properties in electromagnetic shielding, heat conduction, or conversion of mechanical to electrical signals [23, 126, 127].

Novokshonova and Meshkova [128] and Galashina [129] recently reviewed the applications of PFGs based on PE or polypropylene and various fillers such as Al(OH)<sub>3</sub> and Sb<sub>2</sub>O<sub>3</sub>, which provide self-extinguishing composites; expanded perlite for heat-insulating materials; aluminum powder for heat-conducting and dielectric properties; and graphite and carbon black for electricity- and heat-conducting materials. Other more technical fillers [129] have also been used, such as silicon for photoconductivity, magnetic fillers, piezo- and pyroceramics, as well as high-temperature superconducting ceramics (YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>). For such specific fillers, the polymerization-filling technique appears to be the only suitable method for the preparation of these materials since they cannot retain their properties during a melt-blending process.

New types of fillers and the opportunity to extend the technique to the last generation of catalysts such as metallocenes [130-132] opens the polymerization-filling technique to good prospects in the field of material science and technology. Actually, this method involves the fixation of the active polymerization catalyst without the necessity for the presence of neutral-to-acidic species at the surface of the filler [133]. This new development in the polymerization-filling technique allows synthesis of broader kinds of polyolefinic matrices (e.g., HDPE, LLDPE, PP) [134] on virtually every type of filler particles [135] (e.g., kaolin, barite, magnesium hydroxide, ferrites, graphite, carbon blacks, nickel powder, etc.).

## ACKNOWLEDGMENTS

The authors are very much indebted to the Services Fédéraux des Affaires Scientifiques, Techniques et Culturelles for general support to CERM in the frame of the Pôles d'Attraction Interuniversitaires: Chimie et catalyse supramoléculaire. The authors are also grateful to DOW Europe (Terneuzen, The Netherlands) and to Dr. M. Garcia Marti for fruitful discussions.

Ph. Dubois is a research associate of the Belgian National Fund for Scientific Research (FNRS).

## REFERENCES

1. A. A. Berlin, S. A. Volfson, N. S. Enikolopian, and S. S. Negmatov, *Principles of Polymer Composites* (G. Henrici-Olivé and S. Olive, eds.), Springer-Verlag, Berlin, 1986, p. 1.
2. D. M. Kalyon, *Chemtech*, 25, 22 (1995) and the references cited therein.
3. F. R. Eirich, *J. Appl. Polym. Sci. Appl. Polym. Symp.*, 39, 93 (1984).
4. D. G. Thomas, *J. Colloid Sci.*, 20, 267 (1965).
5. E. G. Howard, R. D. Lipscomb, R. N. MacDonald, B. L. Glazar, C. W. Tullock, and J. W. Collette, *Ind. Eng. Chem. Prod. Res. Dev.*, 20, 421 (1981).
6. F. M. Fowkes, *J. Colloid Interface Sci.*, 28, 493 (1968).
7. V. Svehlova and E. Poloucek, *Angew. Makromol. Chem.*, 153, 197 (1987).
8. V. Svehlova and E. Poloucek, *Angew. Makromol. Chem.*, 174, 205 (1990).
9. C. B. Bucknall, *Adv. Polym. Sci.*, 27, 121 (1978).
10. F. Fowkes, D. C. McCarthy, and J. A. Wolfe, *ACS Polym. Prepr.*, 24, 228 (1983).
11. M. Y. Boluk and H. P. Schreiber, *J. Appl. Polym. Sci.*, 40, 1783 (1990).
12. H. P. Schreiber and F. S. Germain, *J. Adhesion Sci. Technol.*, 4, 319 (1990).
13. J. H. Plummer and C. F. Neumeier, *SPI Reinforced Plast. Div. Prepr.*, 28, 1 (1964).
14. S. Serman and J. G. Marsden, *Mod. Plast.*, 125 (July 1963).
15. D. G. Hawthorne and D. H. Solomon, *J. Macromol. Sci.—Chem.*, A8, 659 (1974).
16. L. E. Nielsen, *J. Appl. Polym. Sci.*, 10, 97 (1966).
17. S. J. Monte and P. F. Briuns, *Mod. Plast.*, 68 (1974).
18. C. D. Han, T. Van den Weghe, P. Shete, and J. R. Haw, *Polym. Eng. Sci.*, 21, 196 (1981).
19. M. Arroyo, M. Sanchez, and J. P. Vigo, *Polym. Eng. Sci.*, 31, 245 (1991).
20. M. Arroyo, F. Perez, and J. P. Vigo, *Polym. Compos.*, 7, 448 (1986).
21. M. Arroyo, F. Perez, and J. P. Vigo, *J. Appl. Polym. Sci.*, 32, 5105 (1986).
22. R. Rothon, *Particulate-Filled Polymer Composites* (R. Rothon, ed.), *Polym. Sci. Tech. Series*, Longman Scientific and Technical, Harlow, 1995, Chap. 4.
23. K. Ghosh and S. N. Maiti, *J. Appl. Polym. Sci.*, 60, 323 (1996).
24. Z. Liu and M. Gilbert, *J. Appl. Polym. Sci.*, 59, 1087 (1996).
25. K. Mitsuishi, *Angew. Makromol. Chem.*, 248, 73 (1997).
26. B. Pukanszky, E. Fekete, and F. Tudos, *Makromol. Chem., Macromol. Symp.*, 28, 165 (1989).
27. T. Nakatsuka, *Polym. Sci. Technol.*, 27, 51 (1985).
28. J. Jancar, A. Dianselmo, and A. T. Dibenedetto, *Polym. Eng. Sci.*, 32, 1394 (1992).
29. J. Jancar and J. Kucera, *Polym. Eng. Sci.*, 30, IU (1990).
30. S. Datta, N. Dharmarajan, G. Versstrate, and L. Ban, *Polym. Ekg. Sci.*, 33, 721 (1993).
31. P. R. Hornsby and C. L. Watson, *J. Mater. Sci.*, 30, 5347 (1995).
32. E. Morales, M. C. Ojeda, A. Linares, and J. L. Acosta, *Polym. Eng. Sci.*, 32, 769 (1992).
33. E. P. Plueddmann, *ACS Polym. Prepr.*, 24, 196 (1983).
34. H. Ishida, *ACS Polym. Prepr.*, 24, 198 (1983).
35. L. A. Utracki and B. Fisa, *Polym. Compos.*, 3, 193 (1982).
36. T. M. Malik, *Polym. Bull.*, 26, 709 (1991).
37. G. A. McFarren, T. F. Sanderson, and F. G. Schappell, *Polym. Eng. Sci.*, 17, 46 (1977).
38. J. D. Miller, H. Ishida, and F. H. J. Maurer, *J. Mater. Sci.*, 24, 2555 (1989).
39. J. D. Miller, H. Ishida, and F. H. J. Maurer, *Rheol. Acta*, 27, 397 (1988).

40. Y. Wang, J. Lu, and G. Wang, *J. Appl. Polym. Sci.*, **64**, 1275 (1997).
41. M. Atsuta and D. T. Turner, *Polym. Compos.*, **3**, 83 (1982).
42. H. J. Bixler and G. J. Fallick, U.S. Pat. 3,471,439 (October 7, 1969).
43. R. Hausslein and G. J. Fallick, *Appl. Polym. Symp.*, **11**, 119 (1969).
44. G. J. Fallick, H. J. Bixler, R. A. Marsella, F. R. Garner, and E. M. Fettes, *Mod. Plast.*, **45**, 143 (1968).
45. D. G. Hawthorne, J. H. Hodgkin, B. C. Loft, and D. H. Solomon, *J. Macromol. Sci.—Chem.*, **A8**, 649 (1974).
46. J. H. Hodgkin and D. H. Solomon, *J. Macromol. Sci.—Chem.*, **A8**, 621 (1974).
47. A. Galeski and R. Kalinski, in *Polymer Blends: Processing, Morphology and Properties*, Plenum, New York, 1980, p. 435.
48. B. M. Badran, A. Galeski, and M. Kryszewski, *J. Appl. Polym. Sci.*, **27**, 3669 (1982).
49. R. Kalinski, A. Galeski, and M. Kryszewski, *J. Appl. Polym. Sci.*, **26**, 4047 (1981).
50. A. Galeski, M. Kryszewski, and T. Kowalewski, *Polym. Eng. Sci.*, **32**, 1217 (1992).
51. M. L. Fridman, N. S. Enikolopyan, et al., *Proc. IX Symp. Synthesis of Props. Polym.-Filled Polyolefins*, Chernogolovka (Moscow District), 113 (1982); see Chap. 1, p. 34 in Ref. 1.
52. Y. I. Yermakov, V. A. Zakharov, and G. A. Nesterov, Catalytic Polymerization of Olefins. In *Studies in Surf. and Cat.*, Vol. 25 (T. Keit and S. Kazuo, eds.), Elsevier, Amsterdam, 1986, p. 181.
53. R. L. Banks and C. F. Cook, *Catalyst Technology: Discovery to Commercialisation, Disproportionation of Propylene in Modern Aspect of Catalysis*, Nauka, Novosibirsk, 1978, p. 149.
54. D. C. Bailey and S. H. Langer, *Chem. Rev.*, **81**, 105 (1981).
55. R. D. Lipscomb, U.S. Pat. 3,950,303 (1976).
56. E. G. Howard, U.S. Pat. 4,104,243 (1978).
57. E. G. Howard, U.S. Pat. 4,097,447 (1978).
58. N. S. Enikolopian, USSR Pat. 763,379 (1976); U.S. Pat. 4,241,112 (1980).
59. L. A. Kostandov, USSR Pat. 787,394 (1976); U.S. Pat. 4,241,138 (1980).
60. Idemitsu Kosan, Jap. Pat. 60,106,810 (1983).
61. E. G. Howard, U.S. Pat. 4,151,126 (1979).
62. S. Casenave, A. Ait-Kadi, and B. Riedl, *Can. J. Chem. Eng.*, **74**, 308 (1996).
63. Imperial Chemical Industries, Br. Pat., 1,420,315 (1975).
64. H. Hayashi, K. Matono, S. Asahi, M. Uoi, E.P. Pat. 0 142 143 B1 (1984).
65. F. S. D'yachkovskii, L. A. Novokshonova, and V. I. Tsvetkova, *Intl. J. Polym. Mater.*, **15**, 277 (1991).
66. J. A. Orsino, Ger. Pat. 1,494,876 (1966).
67. Q. Wang, S. Kaliaguine, and A. Ait-Kadi, *J. Appl. Polym. Sci.*, **44**, 1107 (1992).
68. Kruse Uno, U.S. Pat. 3,503,785 (1970).
69. Q. Wang, A. Ait-Kadi, and S. Kaliaguine, *J. Appl. Polym. Sci.*, **45**, i023 (1992).
70. J. M. Patterson and S. Tsai, Reinforcement. In *Encycl. Polym. Sci. Eng.*, (J. I. Kroschwitz, ed.), 2nd ed., Vol. 14, Wiley Interscience, New York, 1988, p. 391.
71. A. K. Dhingra and H. G. Lauterbach, Fibers, Engineering. In *Encycl. Polym. Sci. Eng.*, (J. I. Kroschwitz, ed.), 2nd ed., Vol. 6, Wiley Interscience, New York, 1986, p. 765.
72. H. S. Katz and J. V. Milewski, *Handbook of Fillers and Reinforcements for Plastics*, Van Nostrand, New York, 1978.
73. J. A. Orsino, D. F. Herman, and J. Brancato, U.S. Pat. 3,121,698 (1964).
74. D. F. Herman, U. Kruse, and J. J. Brancato, *J. Polym. Sci.*, **11**, 75 (1965).
75. F. S. D'yachkovskii and L. A. Novokshonova, Ref. 94 in our Ref. 1.
76. J. P. Candlin and H. Thomas, *Adv. Chem. Ser.*, **132**, 212 (1974).
77. V. A. Zakharov, V. K. Dudchenko, E. A. Paukshtis, L. G. Karakchiev, and Y. I.



- Yermakov, *J. Mol. Catal.*, 2, 421 (1977).
78. B. Diedrich, *ACS Polym. Prepr.*, 16, 316 (1975).
  79. A. Munoz-Escalona, *ACS Polym. Prepr.*, 24, 112 (1983).
  80. N. V. Semikolenova, G. A. Nesterov, V. A. Zakharov, G. N. Krjukova, and V. P. Ivanov, *Makromol. Chem.*, 189, 1739 (1988).
  81. W. Schoppel and K. H. Reichert, *Makromol. Chem. Rapid Commun.*, 3, 483 (1982).
  82. D. Damyanov, M. Velikova, and L. Petkov, *Eur. Polym. J.*, 15, 233 (1979).
  83. S. Lin, H. Wang, Q. Zhang, Z. Lu, and Y. Lu, Catalytic Polymerization of Olefins. In *Studies in Surf. and Cat.*, Vol. 25 (T. Keit and S. Kazuo, eds.), Elsevier, Amsterdam, 1986, p. 91.
  84. G. R. Marchand, R. Fuentes, and W. M. Coleman, U.S. Pat. 4,910,272 (1990).
  85. (a) F. Hindryckx, Ph. Dubois, Ph. Teyssie, R. Jerome, and M. Garcia Marti, *J. Appl. Polym. Sci.*, 64, 423 (1997); (b) F. Hindryckx, Ph. Dubois, Ph. Teyssie, R. Jerome, and M. Garcia Marti, *J. Appl. Polym. Sci.*, 64, 439 (1997).
  86. G. A. Nesterov, V. A. Zakharov, V. V. Volkov, and K. G. Myakishev, *J. Mol. Catal.*, 36, 253 (1986).
  87. Y. I. Yermakov, *J. Mol. Catal.*, 21, 35 (1983).
  88. L. Minkova, M. Velikova, and D. Damyanov, *Eur. Polym. J.*, 26, 1161 (1990).
  89. D. Damyanov, I. Ivanov, and M. Velikova, *Eur. Polym. J.*, 24, 657 (1988).
  90. M. Mihailov, L. Minkova, and E. Nedkov, *Makromol. Chem.*, 180, 2351 (1979).
  91. D. Damyanov, I. Ivanov, and M. Velikova, *Eur. Polym. J.*, 24, 657 (1988).
  92. G. A. Nesterov, V. A. Zakharov, E. A. Paukshtis, E. N. Yurchenko, and Y. I. Ermakov, *Kinet. Catal.* [Eng. transl.], 20, 349 (1979).
  93. C. W. Tullock, F. N. Tebbe, R. Mulhaupt, D. W. Ovenall, R. A. Setterquist, and S. D. Ittel, *J. Polym. Sci., Part A; Polym. Chem.*, 27, 3063 (1989).
  94. C. W. Tullock, R. Mulhaupt, and S. D. Ittel, *Makromol. Chem. Rapid Commun.*, 10, 19 (1989).
  95. D. Martineau, P. Dumas, and P. Sigwalt, *Makromol. Chem.*, 184, 1389 (1983).
  96. J. Ulbricht and J. Giesemann, *Makromol. Chem., Macromol. Symp.*, 12, 53 (1987).
  97. A. Akar, N. C. Billingham, and P. D. Calvert, *Polymer*, 24, 889 (1983).
  98. E. G. Howard, U.S. Pat. 4,187,210 (1980).
  99. N. V. Semikolenova, G. A. Nesterov, G. N. Kryukova, V. P. Ivanov, and V. A. Zakharov, *Polym. Sci USSR*, 27, 2248 (1985).
  100. N. V. Semikolenova, G. A. Nesterov, and V. A. Zakharov, *Polym. Sci USSR*, 28, 186 (1986).
  101. D. Damyanov and M. Velikova, *Eur. Polym. J.*, 15, 1075 (1979).
  102. I. N. Meshkova, T. M. Ushkova, I. L. Dubnikova, Y. M. Kazakov, Y. E. Shashkova, N. M. Rudneva, N. K. Portnaya, G. N. Kornienko, V. I. Sergeev, A. I. Petrosyan, A. I. Makhin'ko, and F. S. D'yachkovskii, *Polym. Sci USSR*, 28, 724 (1986).
  103. D. G. H. Ballard, *J. Polym. Sci Polym. Chem. Ed.*, 13, 2191 (1975).
  104. E. G. Howard, U.S. Pat. 4,187,210 (1980).
  105. N. N. Vlasova, V. I. Sergeev, P. Y. Matkovskii, N. S. Yenikolopyan, A. T. Papoyan, B. Y. Vostorgov, L. N. Grigorov, S. A. Bukanova, L. O. Bunina, N. S. Kogarko, L. A. Tkachenko, and V. V. Smirnov, *Polym. Sci USSR*, 27, 2552 (1985).
  106. H. Kothandaraman and M. S. Devi, *J. Polym. Sci., Part A; Polym. Chem.*, 32, 1283 (1994).
  107. N. S. Enikolopyan, N. N. Vlasova, A. T. Papoyan, P. E. Matkovskii, V. A. Shtar-kin, M. P. Gerasina, V. I. Sergeev, and L. O. Bunina, *Doklady Chem.* [Eng. transl. of *Doklady Akad. Nauk SSSR*], 280, 13 (1985).
  108. A. Munoz-Escalona, J. G. Hernandez, and J. A. Gallardo, *J. Appl. Polym. Sci.*, 29.

1187 H984Y

109. T. Garoff, *Techniques and Measurement in Heterogeneous and Homogeneous Catalysis*, lecture given at the University of Liverpool, 6-10 September (1993).
110. D. Damyanov, M. Velikova, I. Ivanôv, and L. Vlaev, *J. Non-Cryst. Sol.*, **105**, 107 (1988).
111. E. G. Howard, B. L. Glazar, and J. W. Collette, *Ind. Eng. Chem. Prod. Res. Dev.*, **20**, 429 (1981).
112. D. G. H. Ballard, E. Jones, R. J. Wyatt, R. T. Murray, and P. A. Robinson, *Polymer*, **15**, 169 (1974).
113. H. E. Evans and W. H. Weinberg, *J. Am. Chem. Soc.*, **102**, 2548 (1980).
114. N. S. Enikolopyan, Filled Polymer I, Science and Technology, *Adv. Polym. Sci.*, **96**, 1990.
115. B. L. Glazar, E. G. Howard, and J. W. Collette, *J. Fire Flammability*, **9**, 430 (1978).
116. R. C. Ferguson, H. J. Stoklosa, W. W. Yau, and H. H. Hoehn, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **34**, 119 (1978).
117. H. L. Chang and A. T. Hu, *Makromol. Chem.*, **192** 2059 (1991).
118. V. Dolâäk and F. Hudecek, *J. Macromol. Sci.—Phys.*, **B15**, 337 (1978).
119. C. G. Ek, *Rheol. Acta.*, **27**, 279 (1988).
120. J. Gahde, V. Müller, Y. V. Lebedev, and Y. S. Lipatov, *Polym. Sci USSR*, **19**, 1446 (1977).
121. V. P. Chacko, F. E. Karasz, R. J. Farris, and E. L. Thomas, *J. Polym. Sci Polym. Phys. Ed.*, **20**, 2177 (1982).
122. L. Minkova and P. L. Magagnini, *Polym. Deg. and Stab.*, **42**, 107 (1993).
123. L. Minkova, M. Velikova, and D. Damyanov, *Acta Polymerica*, **42**, 8 (1991).
124. E. G. Howard, U.S. Pat. 5,352,732 (December 1992).
125. E. G. Howard, B. L. Glazaer, and J. W. Collette, *High Perf. Plast. Nat. Tech. Conf.—Soc. Plast. Eng. (Prepr.)—Cleveland, Fasc. Oct. 5/7*, 36 (1976).
126. H. S. Göktürk, T. S. Fiske, and D. M. Kalyori, *J. Appl. Polym. Sci.*, **50**, 1891 (1993).
127. I. H. Tavman, *J. Appl. Polym. Sci.*, **62**, 2161 (1996).
128. L. A. Novokshonova and I. N. Meshkova, *Polym. Sci USSR*, **36**, 517 (1994).
129. N. V. Galashina, *Polym. Sci USSR*, **36**, 526 (1994).
130. W. Kaminsky, J. Dutschke, H. Meadler, M. Miri, and M. Schlobohm, DE Pat. 3,240,382 (May 1984).
131. W. Kaminsky and H. Zielonka, *Polym. Adv. Technol.*, **4**, 415 (1993).
132. W. Kaminsky, *Macromol. Chem. Phys.*, **197**, 3907 (1996).
133. M. Alexandra, F. Hindryckx, Ph. Dubois, R. Jérôme, and M. Garcia Marti, PCT pat. (pending).
134. Ph. Dubois, M. Alexandre, R. Jérôme, and M. Garcia Marti, communication presented at EuroFillers'97, Manchester, United Kingdom, September 8-11, 1997.
135. M. Alexandre, E. Martin, Ph. Dubois, R. Jerome, and M. Garcia Marti, communication presented at IPCM'97, Eger, Hungary, September 1-3, 1997.