

Catalytic Grafting: A New Technique for Polymer–Fiber Composites I. Polyethylene–Asbestos Composites

QI WANG,¹ SERGE KALIAGUINE,² and ABDELLATIF AIT-KADI*¹

¹CERSIM and ²GRAPS, Department of Chemical Engineering, Laval University, Quebec, Quebec, G1K 7P4, Canada

SYNOPSIS

In this work we present a new technique to prepare polyolefin–fiber composites. This technique is based on chemical anchoring of a catalyst on reinforcing agents containing OH groups on their surface and then conducting an olefin polymerization on the supported catalyst. This technique offers the possibility to approach the challenging problems encountered in polymer composites, namely, the reinforcement–matrix adhesion, the dispersion, and the wetting of the reinforcement by the resin. As a first part of a systematic research, we report on the procedure of fixation of titanium tetrachloride on the surface of asbestos fibers and the Ziegler–Natta polymerization of ethylene on the surface-modified fibers. The procedure as well as the structure and properties of the composite were investigated by means of FTIR, atomic absorption, SEM, solvent extraction, and tensile testing. The experimental results show that the Ziegler–Natta catalyst can be efficiently anchored on the surface of the fibers to conduct successful polymerization and to “synthesize” a new class of polymer composites.

INTRODUCTION

Polymer composites represent a field of intense and growing interest to consumers and producers of polymer materials. They are used to solve the most acute problems, i.e., to improve the properties of polymer materials in order to broaden the spectrum of their end-use applications or to cut down their cost. Their production is growing at a higher rate than that of polymers as a whole.¹ The properties of polymer composites greatly depend on the combined behavior of the fillers or the reinforcing agents, the matrix, and the interface between the filler and the matrix. In this article we shall restrict ourselves to the fiber-reinforcing agents and thermoplastic resins. The fiber element of the composite provides mechanical resistance under applied load, while the matrix ensures the cohesion of the composite material and provides protection of the fibers against environmental conditions.² A third element in a fiber composite material is the fiber–matrix interface. This element is crucial to the stress transfer from

the matrix to the reinforcing agent. The challenging problems usually encountered in plastic polymer composites are the fiber–matrix adhesion, the dispersion of the fibers in the matrix, and the wetting of the fibers by the resin. The research aiming at improving the interface conditions of thermoplastic polymer composites arouses great academic and industrial interest. Many advanced, also expensive, instruments have been developed to obtain a better dispersion of fibers in the matrix (intensive mixers). However, the improved dispersion is made at the expense of a higher fiber attrition. Moreover, adhesion between the fibers and the matrix does not depend on the mixing methods only. A limited choice of a more polar polymer was found to improve wettability and interactions between the reinforcement and the matrix.³ Creating fresh-form surfaces of mineral fillers by milling or grinding may produce high-energy surfaces and favor the interface contact.⁴ Once again such treatment is not suitable for reinforcing fibers due to the loss of aspect ratio. Coupling agents are recognized as another effective means for improving the interface interaction.⁵ However, they cannot offer stable chemical bonding between the matrix and the reinforcement. Moreover, the fiber dispersion in the matrix will still re-

* To whom correspondence should be addressed.

main a problem. The optimum choice to improve interface adhesion would be to establish chemical bonds across the interface.⁶ Many efforts have for example been concentrated on radical grafting polymerization on filler surfaces.⁷ Initiators such as benzoyl peroxide or ammonium persulfate were adsorbed on the surface of several fillers such as Al_2O_3 , TiO_2 , CaCO_3 , ZnO , aluminum, and others. These such modified fillers were then used to conduct graft polymerization of acrylonitrile, acrylic acid, methyl methacrylate, and vinyl acetate.⁸ Ball milling and ultrasonic irradiation of fillers in presence of monomers were also used for surface polymerization.^{9,10} Gamma irradiation of mineral fillers was used by Dinh-Ngoc and Fukano^{11,12} to initiate the polymerization of styrene and methyl methacrylate and to produce composite materials. Plasma treatment of the fillers and reinforcements is also known to activate the surface and to produce grafted fillers for subsequent mixing with thermoplastic resins.¹³ Similar objectives (surface treatment of the fillers) can be achieved by photo-initiated graft polymerization after peroxide,¹⁴ chlorosilanes,¹⁵ or quinone¹⁶ treatment of the fillers. Unfortunately, the radical graft polymerization processes mentioned earlier are not suitable for polyolefins such as HDPE and PP, because these polymers are prepared mainly by ionic-coordinative mechanism. Therefore, anchoring a Ziegler–Natta catalyst onto the filler surface and conducting an olefin polymerization on filler surface offers an attractive challenge to material researchers.¹

Ziegler–Natta catalyst represents one of the most brilliant achievement in both synthetic polymer chemistry and catalyst science during the past 50 years.¹⁷ Several research works have recently been devoted to the so-called supported catalysts¹⁸ such as titanium tetrachloride or derivatives^{19–25} attached to $\text{Mg}(\text{OH})\text{Cl}$, $\text{Mg}(\text{OH})_2$, $\text{Mg}(\text{OR})_2$, MgCl_2 , Al_2O_3 , SiO_2 , and others for an enhanced activity of Ziegler–Natta catalysts. Asbestos fibers were also used as a catalyst support for $(\text{C}_5\text{H}_5)_2\text{TiCl}$, and the activity of such catalyst for hydrogenation and polymerization of olefins was reported.^{26–28} However, it should be pointed out here that most of these efforts have been focused on the catalyst performance rather than producing composite materials.

From the point of view of polymer composite researchers, however, the supported catalyst provides an example of how to fix a Ziegler–Natta catalyst on a filler surface. Since the late 1970s, many fillers, such as minerals, metals, and their oxides (graphite and carbon black) were studied for this purpose.^{29–35} Few works on fiber-filled polyolefin com-

posites made by Ziegler–Natta polymerization have, however, been reported. It should be mentioned that the first experiment using $\text{TiCl}_4/\text{Al}(\text{alkyl})_3$ as catalyst for grafting of polyethylene onto cellulose fibers was carried out in 1964–65,³⁶ but the main objective of the study was to improve the properties of paper rather than to develop polymer composites.

Since the fibers are the highest strength materials, they are the best reinforcement for many applications. If, in addition, they can be used as a support for polymerization catalyst, the resulting composite material is expected to have outstanding properties. The most commonly used fibers, such as asbestos, glass, and wood fibers, have many surface OH groups. This group can be used to chemically anchor catalyst on the fiber surface and to conduct polymerization in order to “synthesize” fiber-filled composites by catalytic graft polymerization. In the present work this idea is applied to such fibers combined with olefins using polyethylene and asbestos fibers as an example. The fibers with the chemically anchored catalyst will serve a dual purpose: a supported catalyst for the olefin polymerization and a reinforcing agent for the final product. This technique is used here for reinforcing agents to handle the major problems encountered in thermoplastic polymer composites. The chemical bonds established between the matrix and the fibers should improve the adhesion while the polymer grafted on the active sites of each fiber should ensure a good dispersion and wetting of the fibers in the synthesized matrix. Compared to the conventional methods of preparing composite materials (by melt blending), the procedure described here avoids the mixing step in the preparation process. With this in mind systematic studies were conducted on the preparation of polyolefin–fiber composites through catalytic grafting. As the first part of a series work, this article focuses on the preparation of polyethylene–asbestos composites with this technique.

Asbestos is a unique mineral combining unusual physical and chemical properties, such as fibrous nature, thermal stability, high tensile strength, flexibility, and incombustibility, which make it highly suitable as a reinforcing material for cement, paper, plastics, etc. The concern of its hazard to health of humans, however, diminishes its application and limits its further development.³⁷ It is worth noticing that, with the formula $\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$ (for chrysotile, the most widely used and versatile member of the asbestos family), asbestos has many OH groups on the surface, which could be used as the reactive sites for anchoring a catalytic species on its surface, and then conducting ethylene polymeriza-

tion under mild conditions. We believe that a product obtained in this way will exhibit higher performance due to chemical bonds across the interface. Furthermore, coating the fiber with polymer will diminish the hazard of asbestos to the health of humans and therefore make it recover its importance in plastic applications. In this study the procedure of anchoring Ziegler-Natta catalysts on asbestos surface and the polymerization of ethylene on the fiber were investigated. The effect of various experimental parameters on the amount of polyethylene grafted on the fibers was examined. The performance of the composites so obtained were then compared with that of the composites made by in situ polymerization and conventional mixing methods. The possibility to use the new material as a modifier for polymer composites was also discussed.

EXPERIMENTAL

Materials

Chrysotile asbestos Plastibest No. 20 (JM Asbestos Inc.) was used as reinforcing fibers. Its nitrogen Brunauer-Emmett-Teller (BET) specific surface area was measured using an Omnisorp 100 instrument. The OH content of the fiber surface was determined by quantitative reaction with triethyl aluminum [$\text{Al}(\text{C}_2\text{H}_5)_3$] under nitrogen atmosphere, followed by quantitative analysis of aluminum using a Perkin-Elmer 1100-B Atomic Absorption Spectrophotometer. The ethylene (Canadian Liquid Air Ltd.) used as monomer was dried and deoxygenated by bubbling through hexane containing a small amount of $\text{Al}(\text{C}_2\text{H}_5)_3$ before polymerization. Hexane was also used as solvent during polymerization after it was dried by sodium for one day and distilled under nitrogen. TiCl_4 and $\text{Al}(\text{C}_2\text{H}_5)_3$ were used as catalysts for ethylene polymerization.

Fixation of Catalyst on the Surface of Asbestos

The reaction of asbestos with the catalyst and the co-catalyst was conducted in a glass vessel using the Schlenk technique. The reactor was charged with pure nitrogen by repeated evacuation and intermediate recharging. Four types of reaction sequences were considered in this work. The reasons that motivate these choices will be explained later. The dried asbestos was first reacted with TiCl_4 at 60°C for 3 h under nitrogen atmosphere in hexane solution. The product was filtrated and repeatedly washed with hexane. One part of the product, labeled AS/Ti, was sampled for subsequent analysis. The other

part of the AS/Ti was reacted with $\text{Al}(\text{C}_2\text{H}_5)_3$ for another half hour, and the obtained product was labeled AS/Ti/Al. Similar reactions were carried out by reacting $\text{Al}(\text{C}_2\text{H}_5)_3$ with the fibers first and then completing the reaction with TiCl_4 . The other two modified fibers obtained after these reactions were labeled AS/Al and AS/Al/Ti, respectively.

The reacted fibers were analyzed using Fourier transform infrared (FTIR) spectra and atomic absorption measurements.

Ziegler-Natta Polymerization of Ethylene on the Surface of Asbestos

One of the main objects of this work is to obtain composite materials with various fiber contents. Among the ways to achieve this objective one can mention a change in the ratio of catalyst to co-catalyst for the polymerization, the variation in polymerization time, and a change in OH content on the fiber surface. From the composite point of view, controlling the OH content represents the most appropriate way. In this way, and by allowing sufficient polymerization time for each OH concentration on the fibers one can, at least in principle, obtain composites with identical matrix properties and different fiber contents. Therefore, the synthesized composite materials will be compared on the same basis. Moreover, in order to carry out successfully the polymerization on the surface of the filler (or in our

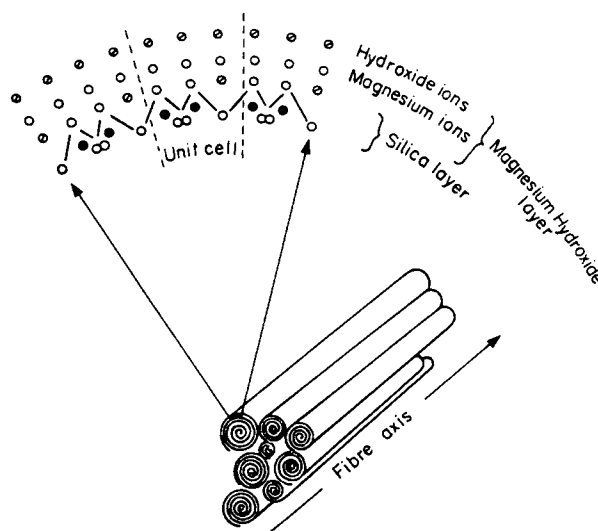


Figure 1 Schematic diagram of the structure of chrysotile asbestos.³⁸ The details of a small section of the scroll show the structure of the double layer and the unit cell based on $\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$.

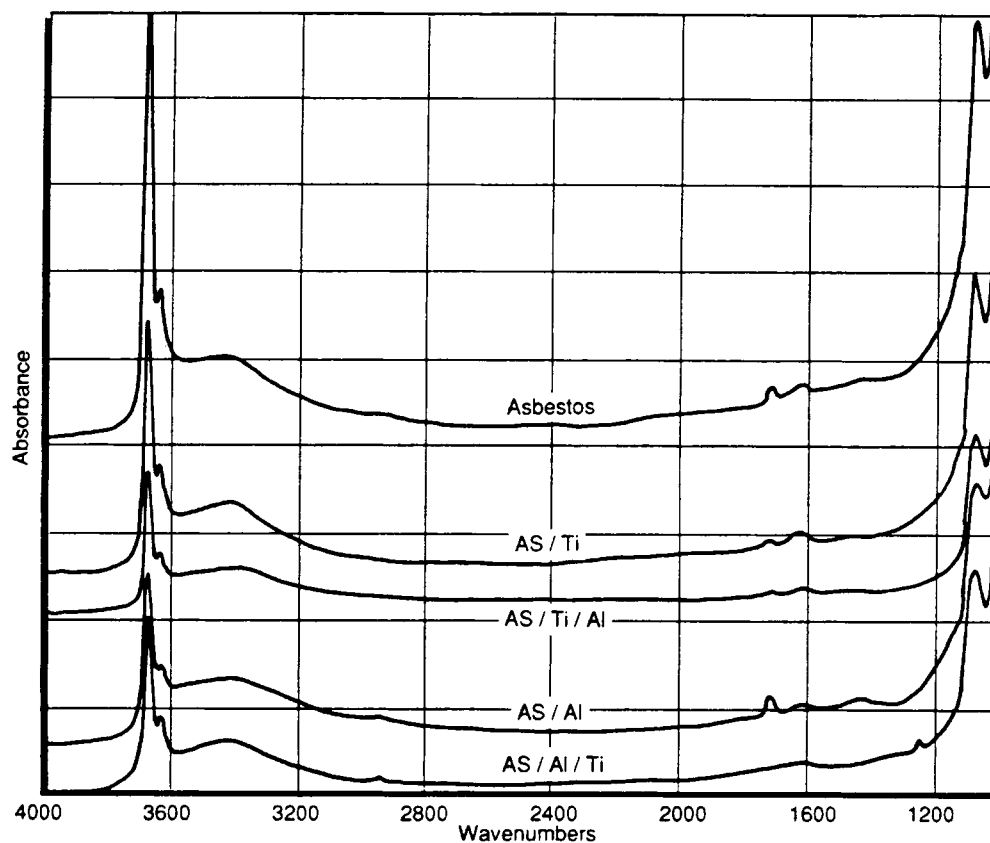


Figure 2 FTIR spectra of asbestos before and after catalysts anchoring.

case the reinforcement), it is necessary to control the OH group concentration on the fiber surface before grafting.¹ The OH group concentration can be controlled by hydrolysis or dehydroxylation by chemical or thermal treatments. In our study the OH content on the surface of asbestos fibers was varied by heating the fibers in an oven for a given period of time at different temperatures.

The Ziegler–Natta polymerization of ethylene on the surface of asbestos fibers was conducted in a four-necked flask equipped with precision-ground

stirrer, thermometer, and a gas inlet and an outlet tube. Air and moisture are completely excluded by heating under vacuum and purging the reactor repeatedly with nitrogen. The asbestos fibers with anchored TiCl_4 together with $\text{Al}(\text{C}_2\text{H}_5)_3$, which acts as a co-catalyst, serve as a supported catalyst for the polymerization. Hexane was used as solvent. The ethylene flow rate was controlled using a gas measuring flow meter. The ethylene fed was adjusted so that as little as possible escaped via the overpressuring mercury column. Therefore, any change in

Table I Results of FTIR Measurement of Asbestos Before and After Catalysts Anchoring

Sample	3692 cm^{-1}		3647 cm^{-1}		1080 cm^{-1} Absorbance
	Absorbance	A_{3692}/A_{1080}	Absorbance	A_{3647}/A_{1080}	
Asbestos	2.58	1.14	0.86	0.38	2.27
AS/Al	1.07	0.80	0.46	0.35	1.33
AS/Al/Ti	1.09	0.86	0.46	0.36	1.27
AS/Ti	1.47	0.88	0.62	0.37	1.66
AS/Ti/Al	0.82	0.87	0.34	0.36	0.94

Table II The Content of Ti and Al of the Four Catalysts

Sample	Ti/Asbestos (mmol/100 g)	Al/Asbestos (mmol/100 g)
AS-Ti	16.5 ± 0.4	
AS/Ti/Al	16.0 ± 0.2	10.9 ± 0.1
AS/Al		16.7 ± 0.1
AS/Al/Ti	19.8 ± 0.2	16.3 ± 0.2

the polymerization process can then be monitored by recording the ethylene flow rate. The polymerization process was terminated by adding ethanol after a given polymerization time. The composition of the composite varied with the OH content on the asbestos surface, and the product was labeled AEG.

For comparison purposes in situ polymerization of ethylene was also conducted in presence of as-received asbestos fibers. Drying was the only treatment performed on the fibers. For this experiment the catalyst, TiCl_4 , was mixed with the co-catalyst, $\text{Al}(\text{C}_2\text{H}_5)_3$, in another schlenk under nitrogen atmosphere. The molar ratio of Al/Ti was 3.0. The solution was then poured into the reactor containing the fibers. The polymerization was once again terminated using ethanol. The composition of the composite was controlled by the amount of asbestos fiber charged in the polymerization apparatus. This kind of composite was labeled AEI.

Pure polyethylene was synthesized in absence of

asbestos as polymeric matrix for the polyethylene-asbestos composite made by a conventional way. The polyethylene and asbestos were blended in a mixer (Haake Buchler Rheocorder System 40) at 200°C for 10 min with a speed of 60 rpm. The composition of the composite was controlled by the ratio of polyethylene to asbestos. The product was labeled AEM.

The morphology and interfacial behavior of AEG and AEI were characterized by SEM (Jeol JSM-III SEM microscope), Soxhlet solvent extraction (in decalin for 20 h), FTIR (BIO-RAD FT-IR spectrometer). The mechanical properties of the three different composites were examined using Instron tensile instrument at a crosshead speed of 0.1 cm/min and a loading ranging from 20 to 50 kg. The samples for tensile testing were moulded with a Carver laboratory press. The size of the specimens was in accordance with ASTM-D638M. The broken section of the samples after tensile testing were vacuum coated with gold and then observed through the SEM microscope.

RESULTS AND DISCUSSIONS

Fixation of Catalyst on the Surface of Asbestos

Chrysotile asbestos is a hydrous magnesium silicate. The structure of a chrysotile fiber formed of several scrolls of individual crystallites is shown in Figure 1.³⁸ Each scroll is formed from a closely connected

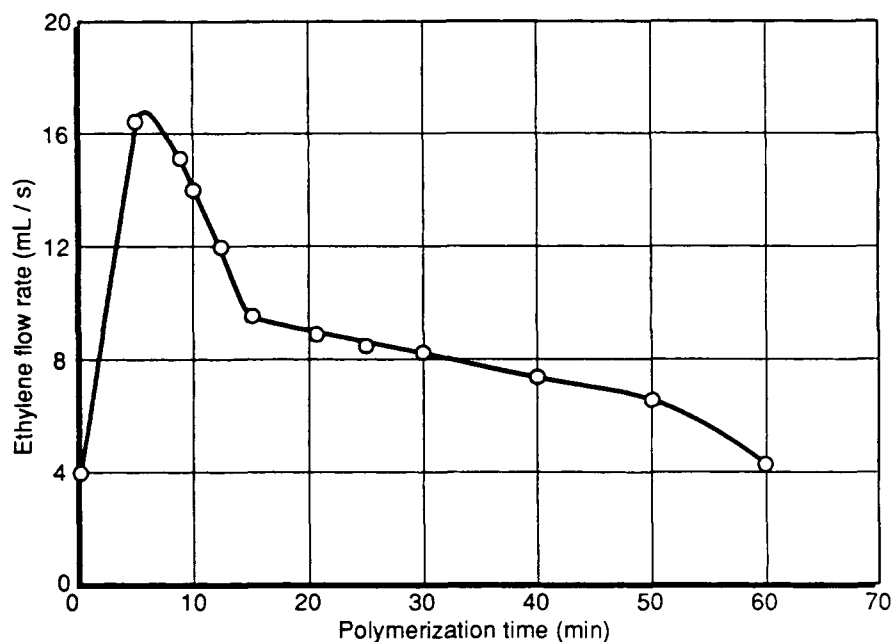
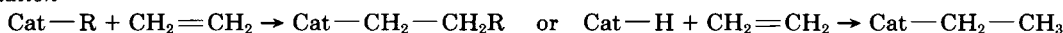
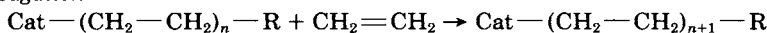
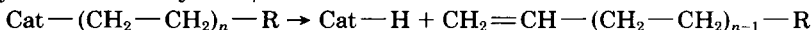


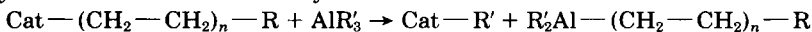
Figure 3 Ethylene flow rate vs. polymerization time. Al/Ti = 3.0.

Table III Kinetic Scheme for Ziegler-Natta Polymerization (Ethylene)^a*Initiation**Propagation**Termination*

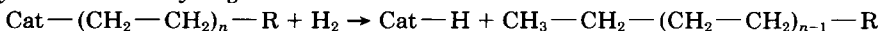
Spontaneous

By transfer with hydride β -elimination

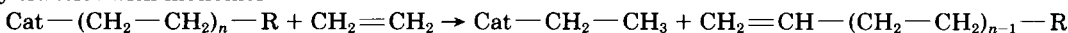
By transfer with aluminum alkyl



By transfer with hydrogen



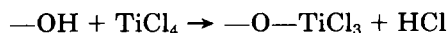
By transfer with monomer



^a Cat is an active center; Cat' is a deactivated center; R and R' are alkyl groups.
From Ref. 41.

double layer having magnesium hydroxide units on its external face and silica units on its inner face. The details of a small section of the scroll show the structure of the double layer and the unit cell based on $\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$. The OH groups on the surface of asbestos can react with $\text{Al}(\text{C}_2\text{H}_5)_3$ stoichiometrically. Therefore the OH content on the asbestos surface could be quantitatively determined by reaction with $\text{Al}(\text{C}_2\text{H}_5)_3$ and followed by measuring the aluminum content using atomic absorption spectrophotometer. For the original asbestos fibers, the surface OH content is 16.7 mmol/100 g asbestos. According to the BET measurement, the specific surface area of asbestos is 19.7 m^2/g . Therefore, it could be calculated that on the surface of asbestos there is one OH group in an average area of 19.6 \AA^2 .

The OH groups on the surface of the fibers are the reactive sites for chemically anchoring TiCl_4 , as described by the following equation:³⁹

**Table IV Dependence of PE Content of AEG on Polymerization Time**

Polymerization Time (min)	Polyethylene Content (wt %)	
	Calculated	Experimental
10	19.3	20.8
30	46.6	47.5
40	61.1	57.2

The reactions of asbestos with TiCl_4 or $\text{Al}(\text{C}_2\text{H}_5)_3$ consume OH groups, and the variation of OH content could be monitored by FTIR. Figure 2 shows the spectra of asbestos before and after it was reacted. The OH stretching vibrations of asbestos give distinctive peaks in the region 3600–3700 cm^{-1} , the strong OH peak at 3692 cm^{-1} attributable to the external hydroxyl groups, and a weaker peak at 3647 cm^{-1} due to the internal hydroxyl groups in chrysotile; the ratio of the intensities of these peaks should be 3 : 1, according to its layered structure described earlier.⁴⁰ The Si–O stretching mode of asbestos appears at 1080 cm^{-1} , which is hardly affected by the reaction of OH groups with catalysts. Therefore, the ratio of the intensity of OH stretching to the intensity of Si–O stretching (A_{3692}/A_{1080} and A_{3647}/A_{1080}) can be taken to monitor the variation of OH content.

The value of A_{3692}/A_{1080} was found to decrease from 1.14 to 0.80–0.88 for the unmodified and the catalyst-grafted asbestos fibers, respectively (see Table I). On the other hand, the ratio of A_{3647}/A_{1080} remains unchanged at a value around 0.36. This indicates that TiCl_4 or $\text{Al}(\text{C}_2\text{H}_5)_3$ reacted only with the external OH groups of asbestos, but hardly attacked the internal OH groups. The results also show that the value of A_{3692}/A_{3647} for the original asbestos fiber, representing the ratio of external to the internal OH groups of asbestos fiber, is in accordance with the theoretical value of 3.⁴⁰

The quantitative determination of the catalyst anchored on the asbestos surface was conducted by atomic absorption. The results are listed in Table II. It should be noticed that the Ti content of AS/

Table V Influence of the OH Content of Asbestos on the Composition of Composites Obtained After 1 H Polymerization

Sample	Heat Treatment		OH/Asbestos (mmol/100 g)	PE (wt %)	PE/OH (g/mmol)
	T (°C)	t (h)			
AEG82	—	—	16.7 ± 0.1	71.0	14.7
AEG3901	390	1	15.6 ± 0.1	65.5	12.2
AEG5401	540	1	12.1 ± 0.1	61.5	13.2
AEG5302	530	2	11.2 ± 0.3	59.2	12.9

Ti and AS/Ti/Al is 16.5 and 16.0 mmol Ti/100 g asbestos respectively, and the Al content of AS/Al and AS/Al/Ti is 16.7 and 16.3 mmol Al/100 g asbestos, respectively, almost the same within experimental error. This indicates that almost the same external surface OH groups of asbestos can react with the first catalytic compound independently of whether it is TiCl_4 or $\text{Al}(\text{C}_2\text{H}_5)_3$. The Al content value of AS/Ti/Al sample and the Ti content value of AS/Al/Ti sample are slightly different from the values obtained for the first catalytic compound anchored. This suggests that the second metallic compound can be complexed in some way by the first one. This particular point is now under investigation and will be addressed in a forthcoming article.

Ziegler-Natta Polymerization of Ethylene on the Surface of Asbestos

The asbestos fibers with chemically anchored TiCl_4 served as a supported catalyst for ethylene poly-

merization. As soon as $\text{Al}(\text{C}_2\text{H}_5)_3$, the co-catalyst, was injected into the reactor under positive pressure of ethylene, the fibers became brownish at once, and the ethylene flow rate increased quickly and then slowed down gradually, as shown in Figure 3, indicating a spontaneous deactivation of the active centers. Table III describes the kinetic scheme for Ziegler-Natta polymerization of ethylene.⁴¹ The insertion of a monomer into Ti-C bond ensures the propagation of the chain growth, and the termination by transfer with the co-catalyst, a monomer or via a β -hydride shift does not destroy the active centers. Only the spontaneous deactivation of the catalyst diminishes the active centers. Such deactivated $\text{Cat}'-(\text{CH}_2\text{CH}_2)_n-\text{R}$ structure, where Cat' is a deactivated center and R are alkyl groups, may be useful for establishing more stable links between the polymer matrix and the reinforcing fibers.

Based on the amount of ethylene consumed, an estimate of the polyethylene content in the polyethylene-asbestos composite can be calculated. Table

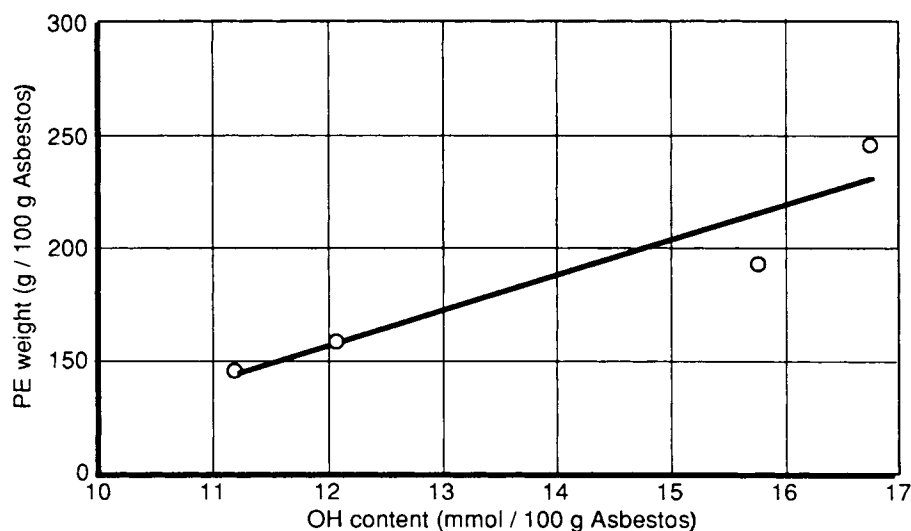


Figure 4 Dependence of PE content of AEG composites on the surface OH content of asbestos. Polymerization time: 60 min. Al/Ti = 3.0.

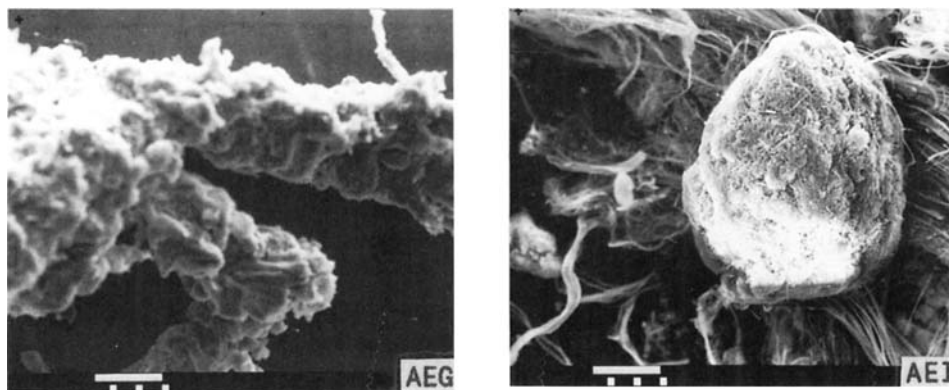


Figure 5 SEM micrographs of AEG and AEI (X150).

IV compares the polyethylene content in the composite determined from the weight increase of the fibers after polymerization with that estimated from the polymerization time. It is therefore possible to control the composition of the new composite by means of terminating the polymerization at a certain time.

However, controlling the polyethylene content by controlling polymerization time, as done for the results presented in Table IV, may lead to composites with different matrices. One way to avoid this problem and to compare the properties of the material on the same basis is to control the OH amount of the fibers and to allow an identical polymerization time in each case. Heat treatment before grafting is among the ways to control the concentration of OH groups on the surface of the fibers. Table V shows the influence of heat treatment on the OH content of asbestos as well as the dependence of the composition of the composites on the OH content when the polymerization time is one hour and the molar ratio of Al/Ti is 3.0 [$\text{Al}(\text{C}_2\text{H}_5)_3$ being introduced in the liquid phase]. Figure 4 shows that the mass of polyethylene grafted on the asbestos fibers de-

pends on the surface OH content. It could be drawn from the experiment that the amount of polyethylene (PE) polymerized per OH mmol in the four samples with different OH content gets a very close value: 13.2 g PE/mmol OH. The effect of fiber content on the mechanical properties will be studied on these composites (see Table V).

As mentioned earlier, AEG is the polyethylene-asbestos composite made with the new technique, while AEI is a composite polymerized in situ in the presence of asbestos (catalyst was not grafted onto the fiber). The two kinds of composites exhibit quite different behaviors. It can be seen from the SEM micrographs (Fig. 5) that the morphology of AEG is much different from that of AEI. For AEG the polymer covers the fiber, and for AEI the PE particles are scattered in the fibers. Thus, when the catalyst is chemically anchored on the fiber, the ethylene is polymerized on the surface of fibers, forming a polymer coating for each fiber, which ensures a good dispersion of fiber in the polymer matrix and avoid mixing at elevated temperature. When the catalyst is not grafted on the fiber, the ethylene was polymerized separately from the fibers, forming scattered polymer particles.

Solvent extraction reflects also clearly that AEG exhibits quite different interfacial behavior from that of AEI. Table VI shows the results of AEG, AEI, and PE extraction by decalin (its boiling point is 185–192°C) for 20 h. These results demonstrate that the polyethylene prepared by homogeneous Ziegler-Natta polymerization (PE) as well as the one polymerized in presence of asbestos fibers (AEI) can be completely extracted by decalin. By contrast, about 57% of the polyethylene produced by catalytic grafting (AEG) cannot be extracted under the same conditions. This result suggests that a strong adhe-

Table VI Results of Solvent Extraction (Decalin, for 20 h)

Sample	Weight (g)	PE in Sample (g)	PE Extracted	
			Weight (g)	Ratio (%)
PE	0.0437	0.0437	0.0438	100
AEI37	0.2045	0.1277	0.1310	100
AEG330	0.1451	0.1101	0.0472	42.9

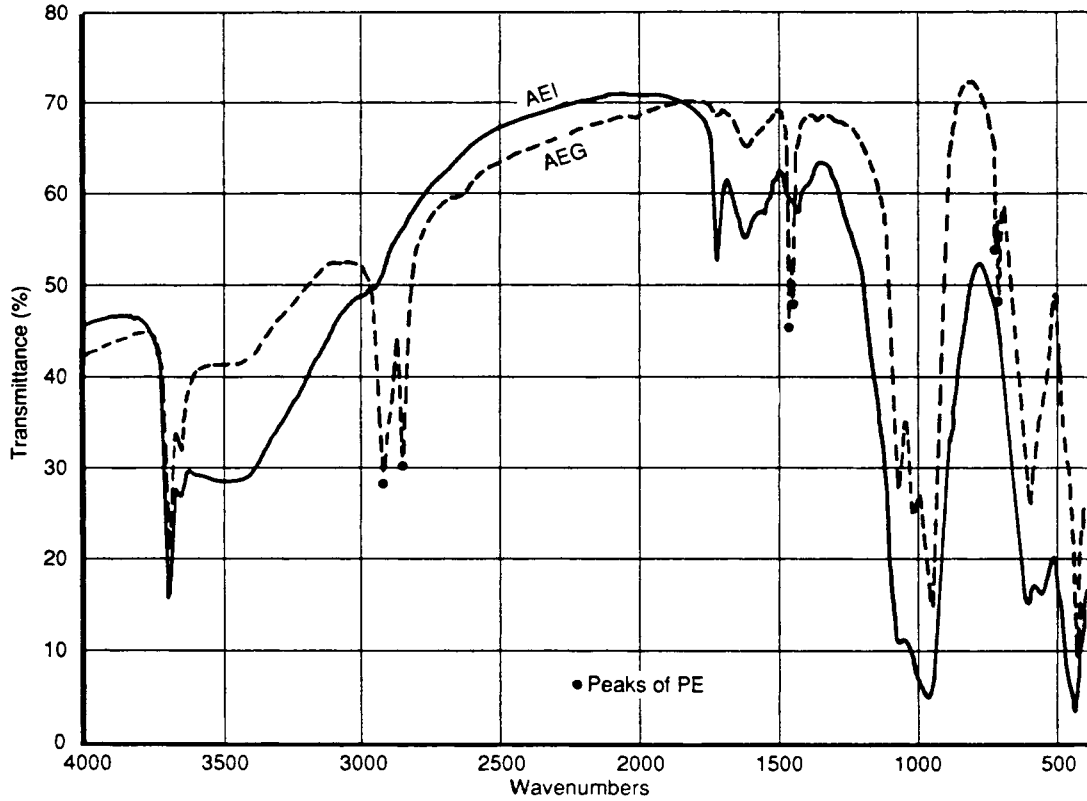


Figure 6 FTIR spectra of AEG and AEI after Soxhlet extraction by decalin for 20 h.

sion between the polymer coat and the fiber surface was developed during the grafting polymerization process.

Figure 6 reports the FTIR spectra of AEG and AEI after decalin extraction for 20 h. For AEG, the

characteristic peaks of PE at 2918, 2850, 1473, 1463, 730, and 719 cm^{-1} remain strong, but for AEI these peaks disappear.

All these experimental results reveal that catalytic grafting polymerization of ethylene on the as-

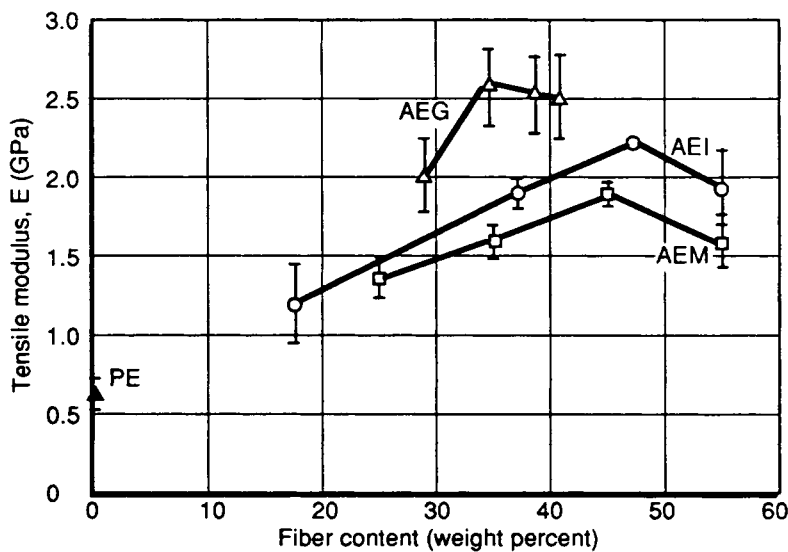


Figure 7 Modulus of AEG, AEI, and AEM types of asbestos-polyethylene composites.

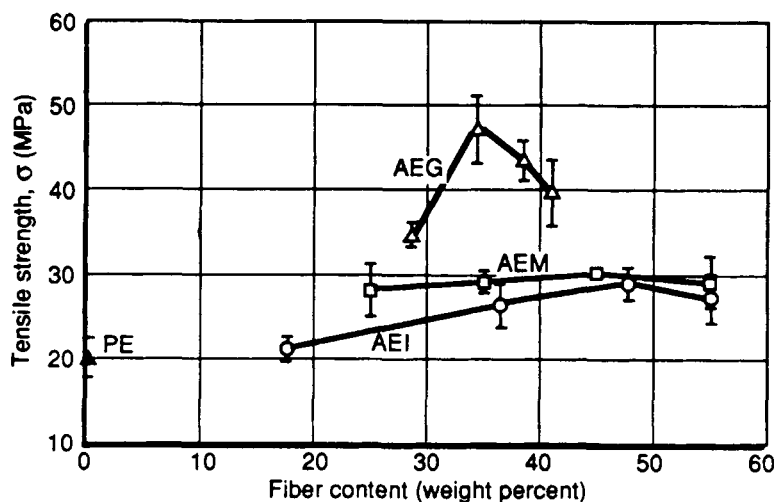


Figure 8 Tensile strength of AEG, AEI, and AEM types of asbestos-polyethylene composites.

bestos fiber surface could result in a new asbestos-polyethylene composite quite different from the conventional composites. The surface polymerization serves to improve the interface adhesion in a way that cannot be achieved by blending with melted polymer or by polymerization in the presence of filler with free catalyst.¹

Mechanical Properties of the New Composite

The catalytic grafting polymerization of olefins on the reinforcing fibers offers an avenue to handle the major problems encountered in thermoplastic polymer composites. The chemical bonds established between the matrix and the fibers should improve

the adhesion while the polymer grafted on the active sites of each fiber should ensure a good dispersion and wetting of the fibers in the composite material. Moreover the procedure avoids the mixing step in the preparation process, which often deteriorates the fiber length and polymer matrix property. The mechanical properties of the composite so obtained should therefore get significant improvement.

Figures 7, 8, and 9 compare the tensile properties of asbestos-polyethylene made by different methods. The tensile properties of the pure polyethylene are also listed for comparison. Note that the value of the elongation for the pure polyethylene is that obtained at yield since the value at break is much higher. As mentioned before, the composition of

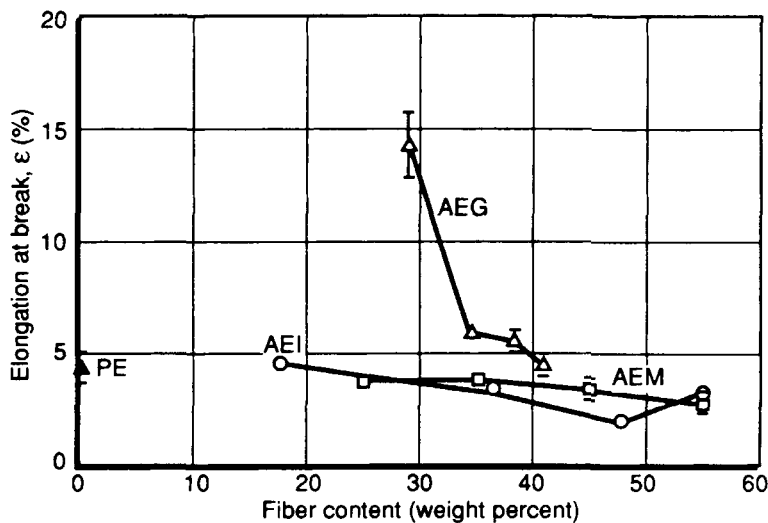


Figure 9 Elongation at break of AEG, AEI, and AEM types of asbestos-polyethylene composites.

Table VII Tensile Properties of AEGR/HDPE and AE/HDPE

Sample	Fiber (%)	<i>E</i> (GPa)	σ (MPa)	ϵ (%)
AEGR/HDPE	34.8	2.49 \pm 0.15	35.0 \pm 3.6	4.04 \pm 1.06
AE/HDPE	34.9	2.04 \pm 0.26	27.9 \pm 6.2	3.25 \pm 0.48

AEG composite is controlled by varying surface OH content of asbestos fibers. The polymerization time and the ratio of catalyst to co-catalyst are the same for preparation of AEG, AEI, and pure PE, which ensures that the properties of the composites made in different ways are compared on the same basis. It is evident that AEG composites with various fiber content is much superior to both AEI and AEM composites in tensile properties. The modulus of AEG is higher than that of AEI and AEM, reaching around 2.5 GPa (Fig. 7). The tensile strength of AEI and AEM (Fig. 8) is only slightly higher than that of pure PE (20.5 MPa), but AEG gets a tensile strength as high as 47.0 MPa. The elongation at break of both AEI and AEM composites is very low (Fig. 9), while AEG composites with given asbestos contents exhibit rather tough behavior. The decrease observed for the mechanical properties (tensile modulus and tensile strength) at high fiber concentration is generally attributable to fiber dispersion problems (possibility of fiber-fiber contact) and to the increase of the number of fiber ends and hence the increase of stress concentration points. The decrease is observed around 50 wt % of fibers in the case of AEM and AEI composites. The decrease observed around 35 wt % of fibers for AEG composites is in our opinion not essentially due to fiber dispersion problems. It might be due rather to the intrinsic properties of the fibers, which were heat treated to control the OH groups on the surface, and to the molecular characteristics of the synthesised matrix, which may be different from one AEG composite to another, even though the polymerisation time is kept constant.

This technique also offers a possibility to prepare a thermoplastic composite with rather high fiber

content. Such composites could be used as modifier for the conventional asbestos-polyethylene composites. Based on this principle, we prepared a new composite with a fiber content of 78.3% (designated as AEGR), then mixed it with the commercial HDPE in a Haake Buchler Rheocorder to get AEGR/HDPE composite with a fiber content of 34.8%. For comparison, we made AE/HDPE composite with fiber content 34.9% by simply mixing dried asbestos fiber with commercial HDPE. Table VII compares the tensile properties of AEGR/HDPE and AE/HDPE, where *E* is modulus, σ is tensile strength, and ϵ is elongation at break. The improvement in mechanical properties of AEGR/HDPE is obvious, demonstrating the effect of the chemical bonding between the interfacial faces of the composite.

Table VIII lists the tensile properties of asbestos-polyethylene composites made by different methods but with almost the same asbestos fiber content. It could be seen that for the composites made by in situ polymerization or conventional mixing, namely, AEM35, AEI37, and AE/HDPE, the tensile properties are poor, while for the composites made by catalytic grafting technique, i.e., AEG3901, all the modulus, the tensile strength as well as the elongation at break increase dramatically, reaching 2.59 GPa, 47.1 MPa, and 6.03%, respectively. Even for the AEGR/HDPE, a composite using AEG as modifier, the improvement in mechanical properties is also obvious. The SEM micrographs of fractured surfaces after tensile testing of different composites (Fig. 10) reveal that the interfacial behavior of these composites does depend on the preparation methods; the coating of polymer on the asbestos fiber could be observed in AEG3901 and AEGR/HDPE com-

Table VIII Tensile Properties of Different Composites

Sample	Fiber (%)	<i>E</i> (GPa)	σ (MPa)	ϵ (%)
AEM35	35.0	1.65 \pm 0.14	28.8 \pm 1.8	3.50 \pm 0.50
AEI37	37.4	1.87 \pm 0.12	25.8 \pm 2.6	2.82 \pm 0.50
AE/HDPE	34.9	2.04 \pm 0.26	27.9 \pm 6.2	3.25 \pm 0.48
AEGR/HDPE	34.8	2.49 \pm 0.15	35.0 \pm 3.6	4.04 \pm 1.06
AEG3901	34.6	2.59 \pm 0.25	47.1 \pm 4.1	6.03 \pm 0.36

posites, responsible for the higher performances of these composites.

CONCLUSIONS

1. Titanium tetrachloride could be anchored on the surface of asbestos, by reacting with the external OH groups of the asbestos fibers, and the anchored catalyst could complex the co-catalyst $\text{Al}(\text{C}_2\text{H}_5)_3$ in some way.
2. The asbestos-fiber-anchored catalyst serves a dual purpose: a supported catalyst for polymerization and a reinforcing agent for the final composites. The morphology and interfacial behavior of such composites are quite different from those of the composites made by in situ polymerization. This suggests that the catalytic grafting improves the interface adhesion in a way that cannot be achieved by blending or in situ polymerization.
3. Catalytic grafting offers an opportunity to

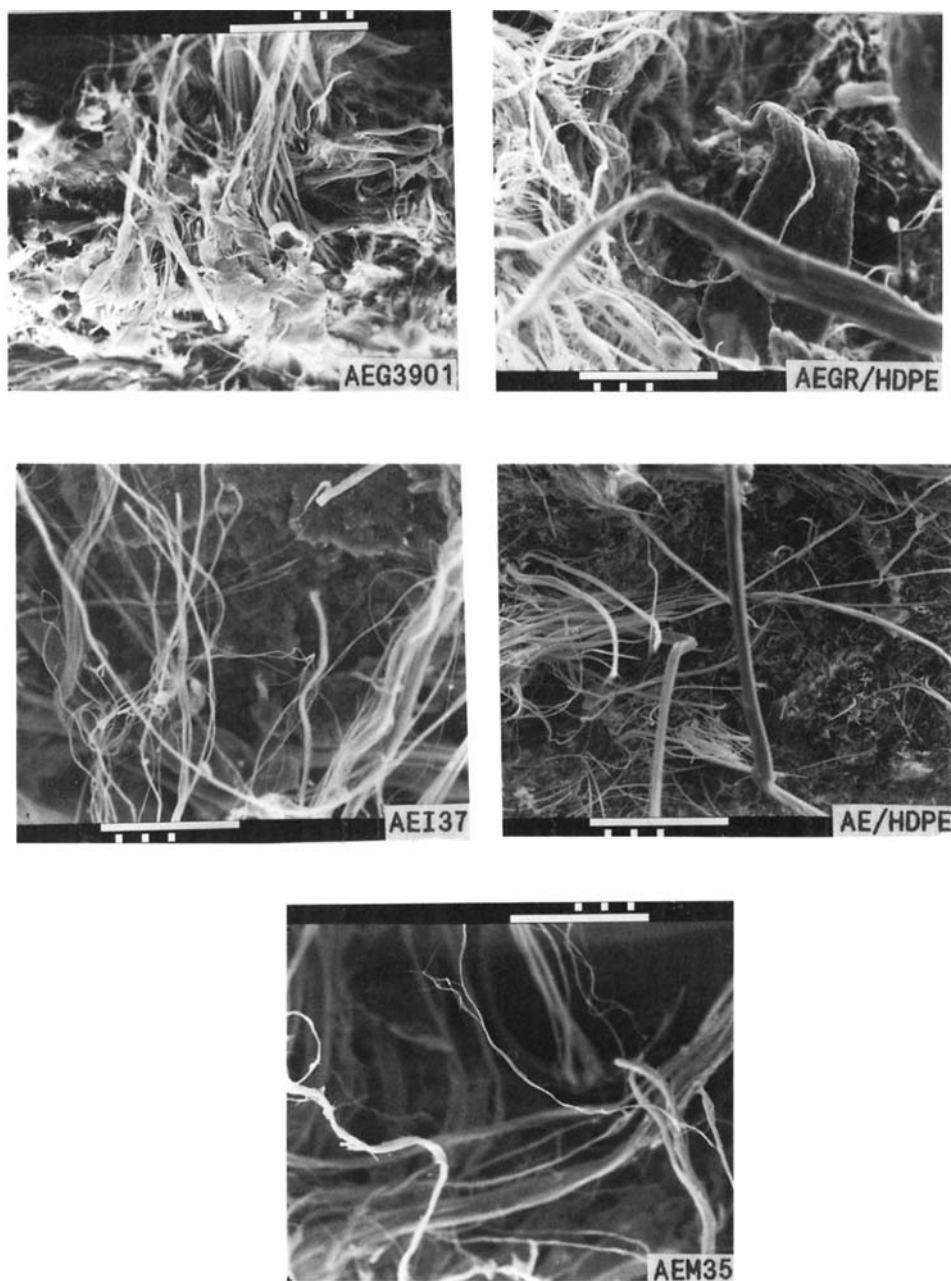


Figure 10 SEM micrographs of different composites (X300).

handle the major problems encountered in thermoplastic polymer composites, and the composites made in this way exhibit much higher performances compared to the composites made by in situ polymerization or conventional mixing. The modulus, the tensile strength, and the elongation at break get significant improvements due to the enhanced adhesion between the matrix and the fibers.

4. The new technique offers several possibilities to control the composition of composites. The composites with high fiber content could be used as modifier for conventional composites to improve their mechanical properties.

There is no a priori reason why the catalytic grafting technique could not be extended to other fiber-polyolefin systems, such as asbestos-polypropylene (PP), high modulus PE fiber (plasma treated)-PE (or PP), Kevlar fiber-PE (or PP), glass fiber-PE (or PP), wood fiber-PE (or PP). Ziegler-Natta polymerization of olefins on various reinforcing fibers lies on the boundary of synthetic polymer chemistry and catalyst chemistry and is a new field of both theoretical and practical importance.

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