

Interfacial Adhesion in Polyethylene–Kaolin Composites: Improvement by Maleic Anhydride-Grafted Polyethylene

F. HINDRYCKX,¹ PH. DUBOIS,^{1,*} M. PATIN,¹ R. JÉRÔME,¹ PH. TEYSSIÉ,^{1,†} and M. GARCIA MARTI²

¹Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman, B6, 4000 Liège, Belgium; ²Dow Benelux N.V., Terneuzen, The Netherlands

SYNOPSIS

Polyethylene–kaolin composites were investigated with a special emphasis on the control of the interfacial adhesion. Both matrix and filler were modified for this purpose. A stearic acid and maleic anhydride-grafted polyethylene were used as potential interfacial agents and the efficiency of aminosilane-surface-treated kaolin was considered. Tensile strength, elongation, impact strength, and melt index were currently measured in relation to the processing conditions. Enhanced interfacial filler–polymer adhesion progressively results in an decreased melt index. This has been clearly shown by comparing the effect of two polymeric additives to the polymer matrix, i.e., a maleic anhydride-grafted HDPE (MAGPE) and an unmodified HDPE of a similar melt index. Compared to low molecular weight additives, such as stearic acid and aminosilane, MAGPE has proved to be a very efficient additive in improving the impact resistance of HDPE–kaolin composites even at low contents. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The economics of production and the cost/performance balance are key parameters for the successful launching of a new material on the market. It is the reason why a sustained effort is made to decrease the price of the final material, so as to improve the processability and to upgrade performance. These targets, which are of vital importance for industry, have stimulated the development of filled polymeric materials.¹ Properties of a filled polymer can indeed be altered by changing the volume fraction, shape, and size of the filler particles and the bulk properties of the polymer matrix. Dimensional stability and increased modulus are commonly expected from polymer composites. Nevertheless, absence of specific interactions between filler and polymer is known to be detrimental to mechanical properties, such as yield strength, ultimate strength, and fracture toughness. A fine and uniform dispersion of the

filler particles within the polymer matrix and, above all, a strong enough interfacial adhesion are prerequisites for high performance.^{2,3}

The approach usually considered to enhance the filler–polymer adhesion at the interphase, also called the mesophase,⁴ is based on the use of a compatibilizer. For instance, the filler surface has been treated with chemicals during the melt blending in order to improve the processability and/or to promote superior mechanical properties. In case of polyolefin/CaCO₃ composites, stearic acid has proved to be one of the cheapest and most effective surface treating agents.^{3,5,6} As an alternative, the filler can be chemically modified prior to processing.^{7,8} In this respect, silane derivatives and organic titanates have been reported to improve the matrix–filler adhesion. Many producers (15 producers in the U.S. since 1981) are now selling fillers treated with one of these coupling agents. Ishida et al.⁹ and McFarren et al.¹⁰ recently used a difunctional coupling agent, i.e., an azidosilane compound. When the reinforcement of high-density polyethylene (HDPE) by kaolin is concerned, this filler has been modified with alkylamines, silanes, and aluminum carboxylates.¹¹ Chemical modification of the polymer matrix by the grafting group reactive toward

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† To whom correspondence should be addressed.

the filler surface is another suitable approach.^{12,13} Accordingly, grafting of maleic anhydride onto a polyolefin is expected to enhance the adhesion to the filler covered with silanol groups.^{14,15} This article was aimed at the efficiency of this strategy in polyolefin-based composites, more precisely, in HDPE-kaolin composites. Tensile strength, elongation, impact strength, and melt index are the main properties of the polyethylene-calcinated aluminum silicate composites to be measured in a systematic way. For the sake of comparison, the efficiency of usual compatibilizers, such as stearic acid, and of aminosilane surface-treated kaolin were investigated.

EXPERIMENTAL

Materials

HDPEs of various density and melt index were used as reported in Table I. Two types of kaolin from Engelhard Co. were used as a filler, i.e., a calcinated aluminum silicate (Satintone W/Whitex) and an aminosilane surface-treated calcinated aluminum silicate (Translink 445). These fillers were flake-shaped particles, with an average size of 1.4 μm , a surface area of 12 $\text{m}^2 \text{g}^{-1}$, and a density of 2.63 kg dm^{-3} .

Sample Preparation

Aluminum silicate and HDPE were mixed in a two-roll mill at 190°C for 5 min. Samples for tensile and impact testing were molded as standard dumbbells and bars, respectively, at 200°C under a pressure of 100 kg m^{-2} .

Calcination

Composites were calcinated in an electrical oven at 500°C for 5 h and the filler was weighed and the filler content calculated.

Additive Materials

Two types of additives were used, i.e., stearic acid ($m_p = 67\text{--}69^\circ\text{C}$; from Sigma) and maleic anhydride-grafted polyethylene (from the Dow Chemical Co.), the maleic anhydride content of which was in the 1.0–1.4 wt % range and the melt index with a load of 2.16 kg ($MI_{2.16} = 0.10 \text{ g/10 min}$).

Melt Index Measurements

Melt-flow measurements were carried out at 190°C with a CEAST 6542 apparatus, according to the ASTM D 1238 norm. Three different loads were used: 2.16, 10.00, and 21.60 kg, respectively.

Impact Testing

U-notched specimens were tested with a Charpy CEAST 6546 apparatus, according to the ASTM D 256 B norm. Length, width, and thickness of the specimens were 50, 6, and 2 mm, respectively. The depth of the notch was 0.35 mm. Testing was carried out at room temperature and repeated for five samples; the average value was then calculated. Impact tests were also recorded with a CEAST 6547 Advanced MK2 Fractoscope System equipped with a 15 J instrumented hammer.

Tensile Testing

Dumbbell samples were tested with an Instron DY.24 apparatus according to the ASTM D 253 norm. Tensile rate was 20 mm/min; length, width, and thickness of the dumbbells were 70, 5, and 2 mm, respectively. Testing was carried out at room temperature and an average value of five measurements was reported.

SEM-EDAX

A Cambridge-Leica scanning electron microscope was used to observe the fracture surface of the com-

Table I Characteristics of HDPEs and Maleic Anhydride-grafted Polyethylene (MAGPE) Used in This Article

Identification	Producer	Density (kg m^{-3})	$MI_{2.16}$ (g/10 min)	$MI_{10.0}$ (g/10 min)	$MI_{21.6}$ (g/10 min)
HDPE 10062	The Dow Chemical Co	962	9.4	—	—
ELTEX B 5924	Solvay S.A.	943	0.1	1.5	10.4
ELTEX B 5920	Solvay S.A.	943	0.2	2.6	15.8
MAGPE	The Dow Chemical Co	—	0.1	2.6	18.8

Table II Modulus, Tensile Properties, and Impact Strength of HDPE 10062/kaolin/MAGPE Composites (M10/F32/MA 0–15): Code M10 = HDPE + Melt Index/F32 = Filler + Wt %/MA 0–15 = MAGPE + Wt % Compared to HDPE

Code	E (GPa)	σ_y (MPa)	ϵ_y (%)	σ_r (MPa)	ϵ_r (%)	I.E. (kJ m ⁻²)
M10/F00/MA 0	1.1	30	7.4	14	170.1	> 39.9 ^a
M10/F32/MA 0	1.7	26	2.8	26	2.8	2.5
M10/F32/MA 5	1.8	33	5.3	19	14.5	8.6
M10/F32/MA 10	1.8	35	5.4	16	18.0	10.7
M10/F32/MA 15	1.7	32	5.3	16	19.3	10.1

^a The impact energy is underestimated since the sample is not completely broken after the test.

posites. An electron de-excitation x-ray analysis (EDAX) detector allowed the chemical composition of the fracture surfaces to be analyzed. Samples were fractured at the liquid nitrogen temperature.

Filler Surface Titration

The number of silanol functions attached to the filler surface was determined by volumetric titration with a triethylaluminum/heptane solution TEA (1 mol/L). The filler (Satintone w/w) was previously dried overnight at 100°C under reduced pressure (10⁻² mmHg). A heptane 20 wt % slurry was then prepared and added with TEA at -78°C. The volume of ethane formed as the reaction product of SiOH with TEA was measured at room temperature.^{16,17}

Solvent Extraction

Polyethylene was extracted from composite samples (1.0 g) with 1,2,4-trichlorobenzene (100 mL) at 160°C under stirring, followed by hot filtration of the filler. No further extraction was reported to occur after 4 days.

RESULTS AND DISCUSSION

Addition of a Chemically Modified Polyethylene (MAGPE) to 32 Wt % Kaolin-HDPE Composites

To enhance the polymer-filler interfacial adhesion, a maleic anhydride-grafted PE (MAGPE) was added to the kaolin-HDPE composites. Actually, two HDPEs of a different melt index (HDPE 10062: $MI_{2.16} = 9.44$ g/10 min, and ELTEX B 5924: $MI_{2.16} = 0.1$ g/10 min) were filled with 32 wt % kaolin (14 vol %) and MAGPE (0–15 wt % compared to HDPE).

Tables II and III show that the elongation at break and the impact energy are significantly improved by the addition of MAGPE. The load vs. time curves confirm this beneficial effect (Fig. 1).

Tensile strength and elongation at the yield point and at elongation break are found to depend not only on the MAGPE content but also on the melt index of the HDPE matrix. Compared to HDPE 10062, ELTEX B 5924 is much more viscous at 190°C and has a higher impact resistance. This superiority is preserved when the polymers are added with 32 wt % filler. The decrease in elongation at

Table III Modulus, Tensile Properties, and Impact Strength of ELTEX 5924/kaolin/MAGPE Composites (M0.1/F32/MA 0–30); Same Codes as in Table II

Code	E (GPa)	σ_y (MPa)	ϵ_y (%)	σ_r (MPa)	ϵ_r (%)	I.E. (kJ m ⁻²)
M0.1/F0/MA 0	0.7	23	8.6	11	147.2	> 60.3 ^a
M0.1/F32/MA 0	1.2	26	6.0	13	38.2	15.2
M0.1/F32/MA 5	1.3	28	6.4	13	50.7	62.4
M0.1/F32/MA 10	1.2	27	7.0	21	83.5	52.5
M0.1/F32/MA 15	1.2	27	6.4	21	115.8	60.5
M0.1/F32/MA 30	1.1	28	6.2	14	57.0	50.0

^a The impact energy is underestimated since the sample is not completely broken after the test.

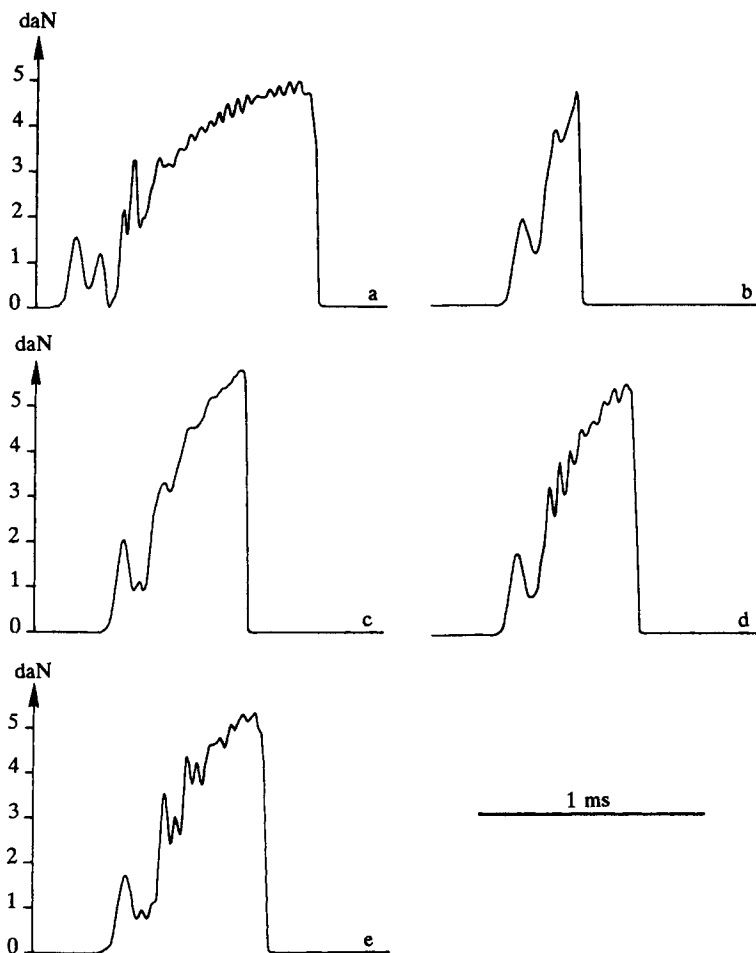


Figure 1 Load vs. fracture time for the M10/F32/MA 0–15 composites (Charpy test; fracture time < 1 ms): (a) M10/F00/MA 0; (b) M10/F32/MA 0; (c) M10/F32/MA 5; (d) M10/F32/MA 10; (e) M10/F32/MA 15.

break and impact energy is less dramatic for ELTEX B 5924 than for HDPE 10062. The addition of increasing amounts of MAGPE does not significantly change the tensile properties at the yield point, nor the ultimate tensile strength, in sharp contrast to the elongation at break and the impact energy, which are remarkably increased. This beneficial effect is much higher for the ELTEX B 5924-based composites for which the impact energy tends to the value for the neat polyethylene. It must, however, be noted that exceeding amounts of MAGPE have a depressive effect on the impact performances as supported by the increase of 15–30 wt % MAGPE in the M0.1/F32 composites (Table III).

Where or when the modulus is concerned, it is essentially independent of the addition of MAGPE. It changes with the melt index of HDPE and it increases upon the addition of kaolin.

To account for the data reported in Tables II and III, it is worth comparing the melt index (MI) at

190°C of MAGPE ($MI_{2.16} = 0.15$), HDPE 10062 ($MI_{2.16} = 9.44$), and ELTEX B 5924 ($MI_{2.16} = 0.1$). It might be anticipated that the addition of the highly viscous MAGPE to HDPE 10062 should increase the melt index of the polymer matrix and, accordingly, the mechanical properties.¹⁸ If it is so, two effects might be operative and could not be discriminated from each other, i.e., a decrease in the polymer MI and the occurrence of specific interactions between the filler and the polymeric additive.

In the second series of composites, the melt index of MAGPE is very close to that of the HDPE ELTEX B 5924. Therefore, modifications in the mechanical performances of the composites could only be attributed to a change in the adhesion between the filler and the polymer matrix. This speculative discussion needs experimental support. It is the reason why the melt index of the two series of composites has been measured as reported in Tables IV and V.

Table IV Melt Flow Index of the M10/F32/MA 0–15 Composites: Comparison of Theoretical [eq. (1)] and Experimental Values

Code	MAGPE (%)	m_A^a	m_B^a	MI _{2.16} (g/10 min)	
				Theoretical	Experimental
M10/F0/MA 0	0	1.00	0.00	9.44	9.44
M10/F32/MA 0	0	0.68	0.00	6.23	6.23
M10/F32/MA 5	5	0.65	0.03	5.42	5.27
M10/F32/MA 10	10	0.62	0.06	4.63	2.55
M10/F32/MA 15	15	0.58	0.10	3.96	2.03

^a m_A and m_B refer to wt % of Dow 10062 and MAGPE, respectively.

The MI of the M10/F32/MA 0–15 composites rapidly decreases upon increasing the MAGPE content (Table IV). This strong dependence essentially results from the much lower MI of the additive compared to the HDPE matrix (Table I). In sharp contrast, the MI of the ELTEX B 5924-based composites (M0.1/F32/MA 0–30) is much lower and essentially independent of the addition of MAGPE. This is clear when the MI is measured with a load of 21.6 kg (Table V). This observation is qualitatively consistent with the close MI of the additive and the polymer matrix. The melt flow index of composites consisting of a blend of polyethylenes of a different MI may be calculated as follows¹⁹:

$$m_A \log(MI_A) + m_B \log(MI_B) + F_p = \log(MI_{\text{theoretical}}) \quad (1)$$

where m_A and m_B are the weight fractions of each polymer, and F_p , the filler interaction parameter. F_p , which is assumed to be constant at a constant filler content, has been calculated as 0.13 from data measured for M10/F32/MA 0. The theoretical melt flow index in the M10/F32/MA 0–15 series has been calculated from eq. (1). It is clear from Table IV and Figure 2 that the experimental MI is lower than is the theoretical value when the MAGPE content is raised. This deviation from eq. (1) might be nothing but the effect of MAGPE on the interfacial adhesion.

To substantiate this assumption, MAGPE has been substituted by an unmodified HDPE of a comparable MI. As HDPE, ELTEX B 5920 has been used since it has an MI value close to that of MAGPE (Table I).

Figure 2 shows that the MI of this new M10/F32/HD 0–10 series is slightly smaller than are the calculated values but definitively higher than the experimental values in the presence of MAGPE. The

small deviation from the theoretical values may be due to the crude approximation that F_p only depends on the filler content and not on the index of the final composites.

Interestingly enough, the addition of 5 and 10 wt % of Eltex B 5920 to the HDPE 10062 matrix does not significantly improve the elongation at break or the impact energy of the composites, compared to the results when MAGPE is used as the additive component (Figs. 3 and 4). It is now obvious that differences among M10/F32/MA 0–15, M0.1/F32/MA 0–30, and M10/F32/HD 0–10 composites do not only result from a difference in the MI of the matrix and the additive but also from the occurrence of an interfacial adhesion or bonding.

Composites with Increasing Filler Contents

As illustrated in Figure 2, favorable interactions between the polymer matrix and the filler result in an decrease in the composite MI, all other conditions being the same. This effect of the filler/polymer interactions on the MI has been confirmed by filling both the neat HDPE 10062 and this HDPE

Table V Melt Flow Index of the M0.1/F32/MA 0–30^a

Code	MAGPE (%)	MI ₁₀ (g/10 min)	MI _{21.6} (g/10 min)
M0.1/F0/MA 0	0	1.5	10.4
M0.1/F32/MA 0	0	1.4	9.3
M0.1/F32/MA 5	5	1.3	9.4
M0.1/F32/MA 10	10	1.2	9.7
M0.1/F32/MA 15	15	0.7	9.5
M0.1/F32/MA 30	30	1.1	9.2

^a MI_{2.16} has not been measured because of too high viscosity.

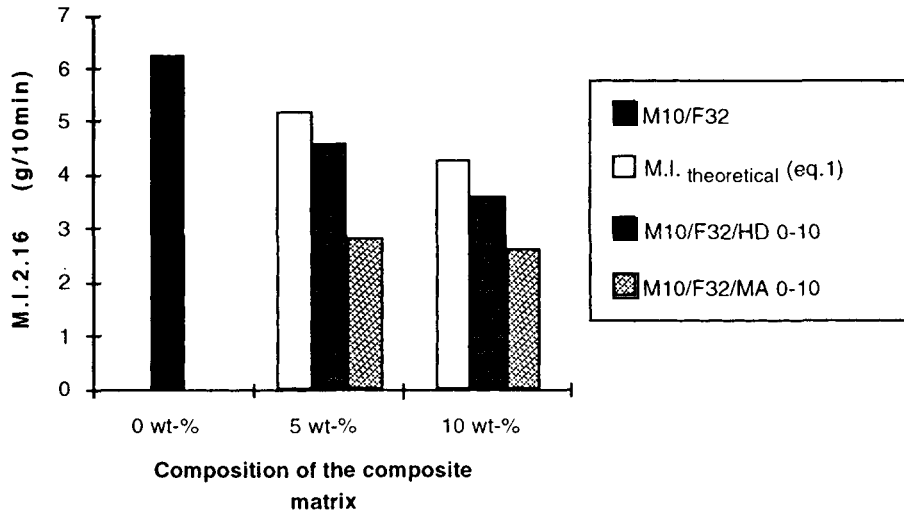


Figure 2 Melt index (2.16 kg) of the M10/F32 composites: unmodified and added with MAGPE (M10/F32/MA 0-10) and ELTEX B 5920 (M10/F32/HD 0-10), respectively.

(added with 10 wt % MAGPE) with increasing amounts of kaolin (0-40 wt % or 0-18 vol %). In the absence of MAGPE, the MI decreases upon increasing kaolin contents (Fig. 5). The best-fitting curve is actually a third-order polynomial. The partial aggregation of the kaolin particles increasing with the filler content might account for this effect as a result of an increase in the apparent mean particle size.

The addition of kaolin to the polymer matrix modified by 10 wt % MAGPE has a dramatic effect on the melt index, the logarithm of which linearly decreases when the vol % of kaolin increases (Fig. 5). This very sharp effect is again consistent with the expected interaction of MAGPE with the filler

particles. Actually, the kaolin particles are assumed to be better deaggregated and thus better dispersed within a possibly reactive polymer matrix. As a result of the expected interfacial interactions, the filler particles would be coated with a MAGPE-HDPE mesophase layer, and their larger apparent size would explain the experimentally observed decrease in the melt index. Two experimental techniques were used in order to give credit to the formation of MAGPE layer around the filler particles:

- Solvent extraction of the polymer matrix, combined with the analysis of the thickness of the

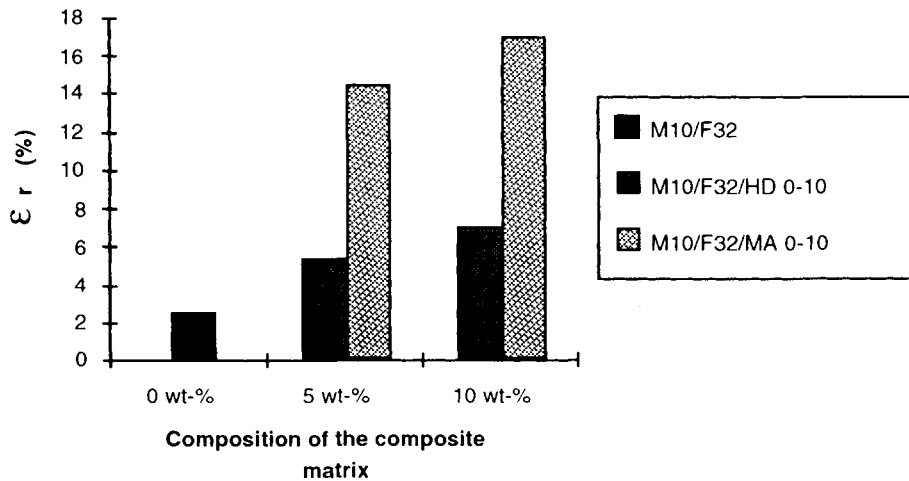


Figure 3 Elongation at break (ϵ_r) of the M10/F32 composite: unmodified and added with MAGPE (M10/F32/MA 0-10) and ELTEX B 5920 (M10/F32/HD 0-10), respectively.

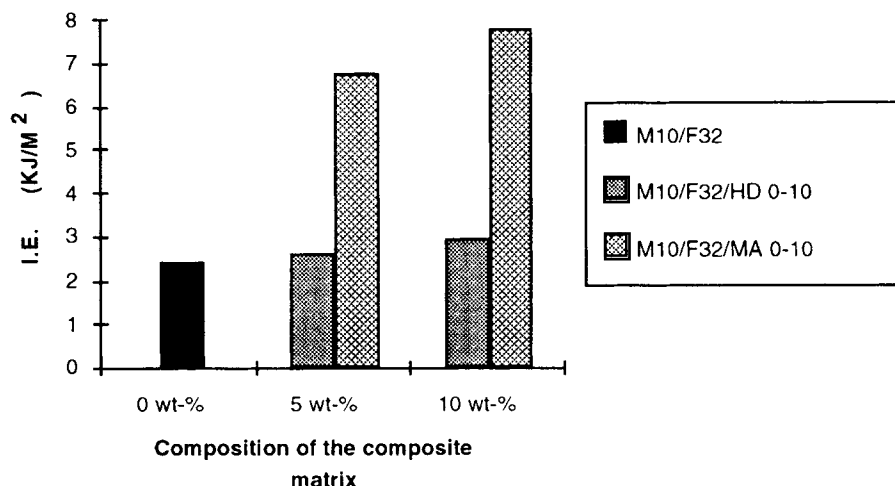


Figure 4 Impact energy (I.E.) of the M10/F32 composite: unmodified and added with MAGPE (M10/F32/MA 0-10) and ELTEX B 5920 (M10/F32/HD 0-10), respectively.

remaining layer of polymer attached to the kaolin particles by thermogravimetry.^{2,20}

- EDAX analysis of the chemical composition of the fracture surface of the composites (fracture at the liquid nitrogen temperature).

Solvent Extraction and Analysis of the Bound Polymer Layer

Recently, several studies have focused on a possible relationship between the properties of polyethylene composites and the existence of a mesophase layer around the filler particles. The authors observed that the whole amount of polyethylene engaged in the composites could not be dissolved by solvent ex-

traction, although the neat polymer is quickly and completely dissolved under the same conditions. The insoluble fraction has been referred to as the bound polymer.

Kendall and Sherliker^{21,22} analyzed various polyethylene-silicate composites and showed that a layer of bound polymer of a ca. 2 nm thickness is formed independently of the filler particle size. They discussed the possible effects of this layer on the fracture properties of the composites. Dolakova and Hudecek²³ observed a residual interfacial fibrillar structure after polyethylene dissolution, and they tentatively drew a relationship between this interfacial situation and the fracture properties of glass bead-, silica-, and kaolin-containing composites.

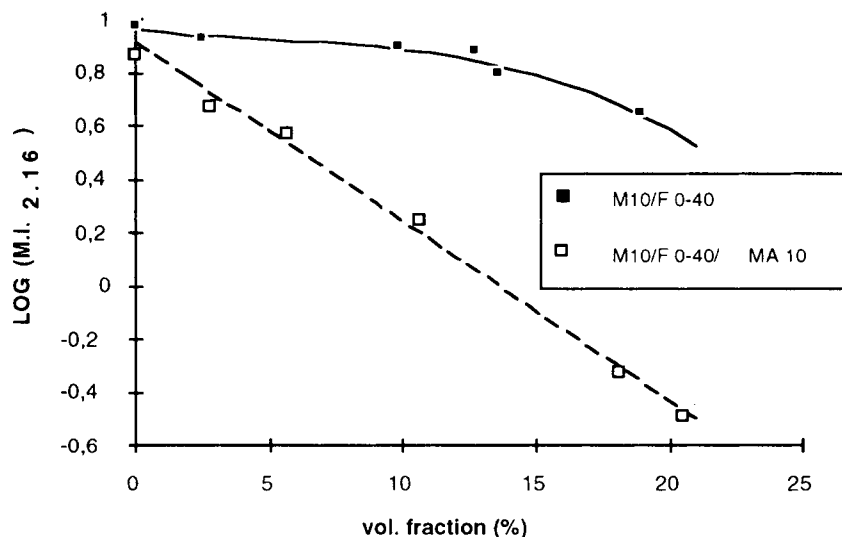


Figure 5 Melt flow index vs. filler vol % for HDPE 10062 (M10)-based composites.

Table VI Bound Polymer in the M10/F32/MA 0, M10/F32/MA 5, and M10/F32/MA 15 Composites

Code	MAGPE (Wt %)	Bound HDPE (Wt %)
M10/F32/MA 0	0	4.5
M10/F32/MA 5	5	15.4
M10/F32/MA 15	15	46.4

Furthermore, a 3.6 nm-thick insoluble layer has been reported in Aerosil (SiO₂)-filled HDPE.²⁰ Maurer et al.²⁰ also showed that the fracture properties of kaolin-filled polymers are dominated by the interfacial interactions rather than by the filler volume fraction.

Composites containing 0, 5, and 15 wt % of MAGPE were extracted with 1,2,4-trichlorobenzene as reported in the Experimental part. The amount of bound polyethylene was measured by thermogravimetric analysis. It clearly increases with the MAGPE content (Table VI). Nevertheless, in the absence of MAGPE, 4.5 wt % of polyethylene remains insoluble under the extraction conditions used in this study. IR spectroscopy might have been a convenient technique to identify MAGPE at the filler surface. Unfortunately, the maleic anhydride content of MAGPE, i.e., 1.0–1.4 wt %, is not high enough to be observed in a reliable way. That the fraction of bound polymer increases with the MAGPE content is convincing, although indirect, evidence for the reaction of maleic anhydride functions in MAGPE and silanol groups on the filler surface. In addition to MAGPE chains chemically attached to the filler particles, long HDPE chains are suspected to be entangled within the interphase polymer layer and accordingly immobilized. Some free kaolin particles may also be entrapped within this layer. The question of the reliability of the extraction technique might also be addressed but in the M10/F32/MA 0 composite; 4.5 wt % bound HDPE has been found in the undissolved fraction according to reported data. Indeed, considering that the (unprocessed) kaolin filler surface (BET = 12 m²/g) is completely covered with bound polymer, a 3.9 nm-thick layer can be calculated. These last results are in complete agreement with Maurer et al.'s²⁰ data where 4.3 wt % bound polymer corresponding to a 3.6 nm-thick layer has been found in kaolin-filled polyethylene. Such an agreement proves the validity of the extraction technique.

SEM-EDAX Measurements

Fracture surfaces prepared at the liquid nitrogen temperature were analyzed by SEM-EDAX. Samples containing the MAGPE additive (M10/F32/MA 5–15) were compared to the M10/F32/HD 5 composite in which MAGPE was replaced by an unmodified HDPE (5%) of a comparable melt index (ELTEX B 5920). It is known that specimens of low tensile strength values have a brittle-fracture behavior and the fracture surface shows uncovered filler particles. In contrast, specimens of high strength are more ductile and fracture occurs within the polymer matrix.^{20,24} Accordingly, an SEM micrograph of the M10/F32/HD 5 has clearly shown neat kaolin particles and some particle fingerprints all along the fracture surface [Fig. 6(a)]. In contrast,

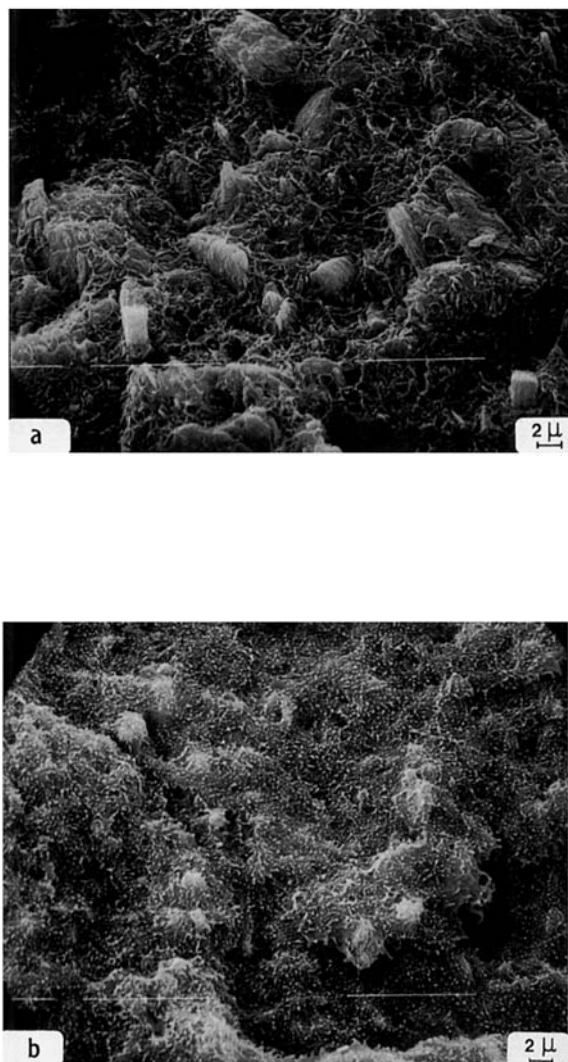


Figure 6 SEM micrographs of fracture surface of (a) M10/F32/HD 5 and (b) M10/F32/MA 15 ($\times 2500$).

Table VII Chemical Composition of Cold Fractured Surfaces: Comparison of the Al/Al + C Atomic Ratio (EDAX) and the Impact Energy (25°C)

Code	$\frac{\text{Al}}{\text{Al} + \text{C}}$ (%)	Impact Energy (kJ m ⁻²)
M10/F32/HD 5	11.7	2.6
M10/F32/MA 5	10.6	6.8
M10/F32/MA 10	10.0	7.8

samples containing the MAGPE additive, e.g., M10/F32/MA 15, have, for the most part, presented smooth polyolefinic surfaces with well-dispersed covered filler particles [Fig. 6(b)]. The chemical surface composition is expected to depend on whether the filler particles on the surface are coated or not with a polymer layer. If the filler-polymer adhesion is high, the filler particles should be covered with polyethylene and the Al/(Al + C) atomic ratio should be lower than in case of a brittle fracture. Table VII shows that this atomic ratio decreases as the MAGPE content increases. This observation is consistent with a more efficient surface coating of the kaolinite particles when MAGPE is added. This effect is nicely parallel to the increase in the impact energy (Table VII). These results confirm the solvent extraction data, although they are essentially qualitative, partly due to a depth of analysis (1 μm) close to the average particle size (1.4 μm).

Addition of a Compatibilizer: Stearic Acid

Stearic acid is often used as a compatibilizer in polyolefin composites.^{25,26} The acid functions may indeed interact and/or react with silanol groups available upon the filler surface. The C₁₇ alkyl chain is considered to be miscible with polyethylene, although it is too short to be effectively entangled within the matrix.^{27,28} Several composites have been prepared, which contain 1.3, 5.2, and 17.6 wt % of stearic acid (SA), respectively (Table VIII).

In the M10/F32/SA 0–18 series, the addition of SA improves the impact and ultimate tensile properties of the composites to some extent. However, an exceedingly high amount of this additive (above 1 wt %) seems to have a detrimental effect (Table VIII and Fig. 9). Surprisingly enough, in the M0.1/F32/SA 0–18 series, stearic acid drastically decreases the impact energy and the elongation at break of the composites, particularly at contents of 5 wt % and higher.

SA which consists of a polar head (carboxylic acid) and a hydrophobic tail (C₁₇ alkyl chain), typically has the structure of a surfactant. In a hydrophobic matrix, it should form micelles with a carboxylic acid core surrounded by alkyl chains. Micellization is expected to occur earlier in an HDPE matrix of a higher molecular weight, i.e., less miscible with the alkyl chains. According to data in Table VIII, the rapid formation of SA micelles in the EL-TEX B 5294 matrix might lead to a brittle material. In the M10/F32/SA 0–18 series, the micelle formation would occur at a higher acid stearic content due to lower molecular weight chains in favor of a

Table VIII Modulus, Tensile Properties, and Impact Strength for the M10/F32/SA 0–18 and M0.1/F32/SA 0–18 Composites

Code	Stearic Acid (Wt %)	<i>E</i> (GPa)	σ_y (MPa)	ϵ_y (%)	σ_r (MPa)	ϵ_r (%)	I.E. (kJ m ⁻²)
M10/F0/SA 0	0	1.1	30	7.4	14	170.1	> 39.9*
M10/F32/SA 0	0	1.7	26	2.8	26	2.8	2.5
M10/F32/SA 1	1.3	1.8	34	5.5	29	10.8	9.1
M10/F32/SA 5	5.2	1.9	33	6.3	29	9.9	6.7
M10/F32/SA 18	17.6	1.8	31	6.2	29	8.8	5.3
M0.1/F0/SA 0	0	0.7	23	8.6	11	147.2	> 60.3*
M0.1/F32/SA 0	0	1.2	26	6.0	13	38.2	15.2
M0.1/F32/SA 1	1.3	2.0	28	5.6	14	30.9	13.2
M0.1/F32/SA 5	5.2	1.9	31	6.3	15	28.0	9.3
M0.1/F32/SA 18	17.6	1.9	29	6.3	28	9.0	6.2

* The impact energy is underestimated as the sample is not completely broken.

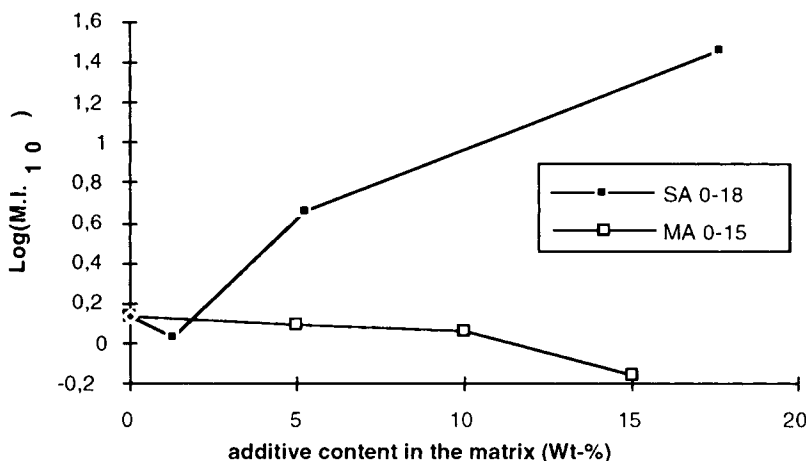


Figure 7 Melt flow index logarithm vs. additive content in the composites based on ELTEX B 5924 (M0.1/F32).

slight decrease in SA miscibility. Figures 7 and 8 show that 1 or 2 wt % SA decreases the MI of composites based on both Dow and ELTEX, which is in favor of an improved filler-HDPE matrix adhesion. However, increasing amounts of SA are responsible for the opposite effect, indicating that SA then behaves as a lubricant at 190°C.²⁷

This observation is in qualitative agreement with the number of the carboxylic acid functions, which is already twice as high as the silanol groups at the filler surface ($2.3 \cdot 10^{-4} \text{ mol g}^{-1}$) (surface titration) when 1 wt % SA is used in the two series of composites. Conversely, Table VIII confirms that a very small amount of SA is required to coat and/or to react with the filler particles and, thus, to increase the impact energy, although the improvement is rather small compared to the MAGPE compound. It is worth pointing out that in PP-CaCO₃ systems

Jancar et al. recently reported that SA decreases the interfacial adhesion.^{27,28}

The beneficial effect that SA can impart to HDPE/kaolin composites clearly depends on both the SA content and the MI of HDPE. The impact resistance of the composite shows no further improvement when the molecular weight of HDPE is too high (i.e., low MI). It is, however, advantageous that only very small amounts of SA (ca. 1 wt %) give rise to the best, although not very high, impact properties. Finally, SA has a low melting temperature, 68°C, which presents a problem for the composite processing at 190°C.

Addition of a Surface-treated Filler

Another traditional way of improving the interfacial adhesion has to be found in the chemical

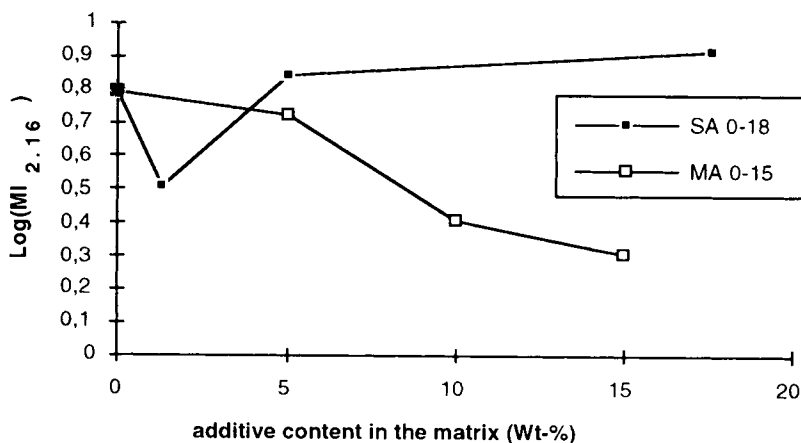


Figure 8 Melt flow logarithm vs. the additive content in the composites based on HDPE 10062 (M10/F32).

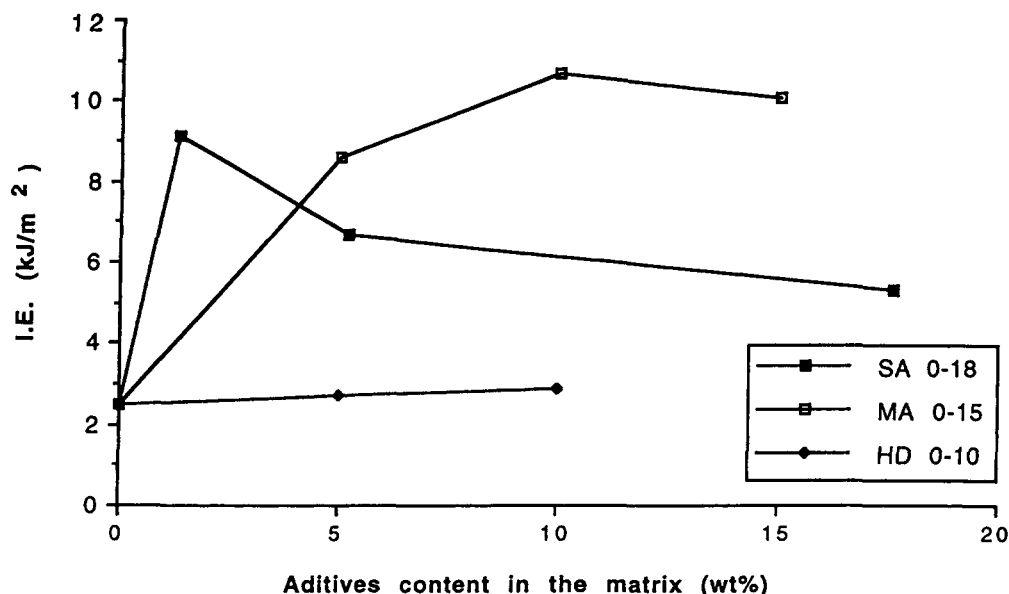


Figure 9 Impact energy (I.E.) vs. the additive content for M10/F32 composites.

modification of the filler surface in order to reduce the interfacial energy of the filler-HDPE system. Silane derivatives and organic titanates are commonly reported as coupling agents very effective in improving filler-polymer interactions. These coupling agents have been first devised and used in glass-filled polymers, particularly unsaturated polyesters. Plueddemann⁷ identified several reasons accounting for the efficacy of the silane coupling agents: improved filler-matrix adhesion, protection of the filler surface against microflaws which initiate failure, reinforcement of the interfacial layer, improved filler wetting and dispersion conditions, and increased hydrophobicity of the surface. If the formation of a silane "monolayer" were first considered, later on, the concept of gradients in multilayers emerged.²⁹ Production and use of silane and titanate coupling agents are still increasing, although they are relatively expensive and scientific assessment of their role is still lacking.

In this study, the efficacy of such a commercially available surface-treated filler has been compared to the MAGPE additive. An aminosilane surface-treated kaolin was compared to neat kaolin of the same average particle size (1.4 μm) in an HDPE 10062 matrix. Table IX shows that the surface-modified filler slightly improves the impact energy and the tensile properties of the composite, but not better than 1 wt % SA. The MI remains essentially unmodified, which may reveal only slight changes in the filler dispersion and the related properties. Consequently, it can be concluded that the amino-

silane surface-treated kaolin usually considered in composite formulation only slightly improves the interfacial adhesion although the filler dispersion is enhanced. The surface coating could explain such a deaggregation by preventing the initial hydrogen bonding between interparticle silanol functions, whereas the very poor interaction between the primary amino group and the polyolefinic matrix could be responsible for the low adhesion improvement observed.

CONCLUSIONS

The interfacial adhesion between kaolin and polyethylene can be improved by the chemical modification of either the matrix or the filler surface. These methods improve the mechanical performance, although it is only the polymeric MAGPE additive reactive toward the filler surface which allows the impact properties to be very significantly improved. This improvement is largely independent of the MAGPE content at least in the range of 5–15 wt %. Solvent extraction of polyethylene has shown that an increasing amount of HDPE is attached to the filler surface as the MAGPE content is increased. Parallel to this observation, the impact resistance is found to be improved. The matrix viscosity is also of critical importance for the mechanical properties of the related composites. It has been observed that the impact resistance is more extensively improved when HDPE is of a lower melt index. Moreover,

Table IX Modulus, Tensile Properties, Impact Strength, and Melt Index for HDPE 10062 Added with 32 Wt % of Neat Kaolin and Translink 445 Kaolin, Respectively

Code	E (GPa)	σ_y (MPa)	ϵ_y (%)	σ_r (MPa)	ϵ_r (%)	I.E. (kJ m ⁻²)	MI _{2.16} (g 10 min ⁻¹)
M10/F32	1.7	26	2.8	26	2.8	2.5	6.3
M10/T445 32	2.1	29	3.9	28	5.0	6.7	6.5

when the MAGPE additive is more viscous than is the HDPE matrix, a substantial decrease in the composite MI is reported to occur. This effect cannot be fully accounted for by the averaging of the MI of each component. An additional contribution has to be found in the improvement of the interfacial adhesion. Indeed, the replacement of MAGPE by an HDPE of a similar MI has confirmed that MAGPE actually behaves as an interfacial agent due to the reactivity of the anhydride functions toward the silanol groups present onto the filler surface. Equation (1), valid to a composite system, has allowed the MI to be predicted and compared to the experimental values.

NOMENCLATURE

MAGPE	maleic anhydride-grafted polyethylene
E	tensile modulus (GPa)
σ_y	tensile strength at the yield point (Mpa)
ϵ_y	tensile elongation at the yield point (%)
σ_r	tensile strength at break (Mpa)
ϵ_r	tensile elongation at break (%)
I.E.	Charpy impact energy (kJ m ⁻²)
M10/F32/X	M: matrix followed by melt index (g/10 min.). F: filler followed by weight %. X: additive, i.e., MA = MAGPE; HD = HDPE. ELTEX* 5920; SA = stearic acid; T445 = Translink 445 kaolinite filler (wt % compared to the polymer matrix)

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