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Polymerization-Filling Technique: An Efficient Way To Improve the Mechanical Properties of Polyethylene Composites

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Melt blending of thermoplastic polyolefins with hydrophilic fillers usually leads to materials with poor mechanical properties, as a result of the weak interfacial adhesion between the hydrophobic matrix and the hydrophilic surface of the filler.[1] To alleviate this problem, fillers have been modified by surface-active agents and coupling agents.[2−5] The encapsulation of the filler by a polymeric matrix[6,7]is another technique, which allows a zone of intermediate modulus between the filler and the matrix to be built up, so reducing local stress concentration responsible for the filler−matrix debonding and the crack propagation and improving accordingly the mechanical and impact properties. However, this technique requires use of functional polymers to cross link the encapsulation layer, which increases the cost of the final material.

We have previously reported on the combination of the polymerization-filling technique (PFT) and metallocene−methylalumoxane catalyst as a successful strategy to load polyethylene and elastomeric ethylene/1-octene copolymers with fillers.[8,9] This technique consists of fixing a catalyst for the olefin polymerization on the filler surface and growing the polymer directly from it. If the reaction is stopped at the early stage of the polymerization, the filler is expected to be completely covered by a thin polymer layer. To test the validity of this technique, glass beads have been encapsulated by polyethylene and ethylene/1-octene copolymer, respectively, and then dispersed in high-density polyethylene (HDPE).

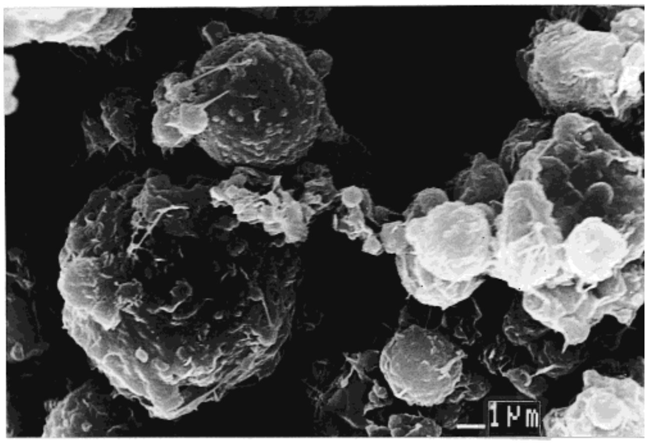

Figure 1. SEM micrograph of glass beads coated by 14.5 wt % polyethylene.

Table 1. Effect of the Precoating of Glass Beads on the Young Modulus (*E*), Strain at Break (σ_r), Elongation at Break (ϵ_r), and Impact Energy (I.E.) of Polyethylene Loaded by 20 wt % Glass Beads

entry	sample[a]	*E* (GPa)	σ_r (MPa)	ϵ_r (%)	I.E. (kJ/m^2)
1	MI 1	n.d.	40.0	996	n.d.
2	MI 1 + GB	1.7	24.7	636	12.0
3	MI 1 + CGB	1.3	28.5	659	150.5
4	PFC	1.4	20.6	80	6.5

[a] MI 1 = DOW HDPE (MI_2 = 1 g/10 min); CGB = coated glass beads; GB = bare glass beads; PFC = polymerization-filled composite (23 wt % glass beads); n.d. = not determined.

The beneficial effect of a polyethylene coating has been first studied. The anchoring of the polymerization catalyst onto the filler has been reported[9] (see Experimental Section). The accordingly treated filler was transferred into an Autoclave Engineers Zipperclave reactor already charged with 1150 mL of dried *n*-heptane. The polymerization was carried out at 70 °C under 9 bar of ethylene (99.95%, Air Liquide) and 1 bar of hydrogen (99.999%, Air Liquide). The reaction was stopped 2 min later, the filler being then modified by 14.5 wt % of polyethylene as determined by thermogravimetric analysis (TGA). Scanning electron microscopy (SEM) confirms that the glass beads are homogeneously coated by polyethylene (Figure 1). The coated filler was finally blended with melted Dow HDPE (melt flow index under 2.16 kg = 1 g/10 min), the purpose being to load the polyolefin with 20 wt % glass beads. The tensile (ASTM D638) and impact (Izod) properties have been measured and compared to Dow HDPE and to two references. The first reference composite was prepared by direct melt blending of DOW HDPE and uncoated glass beads (20 wt %). The second one was prepared by the same polymerization-filling technique except for the polymerization time (47 min) that was long enough to produce HDPE loaded by 23 wt % glass beads. The experimental data are listed in Table 1.

Compared to the neat matrix (entry 1), the ultimate tensile strength and the elongation at break of all the

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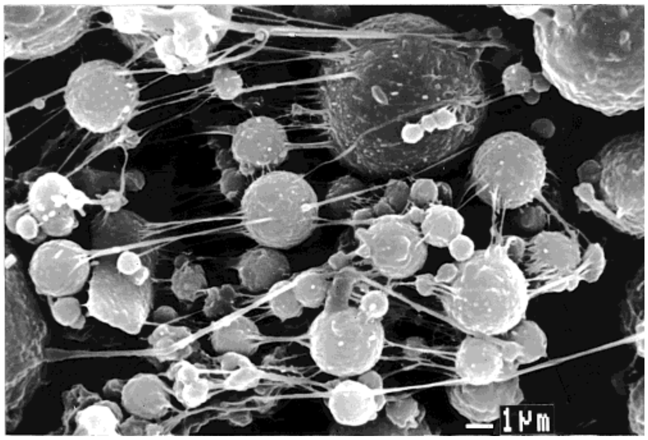

Figure 2. SEM micrograph of glass beads coated with 7 wt % ethylene/1-octene copolymer.

Table 2. Effect of the Precoating of Glass Beads by Ethylene/1-Octene Copolymer on Young Modulus (*E*), Strain at Break (σ_r), Elongation at Break (ϵ_r), and Impact Energy (I.E.) of Polyethylene Loaded by 20 wt % Glass Beads

entry	composite[a]	*E* (GPa)	σ_r (MPa)	ϵ_r (%)	I.E. (kJ/m^2)
1	MI 10	n.d.	22.7	1475	n.d.
2	MI 10 + CGB	1.51	28.9	6.9	41.0
3	MI 10 + GB	1.43	26.4	4.2	14.5

[a] MI10 = HDPE DOW 10062 (MI$_2$ = 10); CGB = coated glass beads; GB = bare glass beads; n.d. = not determined.

composites are expectedly smaller. However, when the glass beads are previously covered by a thin polyethylene layer (entry 3), these properties are improved compared to those of the composite containing unmodified glass beads (entry 2) and the composite directly prepared by the polymerization-filling technique (entry 4). Remarkably, the impact energy is increased by 1 order of magnitude by the precoating of the filler. SEM observation of the cryofracture surfaces indicates that the fracture propagates along the bead/matrix interface in the case of unmodified glass beads. In contrast, the fracture occurs throughout the matrix filled by the coated glass beads, which are thus firmly embedded in polyethylene.

The glass beads have also been coated by an ethylene/1-octene copolymer, to know whether the modulus of the filler coating has an effect on the mechanical properties of the polyethylene composite. The copolymerization was carried out under the same conditions as before, including the reaction time; 7 wt % of copolymer was deposited (TGA), which is enough to coat the glass beads as confirmed by SEM (Figure 2). DSC analysis of the coated beads shows a melting temperature at 127 °C (second heating run at 20 °C/min), in agreement with partial incorporation of 1-octene in the matrix. The coated beads (32 wt %) were kneaded with melted Dow 10062 HDPE (MI$_2$ = 10 g/10 min), and the mechanical properties of the final composite were compared with the HDPE and the two reference composites (Table 2).

The composite that contains coated glass beads (entry 2) is not homogeneous, white aggregates being observed and thought to result from the lack of miscibility between the matrix and the copolymer coating,[10] so leading to the agglomeration of the coated beads. Despite this nonideal dispersion, the comparison of entries 2 and 3 shows that the coating enhances the ultimate mechanical properties, including the impact resistance, even though to a lesser extent than in the case of the polyethylene coating. It must be noted that dispersion of coated or uncoated glass beads in the Dow HDPE of high melt flow index dramatically reduces the elongation at break (Table 2). This observation might be partly due to the relatively low molecular weight of the HDPE matrix, unable to provide the filled material with sufficient plasticity.

In conclusion, the precoating of glass beads by a thin layer of either ethylene or ethylene /1-octene copolymer is beneficial to the impact properties of composites prepared by kneading this modified filler with melted HDPE, at least compared with those of the same composites containing the unmodified particles. The polyethylene coating is more efficient than the ethylene/1-octene copolymer one as a result of a lack of miscibility with the polyethylene matrix.

Experimental Section

The immobilization of the catalyst at the surface of the inorganic filler was carried out under nitrogen using Schlenk techniques.

Polyethylene Coating. Twenty grams of glass beads (CP7000, 90% beads size between 2.4 and 4.5 μm, Potters-Ballotini), previously dried for 16 h under reduced pressure (10^{-2} mmHg) at 105 °C, was suspended in 250 mL of dried *n*-heptane. Twenty milliliters of methylalumoxane solution (MAO, 10 wt % in toluene, Witco) was allowed to evaporate under reduced pressure to eliminate residual trimethylaluminum (TMA) and then dissolved in 20 mL of freshly dried toluene. The TMA-free MAO solution was immediately added to the filler suspension, and the mixture was allowed to react at room temperature for 1 h. Solvents were evaporated and the dry filler was treated at 150 °C under reduced pressure for 2 h. The treated glass beads were then washed twice with 100 mL of dried toluene at 80 °C and finally suspended in 250 mL of dried *n*-heptane. (*tert*-Butylamido)dimethyl(tetramethyl-η^5-cyclopentadienyl) silane titanium dimethyl (CGC) (4.8×10^{-5} mol) was added to the treated beads stirred in 250 mL of dried heptane and they were allowed to react for 1 h at 80 °C.

Ethylene/1-Octene Coating. Twenty grams of dried glass beads, CP7000, was dispersed in 300 mL of dried *n*-heptane. Twenty milliliters of the 10 wt % MAO solution in toluene from Witco was added and the suspension was heated at 80 °C for 1 h. The filler was filtered out and washed at 80 °C by 200 mL of dried toluene. CGC (1.224×10^{-5} mol) was added to the treated beads dispersed in 250 mL of dried heptane and they were allowed to react for 1 h at 80 °C.

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