Effect of interfacial interactions on mechanical properties of composites of low-density polyethylene reinforced with micrometric Boehmite powders were studied in combination with two silane coupling agents vinyltri(2-methoxyethoxy)-silane (VTMES)-SCA 972 and 3-(trimethoxysilyl)-propylmethacrylate (3MPS)-SCA 989. Samples were prepared via melt mixing followed by compression or injection molding. Morphology and mechanical behavior of the composites were investigated as a function of the filler loading. The modulus of the composites increases with increasing contents of micrometric Boehmite particles. Environmental scanning electron microscopy (ESEM) examination reveals formation of fibrous structures upon addition of the treated micro fillers. We presume the fibrillation of the LDPE phase is related to changes of the matrix viscosity. Improvements in mechanical properties are attributed to homogeneous dispersion and good interfacial adhesion between the filler and the matrix, as evidenced by ESEM. POLYM. COMPOS., 30:760–767, 2009. © 2008 Society of Plastics Engineers

INTRODUCTION

It is well known that mechanical, tribological, and thermal properties of polymers can be improved by inclusion of additives including fillers. Since polymers undergo wear easily, methods are being developed to understand polymer wear [1] and to improve polymer tribology [2]. In the case of both mechanics and tribology, the degree of improvement of any property depends on the choice of filler origin, particles size and shape [3–17]. The challenges in this area of high-performance polymers consist in obtaining a significant improvement in the adhesion between the polymer matrix and the additives and to achieve a homogeneous dispersion of the additives in the matrix [18–28].

Thus, control and/or manipulation of the surface properties of the particles are of importance. We know that, during the preparation process, formation of covalent bonding between organic polymers and inorganic components contributes to the enhancement of the compatibility in the composites. This can be achieved through the grafting of a polymerizable group onto oxide surfaces via hydroxyl groups followed by its copolymerization with organic monomers [29–35]. Among others, silane coupling agents have been used to improve dispersion, adhesion, and compatibility in such materials [36–40]. Covalent chemical bonding between the two phases can be achieved by grafting of polymerizable groups onto the oxide surfaces.

Several special techniques are in use for the preparation of polymer-containing composites [41–54]. The surface treatment of the additive particles is useful to efficiently prevent the agglomeration and to gain better solubility of the additives in polymers; it also has large influence on the properties of the composites [55–58].

In our study we have created LDPE samples filled with different weight contents of micro–scale Boehmite particles. To overcome the difficulty of particles dispersion and adhesion, particles are modified through grafting of polymerizable organic silane molecules 3-(trimethoxysilyl)-propylmethacrylate (3MPS) and vinyltri(2-methoxyethoxy)-silane (VTMES) onto surfaces of ceramic oxide powders via hydroxyl groups on the oxides. Organic–inorganic hybrid macromonomers so obtained [59, 60] are mixed with LDPE.

The aim of this work is evaluation of the role and the influence of powder loading and samples morphology on the mechanical behavior.

EXPERIMENTAL PART

Materials

Silane coupling agents (SCA), namely VTMES-SCA 972 and 3MPS-SCA 989 and high purity Boehmite (under the HiQ alumina trade name) with particle size ≈ 55 μm were received as a gift from Struktol Company of America and Engelhard, respectively. Toluene was from Sigma
Chemicals. Low density polyethylene (LDPE) pellets were supplied by Huntsman. All reagents were of analytical grade and were used as received.

**Grafting of SCA onto Ceramic Particles**

Introduction of reactive groups onto the commercially obtained and preheated for 3 h 550°C ceramic surfaces was achieved by a reaction of SCA with the hydroxyl groups of alumina. Two different types of SCA were used and the temperature dependence of the process was characterized. Details have been described in [60].

**Blending and Sample Preparation**

Samples of (LDPE) reinforced with micrometric Boehmite particles were prepared via melt mixing followed by compression and injection molding.

Blends of dried PE and Boehmite powders were melting mixed in a C.W. Brabender D–52 Preparation Station at the rotation speed of 80 rpm and at 150°C. The resulting blends were pelletedized and dried. The blends contained in turn 1, 5, 10 and 20 wt % Boehmite.

Subsequently, the blends were dried for 8 h at 100°C before compressing them in a Carver compression molding machine at 160°C at the compression pressure $2.07 \cdot 10^4$ kPa. The samples were prepared in an AB–100 injection molding machine from AB Machinery. The injection temperature was 187°C and injection pressure 690 kPa.

**Characterization Techniques**

**Environmental Scanning Electron Microscopy.** Micrographs of all samples were taken and determined using a FEI quanta environmental scanning electronic microscope (ESEM). A small portion of the samples were fractured in liquid nitrogen, mounted on a copper stub and coated with a thin layer of gold to avoid electrostatic charging during examination.

**Tensile Testing.** The static tensile behavior of the samples was determined at room temperature with a MTS tester (model QTEST/5). The test was performed in a
FIG. 3. Micrographs of LDPE (a), LDPE + 20 wt% HB (b) and with B and HB filler treated with 3MPS (c, e) and VTMES (d, f).

FIG. 4. Micrographs of the fractured surfaces of the tensile tested LDPE (a) and LDPE with 20 wt% B and HB filler treated with 3MPS (b, d) and VTMES (c, e).
controlled environment and aimed to determine the elongation at break, strain at break, and modulus. The crosshead speed was 5 mm/min; five specimens of each sample were tested, and average values are reported.

MORPHOLOGY OBSERVATION

Morphology of the fracture surfaces of the composites depends on the interfacial structure due to load transfer between particle and polymer matrix. The effect of surface treatment on the interface between Boehmite and LDPE was studied by examination of fractured surfaces of composites with ESEM. Figure 1 shows the ESEM micrographs of composites reinforced with 20 wt % Boehmite (B) and also 20 wt % preheated Boehmite (HB).

We see that morphologies of LDPE + B and LDPE + HB composites are different. No agglomerates of the Boehmite particles (Fig. 1b) can be seen, whereas a few of HB particle agglomerates are observable (Fig. 1c). This can be explained by decreasing amounts of —OH groups on the powder surfaces after heating at 550°C for 3 h (mass loss about 30 wt %). The heating results in an increase of the surface tension [58]. In either case, it is evident from our micrographs that the fillers are well dispersed in the polymer matrices.

FIG. 5. Micrographs of the fractured surfaces of the tensile tested LDPE with 20 wt% B (a) or HB (b, c).

FIG. 6. Variation of the Young’s modulus of the LDPE composites with Boehmite or preheated Boehmite; 20 wt% Boehmite in both cases.

FIG. 7. Variation of the strain at break of the LDPE composites with Boehmite or preheated Boehmite.
We also see that the composites containing the HB powder have rougher surfaces than those with the B powder. Clearly, effects of the samples’ morphology have to be studied carefully to determine contributions of surface characteristics and morphology on mechanical properties of the composite.

Fractured surfaces of the samples with treated Boehmite can be seen in Figs. 2 and 3. We infer from these micrographs that the coupling agents do not affect filler particle dispersion in the polymer matrix (Fig. 2a and b). The agents do favor a better polymer–filler interaction (Fig. 3a–f); this is due to replacement of hydroxide groups on surfaces of ceramic oxide powders with polymerizable organic groups [59, 60].

The micrographs in Fig. 3 indicate that the Boehmite particles can be pulled out easily from the LDPE matrix by breaking the interface due to poor adhesion between particles and LDPE. The reason for poor adhesion is the difference in surface tension (or polarity) between untreated particles and LDPE.

Improvement in interfacial adhesion upon coupling is apparent in Fig. 4a–e. The ESEM micrographs present the tensile fractured surfaces of neat polymer and composites filled with 20 wt % of B and HB treated with 3MPS and VTMES, respectively. All these composites contain polymer fibrils attached to the Boehmite particles—an indication of improved adhesion between the phases. The observations of improved adhesion are consistent with the mechanical performance improvement reported below. In all cases, wetting of the particles by the polymer matrix is clearly improved by the coupling treatment, making the interface between two phases almost indistinguishable. The enhancement of the interface can be explained by a decrease in surface energy of the filler with silane coupling agents, what leads to improvement of compatibility between Boehmite and LDPE. The transformation of LDPE phase and formation the fibrils were observed for all composites. Interestingly, the formation of fibrils of LDPE intensifies with increasing amount of the filler added. When no filler is added as in Fig. 4a, a high shear stress could deform the LDPE phase into very short fibrils. Hence the presence of treated fillers induces longer fibrils. Compared to LDPE + 20 wt % B treated with 3MPS, higher ductility of LDPE + 20 wt % B treated with VTMES composite is evident by the extensive fibril formation at the fracture surface; see Fig. 4c and e. For the other 3MPS coupled samples, the morphology of the fracture surface remained almost unchanged.

In contrast to the above presented results for the grafted samples, Fig. 5 shows an ESEM photograph and a detailed view of an interface between LDPE and 20 wt % untreated Boehmite particles. It is clear that the plastic deformation of composites indicating ductile fracture is lower than that of the treated composites. After tensile fracture, there is no evidence of adhesion between the particles and the polymer matrix; a gap between the two phases is clearly noticeable in high magnification images.

**TENSILE PROPERTIES**

Figure 6 shows the variation of the modulus of the composites filled with 20 wt % Boehmite or with heated Boehmite.

As expected, the tensile modulus increases with the filler content. Modulus of the sample with HB particles is about two times higher than that of pure LDPE. The increase in Young modulus of the Boehmite-filled composites indicates an increase in the rigidity of LDPE related to the restriction of the mobility in LDPE matrix due to the presence of fillers.

The strain at break $\varepsilon_b$ of all samples decreases with increasing Boehmite contents as shown in Fig. 7. We recall that the material brittleness $B$ is inversely proportional to $\varepsilon_b$, namely $B = 1/(\varepsilon_b E')$, where $E'$ is the storage modulus determined by dynamic mechanical analysis (DMA) at the standard frequency of 1.0 Hz [61]. Needless to say, $B$ is a function of temperature.

Thus, Fig. 7 tells us that the brittleness of the hot-pressed composites falls rapidly between 0 and 10 wt %
Boehmite and then continues to fall but at a much slower rate. This on the basis of the assumption that changes of 
$E_0$ with the Boehmite concentration are monotonous and not larger than the changes in $f_b$.

Figure 8 shows the effect of powder loading on the Young modulus of injection molded and hot-pressed composites.

The Young modulus of these composites increased with increasing powder loading. This suggests stress transfer across the polymer—particles interface. Boehmite powder particles in the matrix prevent movement of the matrix phase in the area around each particle, contributing to an overall increase in the modulus. The experimental values for hot-pressed composites are much higher than those obtained for injection molded ones. At the same time, we see that both sets of samples have the same behavior tendency.

Additionally, the effect of the morphology on the modulus of the composites is also evident from these results. It can be clearly seen that the composite filled with HB powder that has rougher surfaces (Fig. 1a–c) attains higher modulus than samples containing B powder.

**EFFECT OF SILANE COUPLING AGENTS ON MECHANICAL PROPERTIES**

Silane coupling agents, namely VTMES-SCA 972 and 3MPS-SCA 989 were applied and effects of the treatment on the mechanical properties of the composites investigated. The results are summarized in Fig. 9. Observed variations in mechanical behavior for the coupled samples are necessarily related to variations in the level of interfacial interaction between polymer matrix and treated Boehmite particles.

Young modulus values for the blends filled with modified powders are about 2.0 times higher than for neat LDPE. The most effective coupling treatments to achieve high modulus are those based on VTMES. Higher modulus $E$ values are seen for all composites. However, $E$ values do not show significant change and remain almost constant after treatment with SCA (as compared to samples with an unmodified powder).

Effects of contents of micrometric grafted Boehmite particles are presented in Fig. 10. As expected, the modu-
lus E goes symbatically with the Boehmite particle concentration.

Inspection of Fig. 7 led us to the conclusion that the composite brittleness increases with increasing Boehmite concentration. We now return to the strain at break $C_b$ to see effects of powder treatment. Figure 11 shows pertinent results. The tensile ductility appears to decrease slightly with the addition of 1 and 5 wt% treated Boehmite powder. The strain at break then decreases continuously with increasing filler content. This decrease indicates that the composites become brittle with increase in Boehmite loading owing to the stress concentration effect of the filler.

The strain at break values increase with a silane treatment and decrease with an increase in filler loading. The increased strain at break of our composites with a treatment indicates that SCA probably provide a lubricating or plasticizing effect. We envisage formation of physisorbed layers at the interphase causing a reduction in viscosity. We also see that for compression molded samples $C_b$ decreases faster than in the injection molded samples. This can be due to lesser molecular orientation in the compressed samples than in injection molded ones. As discussed by Michler et al. [62], orientation has large effects on mechanical performance.

We now focus on 20 wt% concentration of treated Boehmite to see effects of various treatments. The results are presented in Figure 12. We attribute them to improved interfacial adhesion between the treated powder and polymer matrix as compared to untreated powders. The importance of interfacial adhesion has been stressed for instance by Kopczynska and Ehrenstein [63]. We have achieved a fairly uniform distribution of the dispersed phase in the matrix—what is essential also [64].

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