Rheology of Low-Density Polyethylene + Boehmite Composites

Piotr Blaszczak,[1,2] **Witold Brostow,**[1,2] **Tea Datashvili,**[1,2] **Haley E. Hagg Lobland**[1,2]
[1]*Department of Materials Science and Engineering, Laboratory of Advanced Polymers and Optimized Materials (LAPOM), University of North Texas, Denton 76203-5017, Texas*

[2] *Department of Physics, Laboratory of Advanced Polymers and Optimized Materials (LAPOM), University of North Texas, Denton 76203-5017, Texas*

Polyethylene is already one of the most commonly used polymers due to its solvent resistance and easy processing. Low-density polyethylene (LDPE) also has excellent flexibility and resilience. However, the mechanical properties of LDPE are often poor. We added the inexpensive ceramic filler Boehmite to LDPE, simultaneously improving mechanical properties and reducing production cost—as Boehmite is cheap and abundant while the filler reduces the amount of petroleum-derived polymer per unit weights of product. Additionally, less environmental contamination results at the end of service life since the Boehmite need not undergo degradation as the LDPE does. To aid adhesion between the matrix and filler, we introduced silane coupling agents (SCAs) to bond the hydrophobic LDPE to the hydrophilic Boehmite. Furthermore, since fillers ordinarily increase viscosity, it was essential to maintain a low viscosity for easy processability. We evaluated by rheometry the effect of the Boehmite on the melt viscosity of the LDPE + Boehmite composites and determined that the addition of any type of Boehmite decreases the viscosity compared to that of neat LDPE. The effects were explained by fiber formation and enhanced rigidity while the allowance for a lower processing temperature results in further energy and therefore cost savings. We also show that high-temperature exposure of Boehmite during any part of the sample processing results in a decrease in the coupling efficiency of the matrix to filler and in a higher melt viscosity; yet the viscosity is still lower than for neat LDPE. **POLYM. COMPOS., 31:1909–1913, 2010. © 2010 Society of Plastics Engineers**

INTRODUCTION AND SCOPE

The use of polymer-based materials (PBMs) continues to increase due to their low-density, low cost and ease of processing [1]. Among PBMs, polyethylene is already one of the most commonly used due to its simple structure, low reactivity, and ease of processing. Low-density polyethylene (LDPE) also has excellent flexibility and resilience; however, the mechanical properties of neat LDPE are not sufficient to meet the high requirements of certain applications [2].

The addition of fillers is a common, easy and often inexpensive way to modify the properties of the base polymer matrix [3–5] while other options involve the use of fibers [6, 7] or else irradiation [8]. The extensive use of fillers in PBMs has allowed the development of composites for a wide range of applications owing to the fact one can judiciously maintain the desirable traits of the component materials while improving or eliminating undesirable ones. For instance, carbon black has been added to poly(vinylidene fluoride) + polyethylene blends with resultant improvements in friction and electrical conductivity [9]. Due to hardness and typically higher elastic modulae and compressive strengths, ceramics are often added to polymer matrices to improve their mechanical properties [10–17]. Boehmite [AlO(OH)], a mineral component of the aluminum ore bauxite, is an inexpensive material already under investigation for various applications [18–23]. The heat treatment of Boehmite produces a variety of transition aluminas (γ-Al_20_3, η-Al_20_3, δ-Al_20_3, θ-Al_20_3), all of which exhibit large surface areas and thermal stability up to 1,000°C. Dehydration of heated Boehmite yields alumina along with a remaining small quantity of undehydrated Boehmite.

Rheological properties of filled polymers can be characterized by the same type of parameters that would describe any fluid medium: these include shear viscosity and its dependence on the applied shear stress and shear

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Correspondence to: Witold Brostow; e-mail: brostow@unt.edu

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rate, as well as elongation viscosity under conditions of uniaxial extension. The creep recovery behavior of LDPE and linear low-density polyethylene (LLDPE) are discussed by Münstedt and coworkers [24] with their results highlighting the influence of molecular structure on rheology. In oscillatory tests where a frequency is imposed, real and imaginary components of the complex dynamic viscosity can be evaluated. For pure rotational tests, we can find not only viscosity but also the normal stress that results from the elastic component of viscoelastic polymer melts.

There is a thorough study of rheology and morphology of PP + LDPE blends by Levij and Maurer [25]. Studies on PP + Boehmite composites are readily found [26–28]. However, there are comparably fewer articles on composites of PE + Boehmite (e.g., [29]). We have prepared blends by adding Boehmite powders to an LDPE matrix. The studies just mentioned on polyolefin + Boehmite composites address specifically nanocomposites that incorporate Boehmite nanoparticles while we have used microparticles—which are less expensive—to advantage. Since LDPE is a hydrophobic organic compound that would not normally bind tightly to polar Boehmite, we have also introduced silane coupling agents (SCAs). The SCAs, having at least two reactive groups, bond to organic constituents at one group and to inorganic constituents at the other. The coupling agents, which link polar to nonpolar groups, improve compatibility of the component materials over that which occurs in a simple physical mixture. A further and desired effect of the improved matrix-filler adhesion is an improvement of mechanical properties [22], and also tribological [23] and thermophysical ones [20]. Generally, much more attention has been paid to improvement of mechanics of PBMs rather than tribology [30] or thermophysics [31–33]. This while PBMs can be scratched easily and can suffer extensive wear, with Teflon as a notorious example.

While the physical and chemical nature of the filler are determinants of the efficacy of that filler in improving polymer function, the presence of solid additives in thermoplastic melts inevitably influences their processability. The extent to which processability is altered depends on the amount of filler present and the strength of interactions—both filler-polymer and filler–filler interactions—together with the melt processing conditions which include the shear and/or elongation flow fields developed. Thus, it is imperative to define the polymer + filler composite rheology to develop formulations with the desired end-use properties that are economically viable for processing. The rheological study by Marcinčin et al. [34] on PP + Boehmite nanocomposites reports non-Newtonian behavior for fibers. Elsewhere in work by Streller et al. [27, 35] on similar composites there is no mention of rheology of the materials. For Boehmite-based PE nanocomposites, Halbach and Mülhaupt [29] likewise have not reported on rheological properties. We have prepared Boehmite-containing LDPE composites for reasons already explained, in a variety of concentrations. To determine the effect of Boehmite on viscosity of the LDPE—which alone is easily processed—we have performed rheological tests and analyzed the results for our entire set of LDPE + Boehmite hybrids.

SAMPLE PREPARATION

Materials

SCAs, namely VTMES-SCA 972 (abbreviated VS) and 3MPS-SCA 989 (abbreviated MPS) were received as a gift from Struktol Company of America. High-purity Boehmite, under the HiQ alumina trade name, with particle size of 55 μm was received as a gift from Engelhard. Toluene and low-density polyethylene (LDPE) were from Huntsman. All reagents received were of analytical grade and were used without additional processing.

Grafting of SCA Onto Ceramic Particles

Reactive groups were introduced onto the surfaces of either the unmodified commercial Boehmite (CB) or heated Boehmite (HB)—preheated at 550°C for 3 hours—by reacting a SCA with the hydroxyl groups of the alumina powders. The two different types of SCAs were those already mentioned, VS and MPS, and were used at room and elevated temperatures as described before [22].

Blending and Sample Preparation

Samples of LDPE reinforced with micrometric Boehmite particles were prepared via melt mixing followed by compression molding. Blends of dried PE with 1, 5, 10 and 20 wt % Boehmite were melt mixed in a C.W. Brabender D –52 Preparation Station at a rotation speed of 80 rpm and at 150°C. The resulting blends were then pelletized and dried for 8 hrs at 100°C. Subsequently, the blends were compressed in a Carver compression molding machine at 160°C at a pressure of 20.7×10^3 kPa.

RHEOLOGICAL MEASUREMENTS

The viscosity η of the samples was determined on a TA ARES-LS2 machine using stainless-steel parallel plates of diameter 25 mm. A steady rate sweep test (rotational mode) of each blend was conducted, measuring η and shear stress τ every 10 s while the shear rate $\dot{\gamma}$ was ramped logarithmically from 10^{-4} to 10 s^{-1}. Two specimens of each sample type were analyzed, with the results showing good reproducibility.

Since the LDPE matrix was identical for all samples, every specimen was tested in the rheometer at 150°C, which is 30° above the approximate melting temperature T_m of LDPE. Samples were placed in the preheated machine and allowed to melt. After 5 min the geometries were closed to 0.05 mm above the test gap (1.50 mm), and the samples were trimmed to size. An additional 15 min were allowed for the temperature of the sample and machine to equilibrate; afterward the upper parallel plate was lowered to the test gap and the test was run.

Graphs relating viscosity and shear rate are often presented as [log η] versus [log $\dot{\gamma}$]. Because the logarithmic scale may exaggerate a simple relationship between variables, this method was abandoned in favor of straightforward plots of viscosity vs. shear rate.

RESULTS

The plots of viscosity as a function of shear rate for all samples are provided in Figures 1–3. Samples prepared with CB are compared to neat LDPE in Figure 1, while blends prepared from the 550°C preheated Boehmite HB are compared to LDPE in Figures 2 and 3. Samples that were mixed with SCA under reflux at the boiling temperature(~95°C) of the solution for 24 hrs are labeled highT. Room temperature (roomT) samples were prepared at the room temperature (~20°C) during 24 h. Data are for samples loaded with 20 wt % of Boehmite (given results from earlier reports [22, 23]).

We observe in Figures 1–3 that all the LDPE + Boehmite hybrids exhibit shear thinning; the high viscosity at low shear rates decreases with the increasing shear rate. Moreover, we do not observe significant changes in the curve shape among the various samples. The inclusion of any Boehmite filler in LDPE results in a general downward translation of the viscosity curve from that of the neat LDPE.

Comparing samples with CB to the neat LDPE in Figure 1, we see that there exists a sizeable difference between the various CB blends and LDPE but a smaller difference among the CB-containing samples. The coupling agents clearly affect the viscosity of the CB blends; CB + MPS + highT has the lowest viscosity of all shear rates; it also exhibits a double hump pattern that, though seen in a few other samples, is well defined for this sample at very low shear rates. While the MPS agent lowers viscosity, the VS coupling agent increases η slightly compared to that of the CB blend without a coupling agent.

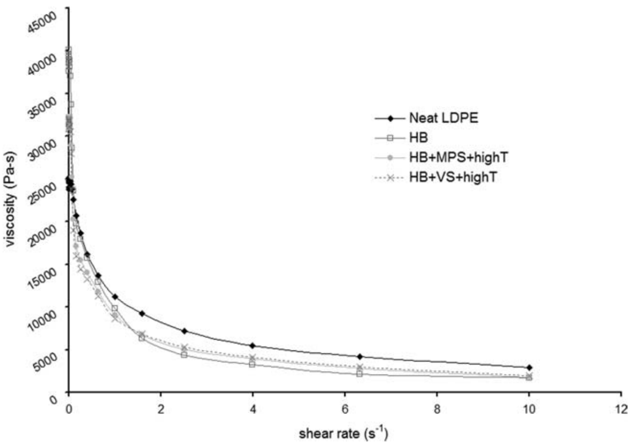

FIG. 2. Dependence of viscosity on shear rate for LDPE and composites containing heated commercial boehmite (HB), with and without modification by silane coupling agents at an elevated temperature (highT).

Figures 2 and 3 show the viscosity curves for all blends containing heated Boehmite HB. To avoid multiple overlapping curves, the data was split according to whether samples were prepared at high temperature or at room temperature. We notice first in Figure 2 that while each HB-containing sample has lower viscosity than the neat LDPE, the curves are closer to that of LDPE than were similar curves for the CB samples. This suggests that HB has less effect than CB on the viscosity of LDPE, especially at low shear rates (below 4 s^{-1}). The highT HB blends form a very tight group (Fig. 2), with very little viscosity variation as a result of the addition of the SCAs. An interesting feature, however, is that all three HB curves in Figure 2 intersect a distinct shear rate, after which the previously most viscous sample becomes the least viscous and vice versa.

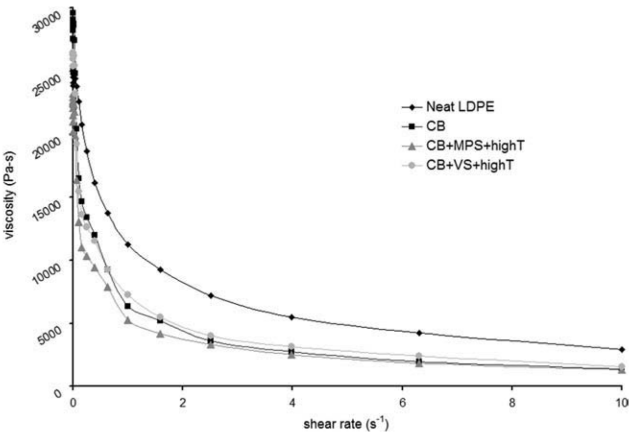

FIG. 1. Dependence of viscosity on shear rate for LDPE and composites containing unheated commercial boehmite (CB), with and without modification by silane coupling agents at an elevated temperature (highT).

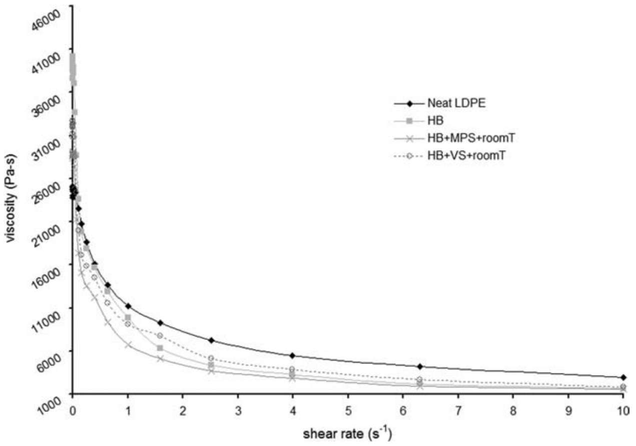

FIG. 3. Dependence of viscosity on shear rate for LDPE and composites containing heated commercial boehmite (HB), with and without modification by silane coupling agents at room temperature (roomT).

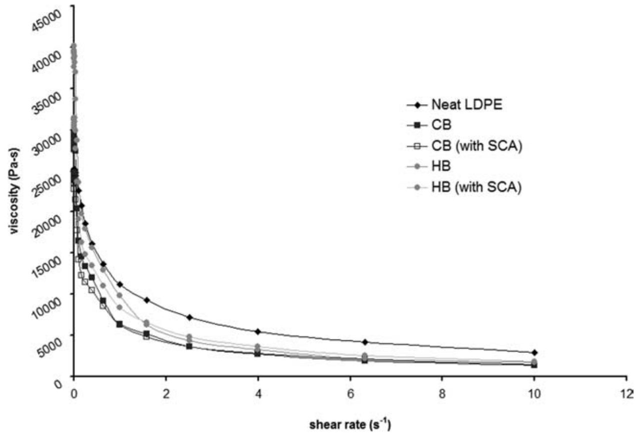

FIG. 4. Dependence of viscosity on shear rate for LDPE, composites containing CB and HB, and averages for composites containing modified boehmite.

In Figure 3 we see that viscosity curves for HB samples prepared at room temperature are similarly lower than the curve for neat LDPE. Contrasted with the highT preparation of HB blends, the addition of SCAs to roomT HB samples causes a wider deviation from pure HB. The HB and HB + VS + roomT curves lie closer to that of the LDPE sample, while only the HB + MPS + roomT sample approaches the low viscosities obtained by the CB samples. Another notable aspect is the strong double hump pattern exhibited by HB + VS + roomT and similar to what we saw earlier for CB + MPS + roomT. This pattern results in the sample HB + VS + roomT having a higher viscosity at high shear rates and lower viscosity at low shear rates than the plain HB blend.

DISCUSSION

Often solid fillers tend to increase viscosity of polymer melts [36]. The lowering of viscosity by our addition of Boehmite to LDPE opposes that general trend. It has been demonstrated elsewhere that the filler is well dispersed for both CB and HB blends [22]. We know that while the coupling agents do not affect particle dispersion, they do alter the matrix-filler interactions. Kopczynska and Ehrenstein [37] discuss how important interfaces are for properties of multiphase polymeric materials.

Micrograph images obtained by environmental scanning electron microscopy (ESEM) show that matrix-filler adhesion is improved by the reaction with SCAs, see Figure 4 in [22]. Specifically, we observe in our LDPE + SCA-modified Boehmite composites that the Boehmite particles are covered with attached (bonded) polymer fibrils. How does this variation of the matrix-filler interactions affect viscosity of the melted polymer system? As a result of good adhesion between the polymer matrix and the mineral filler, the polymer melt with filler flows more uniformly, thus at a lower viscosity despite adding solid filler. Another contribution is that more rigidity facilitates the flow and lowers melt viscosity. For polymer liquid crystals (PLCs) that necessarily contain rigid chain sequences this has been predicted by statistical mechanics [38] and confirmed experimentally [39]. Both mechanisms can be in operation simultaneously, in fact each supporting the other.

The preparation of samples at high temperatures (HB instead of CB) can decrease reactivity of Boehmite by dehydration. A lower reactivity results in weaker bonding between the polymer matrix and Boehmite filler. If our assumption is true, then this would lead to somewhat higher viscosities. Figure 4 confirms this, comparing CB and HB to one another, to LDPE, and to averages of the samples modified by coupling agents. We also see that the higher reactivity of CB over HB counteracts the effect of highT preparation resulting in samples with lower viscosity overall.

Furthermore, evidence from the ESEM and mechanical properties [22] also suggests that, in the absence of coupling agents, adhesion between LDPE and Boehmite is quite poor. This is coupled with the interesting result that the addition of any Boehmite filler, regardless of previous heating or presence of SCAs, is accompanied by a drop in viscosity. Though the magnitude of the reduction is affected by these variables, the existence of some amount of a viscosity decrease is present in all samples. Since LDPE is a highly branched polymer whose chains would tend to get entangled, apparently even poorly bonded plain CB and HB particles fill in the spaces between chain branches, provide some rigidity, and enable easier flow.

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