Rheological characterization of a polyethylene melt, filled with different concentrations of fumed silica at 453 K

D Hadjistamov1,3 and T Schweizer2
1DECE GmbH, Helvetierstr. 15, CH-4125 Riehen, Switzerland
2ETH Zürich, Institute of Polymers, CH-8093 Zürich, Switzerland
E-mail: dhadjistamov@datacomm.ch

Abstract. Fumed silica is widely used as filler / thickening agent to increase the viscosity or to change the flow behavior type of a suspension. Strong hydrogen bonds between silica-silica and silica-matrix can lead to a suspension with a yield stress. We wanted to know if fumed silica can also form a three-dimensional network in a polyethylene melt at 453 K. The systems with the polyethylene LDPE 1810H (LDPE) filled with different concentration of the fumed silica Cab-o-sil TS720 (silica) were investigated with the MCR300 rheometer from Anton Paar at 453 K. The shear stress $\tau$ and the 1st normal stress difference were measured simultaneously in stress growth experiments. The points of the flow curves represent the steady state values from the start-up experiments with a constant shear rate. Just after the steady state values are reached, the stress deformation is stopped, and the stress relaxation begins. The relative residual shear stress is an important value. The absence of residual shear stress means that the structure of the system is destroyed in the stress growth experiment and the system has shear-thinning flow behavior. The systems with high residual shear stress form a strong network that leads to a system with plastic flow behavior with a yield stress. The shear stress changes insignificantly in the yield stress region with the shear rate. The yield stress can be determined also from the relative residual shear stress curve.

1. Introduction
Fumed silica is used in paints, tooling systems, food, toothpaste etc. [1]. Silica can be added to avoid the sedimentation of the fillers [2]. Systems with fumed silica are studied in polydimethylsiloxane rubber [3,4], in different rubbers [5-7], in the epoxy resin Araldite GY 260 [8], in polydimethylsiloxane [9-18], in polyethylene terephthalate [19]. Recently, the rheological behavior of precipitated silica in polydimethylsiloxane [20] and CPE/NR blends [21] has been investigated. A thermodynamic approach describes the rheological behavior of fumed silica in polystyrene [22,23]. Measurements of the 1st normal stress difference $N_1$ in colloidal suspensions are scarce, although special effects like negative $N_1$ have been reported [24]. Cassagnau [25] reports about rheology of silica in organoclay nanocomposites.

No publications exist about the rheological characterization of fumed silica in the LDPE 1810H.

The fumed silica increases the viscosity of a suspension through hydrogen-bonding that builds a three-dimensional network. Depending on the concentration of the fumed silica, the effect can be only an increase in the viscosity or an increase in the viscosity and a change in the flow behavior of the system - to a system with plastic flow behavior [1,8,16]. The main feature of the systems with plastic flow behavior is the existence of a yield stress $\tau_y$ or a yield stress region. It can be identified from the
flow curve as a region where the shear stress changes insignificantly with increasing shear rates. Many suspensions – e.g. paints, adhesives, pigment dispersions and others show plastic flow behavior.

The main purpose of this paper is to find out whether fumed silica can induce plastic flow behavior in a melt of LDPE at 453 K.

2. Experimental
The LDPE 1810H (BASF AG) is a low-density polyethylene with a weight average molecular weight of 186 kg/mol. The fumed silica Cab-o-sil TS 720 (hydrophobic) has a specific surface area of 100 ±20 m²/g. The specific gravity is 1.8 g/cm³.

LDPE granules with different concentrations of silica were mixed on a Brabender kneader in a 30 cm³ chamber at 30 rpm and 453 K until torque was constant. The resulting mixtures were hot pressed to tablets and investigated with the MCR 300 rheometer from Anton Paar at 453±0.5 K, with a cone-plate measuring system of 4° cone angle.

The points of the flow curves represent the steady state \( \tau_S \) values from the shear flow start-up experiments with a constant shear rate \( \dot{\gamma} = \text{const} \). (figure 1).

\[ \text{Figure 1. Shear flow start-up experiment – stress relaxation [1].} \]

A shear flow start-up experiment – stress relaxation without residual shear stress \( \tau_R = 0 \)

B shear flow start-up experiment – stress relaxation with residual shear stress \( \tau_R \)

When steady state flow is reached, the shear deformation is halted, and the stress relaxation is measured. If an existing structure has been destroyed during shear, no residual shear stress \( \tau_R \) is observed (figure 1A). If the structure is only partially destroyed after the start-up experiment, a residual shear stress \( \tau_R \) is observed (figure 1B). The relative residual shear stress \( \tau_{RR} = \frac{\tau_R}{\tau_S} \) is the
ratio of residual shear stress to steady state shear stress. It is assumed that the relative residual shear stress represents the part of the structure that has not been destroyed during shear. A system with a better-preserved structure exhibits a larger \( \tau_R \) and \( \tau_{RR} \) respectively.

3. Results and discussion

Figure 2 represents the loss modulus curve of LDPE and the flow curve of the system with LDPE, filled with 5wt% silica.

The LDPE melt shows shear-thinning flow behavior with a first Newtonian region up to the onset of shear thinning at 340 Pa. The zero-shear complex viscosity has a value of 22.6 kPas. The addition of 5wt% Cab-o-sil to the LDPE causes only an increase in the shear stress. This melt exhibits shear thinning flow behavior with a zero-shear viscosity of 400 kPas. This value is about 18 times larger than the zero-shear viscosity of unfilled LDPE. The first Newtonian region of the filled melt runs up to the onset of shear thinning of 360 Pa, which is almost equal to the value for the unfilled LDPE. The LDPE, filled with 5wt% fumed silica, as a system with shear-thinning flow behavior, does not indicate any residual shear stress.

The rise of the silica concentration from 5wt% to 10wt% causes at given shear rate a considerable increase in the shear stress (figures 2 and 3), and in the viscosity respectively. The melt with 10wt% silica builds a strong network formation that leads to a change in the flow behavior from shear-thinning (figure 2) to plastic (figure 3).
The flow curve of the LDPE melt with 10wt% silica demonstrates two regions where the shear stress changes insignificantly with the shear rate. These sections can be assumed to be yield stress regions at 3.9 kPa and 6.2 kPa. Two yield stress regions have also been experimentally observed for systems with 20wt% and 25wt% Bentone 27 (organoclay) in Araldite GY [1].

The first point of the relative residual shear stress curve has a value of 0.79. About 79% of the three-dimensional structure is still retained or 21% of the structure is destroyed in the shear flow start-up experiment. The values of the relative residual shear stresses (figure 4) decrease in the yield stress regions and consequently a strong distortion of the structure occurs in these regions. Between the first and second yield stress regions there is a transition section (figure 4), where the destruction of the structure and the decrease of the relative residual shear stress slows down with the shear stress.

It is possible to determine the yield stress regions of the filled polyethylene melts also from the relative residual shear stress curve (figure 4). The evaluated yield stress regions are 3.9 kPa and 6 kPa for LDPE, filled with 10wt% silica. There is a good agreement between the yield stress values obtained from the flow curve (figure 3) and from the relative residual shear stress curve (figure 4).

The addition of 15wt% silica (figure 5) leads also to a system with plastic flow behavior.

**Figure 3.** Flow curve of LDPE, filled with 10wt% silica (MCR 300 rheometer, Anton Paar 453 K, CP 50-4).

**Figure 4.** Relative residual shear stress of LDPE with 10wt% silica.

**Figure 5.** Flow curve of LDPE, filled with 15wt% silica (MCR 300 rheometer, Anton Paar, 453K CP 50-4).

**Figure 6.** Relative residual shear stress of LDPE with 15wt% silica.
The flow curve of the melt with 15wt% fumed silica (figure 5) shows nearly equal shear stress values compared with the system with 10wt% (figure 3). The higher silica concentration leads to a higher shear stress but does not promote to the expected much bigger strengthening of the structure. The concentration of 10wt% seems to be optimal. The system with 15wt% shows plastic flow behavior with a yield stress section at 3.8 kPa and a second yield stress region at 5.7 kPa (figure 5).

Figure 6 represents the dependence of the relative residual shear stress on the shear stress for the systems with 15wt% silica in LDPE. The first point has a relative residual shear stress of 0.58. About 58% of the three-dimensional structure is still left or 42% of the structure has been destroyed during shear. The relative residual shear stress of the first point has a lower value (figure 6) compared to that of the system with 10wt% silica (figure 4).

Considering the relative residual shear stress curves (figure 6) we can evaluate the yield stress regions of the filled with 15wt% polyethylene melt with 3.9 kPa and 5.6 kPa. There is a good agreement between the yield stress values obtained from the flow curve (figure 5) and from the relative residual stress curve (figure 6).

4. Conclusion
The LDPE shows shear-thinning flow behavior. Silica works at a concentration of 5wt% only as a filler – a large increase of the shear stress is observed (figure 2), but the system retains the shear-thinning flow behavior.

Additions of 10wt% and 15wt% fumed silica form a three-dimensional network which is strong enough to lead to systems with plastic flow behavior with two yield stress regions (figures 3 and 5). The shear stress changes insignificantly with shear rate in these regions, there is a strong decrease in the viscosity respectively. Between the two yield stress regions is the transition section. A rearrangement of the structure takes place in this region. The high values (0.79 and 0.58) of the relative residual shear stress reveal a strong structure in the melt. It is possible to determine the yield stresses from the flow curve and from the relative residual shear stress curve.

The flow behavior of a polyethylene melt with fumed silica depends obviously on the silica concentration. One can now conclude that the fumed silica Cab-o-sil TS720 is able to form a three-dimensional strong structure not only in suspensions with a low viscosity matrix like epoxy resins [8] at room temperature, but also in the polyethylene melt LDPE 1810H at 453 K.

References
[1] Hadjistamov D 2010 Polym. Eng. Sci. 50 811-8
[2] Hadjistamov D 1978 Colloid Polymer Sci. 256 770-83
[3] Southwart D W 1970 J. Inst. Rubber Ind. 4 77-81
[4] Boonstra B et al 1975 Rubber Chem. Technol. 48 558-76
[5] Okel T A and Wadell W H 1995 Rubber Chem. Technol. 68 59-76
[6] Shailes D et al 1998 Rubber World 218 1-21
[7] Mongrue L A and Cartault M 2006 J. Rheol. 50 115-35
[8] Hadjistamov D 2003 Appl. Rheol. 13 209-11
[9] Cantu T S and Caruthers J M 1982 J. Appl. Polym. Sci. 27 3079-88
[10] Ziegelbaur R S and Caruthers J M 1985 J. Non-Newtonian Fluid Mech. 17 45-68
[11] Kosinski L E and Caruthers J M 1986 Rheol. Acta 25 153-60
[12] DeGroot J V et al 1994 J. Colloid Interface Sci. 166 404-13
[13] Piau J-M et al 1999 J. Rheol. 43 305-14
[14] Hadjistamov D 1993 Appl. Rheol. 3 113-9
[15] Hadjistamov D 1995 Appl. Rheol. 5 29-33
[16] Hadjistamov D 2002 Appl. Rheol. 12 297-301
[17] Selimovic S et al 2007 J. Rheol. 51 325-40
[18] Ma T et al 2017 J. Rheol. 61 205-15
[19] Chung S C et al 2002 Macromol. Res. 10 221-9
[20] Shim S E and Isayev A I 2004 Rheol. Acta 43 127-36
[21] Phewthongin N et al 2006 J. Appl. Polymer Sci. 100 2565-71
[22] Havet G and Isayev A I 2001 Rheol. Acta 40 570-81
[23] Havet G and Isayev A I 2003 Rheol. Acta 42 47-55
[24] Lee M et al 2006 J. Rheol. 50 293-311
[25] Cassagnau P H 2008 Polymer 49 2183-96