Effects of volume fraction, size and geometry of different fillers on interparticle interactions in LDPE melts

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Abstract. This study focuses on the effects of volume fraction, size and geometry of different fillers on interparticle interactions in low-density polyethylene (LDPE) melts. For this purpose, the rheological properties of LDPE filled with various fillers have been investigated by means of high pressure capillary rheometry in consideration of different particle sizes. It has been shown that interparticle interactions vary depending on volume fraction of the fillers. Furthermore the aspect ratio of the particles has a great impact on tendency of particles to interact with one another. While fibrous and flake shaped particles have a great tendency to interact with one another, spherical particles, depending on the particle size, exhibit a transition from negligible to non-negligible interactions. It has been shown that on the basis of a generalized interaction function, that considers the transition from negligibly interactions to the domain of pronounced interactions, interparticle interactions can be taken into account mathematically for describing the flow behaviour of particle filled LDPE melts.

1. Introduction

Viscosity functions of particle filled polymer melts are shifted to higher values in comparison to the viscosity function of the unfilled polymer melt (Figure 1). The offset depends on the volume content of the wood particles as well as the applied shear rate.

Figure 1. Viscosity functions of LDPE-based WPC with varying wood content (T = 190 °C)
W. Gleißle and M. K. Baloch developed a very vivid description for the offset of the vertical shift on the basis of the concept of shear-stress-equivalent inner shear rate. Within this concept, the hydraulic gap is reduced by the volume content of the solid particles. This leads to an increase in the shear rate of the continuous phase between these particles, the so-called inner shear rate [1]. Taking into account the shear thinning flow behaviour of particle filled polymer melts the relative increase of the inner shear rate to the shear rate of the suspension is expressed by the shift factor \( B \), Eq. (1), which is influenced by a number of factors [2-5].

\[
B \left( \tau_0 \right)^{n_0} = \frac{K_c}{K_0^\chi} \cdot \tau_0^{(\chi-1)}
\]  

with:

- \( B \): shift factor [-]
- \( \tau_0 \): apparent shear stress [Pa]
- \( K_c \): consistency of suspension [Pas^n]
- \( K_0 \): consistency of matrix polymer [Pas^n]
- \( \chi \): interaction exponent = \( n_c/n_0 \) [-]

Within this study the effects of volume fraction, size and geometry of different fillers on interparticle interactions in low-density polyethylene (LDPE) melts are investigated. The aim of this study is to find a general approach describing the flow behaviour of particle filled polymer melts, which takes into account interaction effects of different types of fillers.

2. Materials and methods

The matrix polymer that has been used in this study is a low-density polyethylene (LDPE, Lupolen 2420 K), a highly branched polymer which exhibits shear thinning flow behaviour even at low shear rates. As filler particles glass beads and natural graphite have been used, in each case in two different particle size fractions. The particle size distributions were determined by laser diffraction using Mastersizer 3000 (Malvern Instruments GmbH) (Fig. 2–5 (a)). The geometry of the filler particles were characterized by microscopy using VHX 2000D (Keyence Microscopes) (Fig. 2–5 (b)).

Figure 2. Soda-lime glass (60), particle size distribution (a), transmitted light microscopy, magnification 200x (b)
Figure 3. Soda-lime glass (346), particle size distribution (a), transmitted light microscopy, magnification 200x (b)

Figure 4. Natural graphite (77), particle size distribution (a), transmitted light microscopy, magnification 100x (b)

Figure 5. Natural graphite (267), particle size distribution (a), transmitted light microscopy, magnification 100x (b)

The preparations of all formulations were carried out by compounding on the co-rotating twin screw extruder, with a melt temperature of 190 °C and a mass output of 3 kg/h. All rheological analyses were performed on a high pressure capillary rheometer (HKR) Smart RHEO 5000 twin bore (CEAST,
Instron®) using a round die with a diameter of 2 mm and a length of 40 mm. The measured data were analysed on the basis of the apparent shear stress and shear rates.

3. Results and discussion

3.1. LDPE filled with glass beads (d50 = 346.150 µm)

Figure 6 shows the flow functions of the unfilled LDPE and LDPE which is filled with different content of glass beads. All flow functions clearly exhibit shear thinning flow behaviour. The corresponding power law model parameters are listed in Table 1.

![Figure 6. Flow functions of LDPE filled soda-lime glass (346) (T = 190 °C)](image)

| LDPE-GB      | glass beads | K          | n  |
|--------------|-------------|------------|----|
|              | volumetric content [%] | [Pa s^n] | [-] |
| LDPE         | 0           | 5231       | 0.496 |
| LDPE-GB5.9   | 5.9         | 5806       | 0.502 |
| LDPE-GB19.4  | 19.4        | 8181       | 0.502 |
| LDPE-GB36.0  | 36.0        | 13490      | 0.465 |
| LDPE-GB45.7  | 45.7        | 17712      | 0.453 |
| LDPE-GB56.7  | 56.7        | 25936      | 0.443 |

With increasing volume content of the glass beads the flow functions are shifted to higher values. Accordingly, the consistency (K) increases with increasing volume content of the glass beads (Fig. 7 (a)).
The quantitative impact of the volumetric filler concentration \((\phi_v)\) on the consistency can be approximated by an empirical equation, Eq. (2).

\[
K_c = K_0 \cdot \left(1 + A \cdot \phi_v^\alpha \cdot e^{\beta \cdot \phi_v}\right)
\]  

The model parameters have been found by regression analysis, \(A = 2.179, \alpha = 1.079, \beta = 2.114\).

Figure 7 (b) shows the correlation between interaction exponent and consistency. In case of negligible interparticle interactions only the consistency changes as a function of the volumetric filler content, while the flow index and the interaction exponent remains constant. The interaction exponent of the investigated glass bead filled LDPE melts remains almost constant up to a volume content of 19.4 vol.%. Thus, interparticle interactions are negligibly small in this region. At higher volumetric filler fractions, a transition to non-negligible interactions can be observed. In order to describe the correlation between interaction exponent and consistency with consideration of the transition from negligible interactions to the domain of non-negligible interactions a generalized interaction function has been used.

\[
\chi = \frac{1}{\left(1 + \left(\frac{K_c}{K^*}\right)^a\right)^{\frac{1}{a}}}
\]  

The model parameter \((K^*)\) describes the transition from negligible interactions to non-negligible interactions, whereas \((a)\) expresses the width of the transition. The intensity of interaction effects is considered by parameter \((b)\). For the glass bead filled LDPE melts the following model parameters have been found by regression analysis: \(K^* = 8056, a = 49.238, b = 0.107\).

On the basis of Eq. (2) and Eq. (3) the influence of the volumetric filler concentrations and the transition of negligible to non-negligible interaction effects can be taken into account in the Equation for the shift factor B Eq. (1). Finally, the offset of the vertical shift of the flow functions of LDPE filled with different amounts of the big glass bead fraction \((d_{50} = 346 \mu m)\) can be well described by using shift factor B in the following equation:

\[
\tau_c = B^{\eta_0} \cdot \tau_0 = B^{\eta_0} \cdot K_0 \cdot \dot{\gamma}^{\eta_0}
\]  

Based on this approach a good match between approximated and measured flow function have been achieved (Fig. 8).
In order to validate the equations and the calculated model parameters which have been used to approximate the measured values, different compounds have been prepared in which the volume contents of the glass beads were varied. On this basis, the flow curves of the validation compounds have been estimated. The results show a good match between estimated flow curves and measured values (Fig. 9).

3.2. LDPE filled with glass beads (d50 = 60 µm)
In contrast to the large particle size fraction of the glass beads (d50 = 346 µm), the small glass beads (d50 = 60 µm) show interparticle interactions even at low filler concentrations (Fig. 10). This means that not only the particle geometry but also the particle size influence the tendency to form interparticle interactions. The generalized interaction function is also suitable for describing the correlation between interaction exponent and consistency with consideration of directly occurring interparticle interactions (Fig. 10).
Figure 10. Interaction exponent as a function of consistency

The same model approaches Eq. (2) and Eq. (3) as for the large particle size fractions of the glass beads have been used for approximating and estimating the flow functions of LDPE filled with the small particle size fraction of the glass beads. The following model parameters have been found by regression analysis:

Equation (2): \[ A = 0.276 \quad \alpha = 0.180 \quad \beta = 5.627 \]
Equation (3): \[ K^* = 6744 \quad a = 4.308 \quad b = 0.133 \]

On the basis of the calculated model parameters, the flow curves have been approximated and estimated, respectively. The results show a good match between calculated flow curves and measured values (Fig. 11).

Figure 11. LDPE filled soda-lime glass (60) (T = 190 °C), comparison of approximated and measured flow functions (a), comparison of estimated and measured flow functions of the validation compounds (b)

3.3. LDPE filled with natural graphite

Lastly, the applicability of the generalized interaction function Eq. (3) on plate-shaped particles has been investigated. For this purpose, compounds with different volume contents and particle size fractions of natural graphite as filler particles in LDPE were prepared.

The following model parameters have been found by regression analysis:
Natural graphite (267) – large particle size fraction

Equation (2): \( A = 4.916 \) \( \alpha = 1.443 \) \( \beta = 3.017 \)
Equation (3): \( K^* = 5288 \) \( a = 214.295 \) \( b = 0.189 \)

Natural graphite (77) – small particle size fraction

Equation (2): \( A = 4.842 \) \( \alpha = 1.624 \) \( \beta = 3.643 \)
Equation (3): \( K^* = 7545 \) \( a = 2.841 \) \( b = 0.213 \)

Figure 12 illustrates the good match between estimated flow curves and measured values for the large fraction of natural graphite as well as for the small fraction.

![Figure 12](image)

(a) (b)

Figure 12. Comparison of estimated and measured flow functions for LDPE filled with natural graphite, large particle size fraction (a) small particle size fraction (b)

4. Conclusions

In this study, the flow behaviour of LDPE which was filled with different volume and size fractions of different fillers have been investigated. On the basis of a generalized interaction function that considers the transition from negligible to non-negligible interparticle interactions, the flow behavior of the investigated compounds have been described mathematically with good consistency to the measured values. With this approach, flow functions for arbitrary volumetric filler concentrations can be estimated with good accuracy, independently from geometry and size of the particles. The calculated model parameters for describing the flow behavior of the particle filled LDPE melts have been successfully validated.

References

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