Practical material characterisation of SEBS-based carbon black compounds – processing properties

Product designation Part 1

As a consequence of the constantly rising need for electronic components, and also as a result of developments, for example, in the area of e-mobility, there is a growing interest in highly filled specialist polymer compounds. In particular, compounds with good electrical conductivity combined with a low tendency to corrosion are now indispensable for various application areas. In fuel cells, batteries and electronic components, electrically conductive polymer mixtures are increasingly taking over new functions. Improved workability and shaping in comparison with metals along with the better energy balance in the manufacture of the components also have a part to play here. One factor that many commercially available compounds that focus on high electrical conductivity have in common is a very high fill level of carbon-based functional fillers such as carbon black or graphites. One example of developments of this type are the compounds in the NEFA MB EL product group. The particular manufacturing method and the associated properties of these systems have already been described in a previous publication [1].

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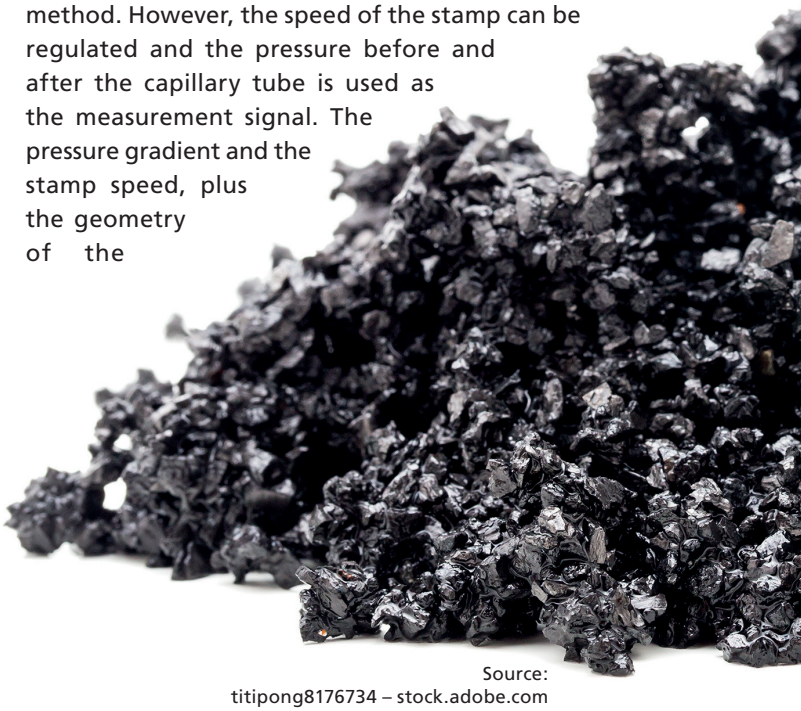
1 Introduction

In general, in the development of conductive compounds, mechanical and electrical characteristic values take priority. The rheological properties often result from the product development, even though the flow properties of a compound also play a major part in deciding on its possibilities for use. For injection moulding, for instance, the flow properties determine quality-defining parameters such as the pressure gradient, mould filling time or mould breathing. These data are necessary in order to be able to carry out filling simulations, among others, to support moulded part design and tool construction and to avoid expensive design errors from the start. The characterisation and assessment of rheological properties is particularly complex in the case of polymer compounds with very high filler contents. The following article describes possible methods for carrying out an assessment of the rheological properties of compounds in a way that is practically oriented and relevant in practice.

2 Rheological characteristics for the processor in the test laboratory

A rheological one-point value that is widespread in industrial practice is the "melt flow index" (MFI) [2]. To determine this value, a polymer melt is pressed through a defined capillary tube in a standardised measurement set-up in fixed conditions (temperature, pressure). The test determines the mass of polymer that flows through the capillary tube in 10 min. The advantage of MFI measurements lies in the relatively simple apparatus configuration and relatively simple measurement to determine the characteristic value. In addition, the melt flow index provides a fast indicator for the processing behaviour of polymers. The usefulness of the characteristic values determined using this method, however, is clearly limited, especially with highly filled compounds. Because MFI measurements only show very low shear velocities, the measured values for highly filled compounds are often only small or even non-existent. Using the examples of the compounds NEFA MB EL 23381S and 21845S, at 270 °C and a test weight of 21.6 kg, MFI values of less than 0.3 g/10 min were determined. Despite this, the materials can be processed in the injection moulding process. The usefulness and meaningfulness of this characteristic is thus inadequate for highly filled compounds.

To obtain rheological values for simulations, more complex methods are needed that record the non-Newtonian flow behaviour of the compounds in a wider shear velocity range. High-pressure capillary rheometers (HCR) in particular are considered to be the state-of-the-art method for determining flow curves of polymer melts [3]. As with MFI measurement, a polymer melt is pressed through a capillary tube in this method. However, the speed of the stamp can be regulated and the pressure before and after the capillary tube is used as the measurement signal. The pressure gradient and the stamp speed, plus the geometry of the



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capillary tubes, can determine, using physical-mathematical models, flow curves that show the apparent viscosity of a polymer melt as a function of the shear velocity.

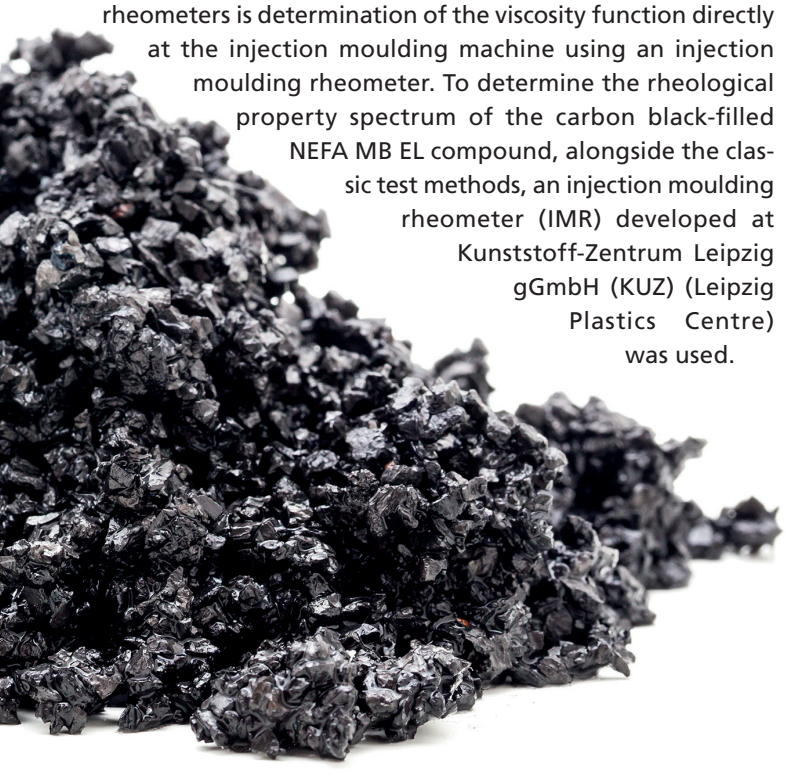
Figure 2 shows the flow curves measured using a high-pressure capillary rheometer for a PP homopolymer and two highly filled NEFA MB EL compounds.

The curves prove, in the first place, that the highly filled compounds are also flowable and are thus materials suitable for injection moulding with a marked structural viscose behaviour – information that could not have been derived from the MFI measurements. It can also be seen that the viscosity of the highly filled compounds through the entire shear velocity range is clearly greater than that of pure polypropylene. It can therefore be assumed, on the basis of the course of the flow curves, that the NEFA MB EL compounds are considerably more difficult to work than pure PP. This purely qualitative statement can also be quantified on the basis of flow simulations. The simulation is based on the viscosity values measured using HCR. In practice, this is precisely where a bottleneck can occur, as only a few companies operate rheometers of this type themselves and external measurements are often time-consuming and expensive.

3 Practical rheological characterisation in injection moulding technology

3.1 Viscosity function directly at the injection moulding machine

A practical method as an alternative to high-pressure capillary rheometers is determination of the viscosity function directly at the injection moulding machine using an injection moulding rheometer. To determine the rheological property spectrum of the carbon black-filled NEFA MB EL compound, alongside the classic test methods, an injection moulding rheometer (IMR) developed at Kunststoff-Zentrum Leipzig gGmbH (KUZ) (Leipzig Plastics Centre) was used.



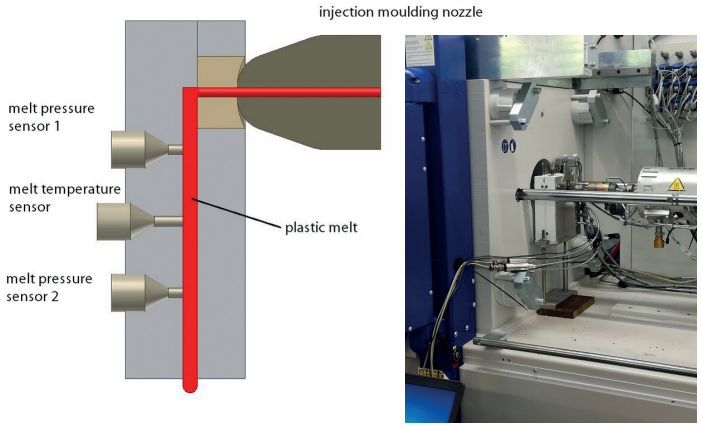


Fig. 1: Injection moulding rheometer with flat-slit channel, schematic layout (left), and use on the injection moulding machine (right).

Injection moulding rheometers have the advantage that they can be used directly at the processing machine and thus provide practically based information about the flow behaviour or the studied plastics or compounds under real plastification conditions. In addition, the apparatus requirement for an IMR is much lower compared with high-pressure capillary rheometers. The rheological results obtained in the IMR contain information about the effects on the material from the shearing occurring in the injection moulding during the melting process and findings about the material alteration caused by the dwell time of the polymer melt in the plastifying cylinder. Furthermore, viscosity changes caused by the use of additives or the effects of residual moisture can be directly proved without needing to mix the material in a separate external step.

Injection moulding rheology requires a horizontal injection moulding machine and the actual IMR. The measuring device is placed in the nozzle prechamber of the injection moulding machine and clamped between the injection unit and a counter bearing to the injection moulding tool (fig. 1, right). The plastic melt passes from the injection unit through the sprue bush into the measuring channel of the injection moulding rheometer (fig. 1, left).

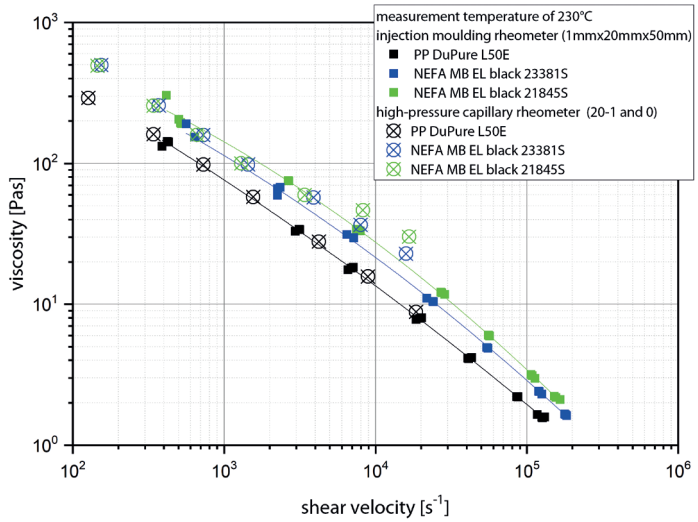
For this, the plastic to be investigated is first melted as standard in the plastifying cylinder of the injection moulding machine. Through the forward action of the reciprocating screw, controlled by the setting of an injection speed or a volume flow, the plastic melt is set in motion out of the screw prechamber and pressed into the injection moulding rheometer. The pressure loss at a specified injection speed or specified volume flow is determined via the pressure sensors in the measurement channel. The following statistical values are obtained from these raw data:

Apparent wall shear stress $$\tau_w = \frac{\Delta p \cdot H}{2 \cdot L}$$ (Eq. 1)

Apparent shear velocity $$\dot{\gamma}_s = \frac{6 \cdot \dot{V}}{B \cdot H^2}$$ (Eq. 2)

Apparent viscosity $$\eta = \frac{\Delta p \cdot B \cdot H^3}{12 \cdot \dot{V} \cdot L}$$ (Eq. 3)

Fig. 2: True viscosity functions of PP DuPure L50E in comparison with the carbon black-filled compounds NEFA MB EL 23381S and 21845S



t_w apparent wall shear stress
D_p pressure loss
H capillary height
L distance between pressure sensors
$\dot{\gamma}_a$ apparent shear velocity
$\dot{V}$ volume flow
B capillary width

This procedure is repeated with selected volume flows and a viscosity function is generated as the result of this multi-point measurement.

Because these calculations are based on a Newtonian flow behaviour and the examined carbon black-filled compounds show non-Newtonian, i.e. a shear-thinning, behaviour, the Weissenberg-Rabinowitsch correction must finally be carried out. The results curves of two NEFA MB EL compounds with a standard PP as a reference curve are also shown in comparison with the curves measured in the HCR in figure 2 .

In the shear velocity range relevant for injection moulding processing of 103 to 105 s-1 and beyond, the measurements were successfully carried out with both carbon black-filled compounds. In comparison with the reference curve for the PP DuPure L50E, it becomes clear that the carbon black-filled compounds show much higher viscosity values at a measurement temperature of 230 °C. Out of the material characteristics of the two NEFA MB EL types, the variant 21845S is seen to be the most slow-flowing.

Whilst, with the unfilled PP, a good correlation of the flow curves from both methods can be observed, with the highly filled systems, major deviations are seen specifically in the shear velocity range relevant for injection moulding processing. However, the viscosity of the highly filled systems is much lower under real injection moulding conditions than that measured in laboratory conditions. For the materials critical for injection moulding processing in particular, this deviation is relevant – especially considering that this information has an influence on the flow simulation for the design of injection moulding tools.

Irrespective of the process-oriented determination of viscosity values, the injection moulding rheometer developed in the KUZ also opens up the option of an in-process error analysis, quality assurance or even a direct process control. Above all, because of its ease of use and supporting software, injection moulding rheology offers the practician a good opportunity for evaluating the flow properties of the material currently in use without having to wait a long time for flow curves from in-house or external test laboratories. Because of the real flow channels and real material plastification, the viscosity values determined are very practically oriented.

Fig. 3: Comparison of the achieved flow distance in the flow spiral tool with the same injection moulding conditions, starting on the left, of PP DuPure L50E, NEFA MB EL 23381S and NEFA MB EL21845S

Fig. 4: Test spiral measuring template

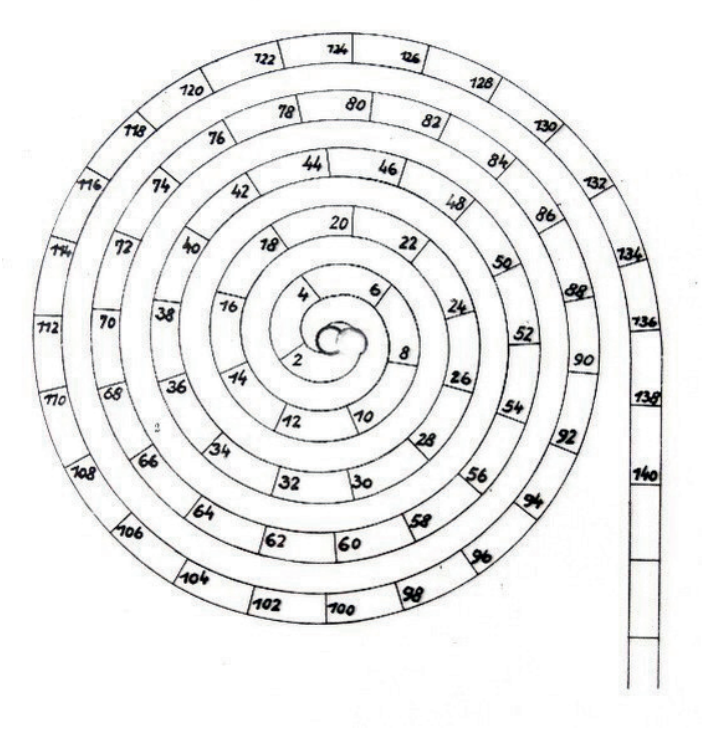
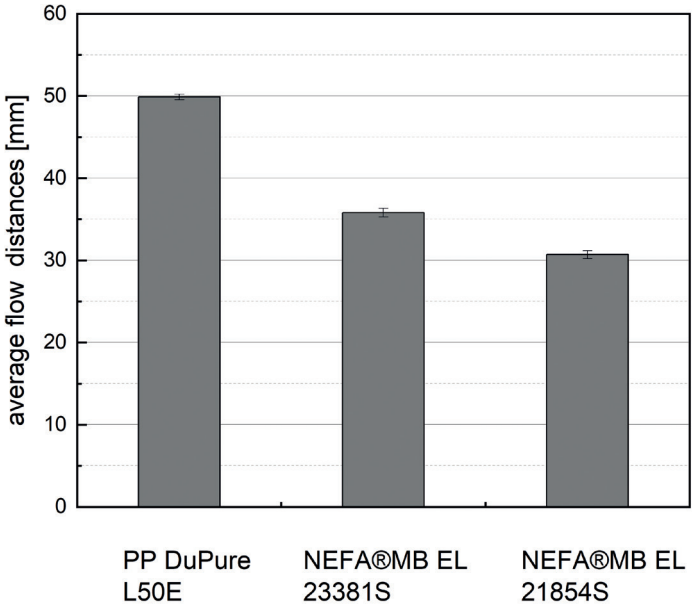


Fig. 5: Resulting flow distances from the injection moulding tests with identical framework conditions



3.2 Achievable flow distances in the test spiral tool

Another process-oriented method for the qualitative assessment of the flow behaviour of unfilled and filled polymer melts is the determination of achievable flow distances in the test spiral tool. Under defined injection moulding conditions, such as volume flow, injection pressure, mass temperature or tool temperature, a polymer melt is injected into a spiral-shaped cavity with a very long flow distance. The flow distance achieved can be determined on the finished injection moulded part. With measurement under constant processing conditions, this method provides comparative information about the flow behaviour of polymer melts. Alongside the actual flow behaviour of the injected compounds, however, the tool temperature and the resultant solidification processes also have an effect on the achievable flow distances. This process thus provides important results for material-appropriate tool design with the focus on realisable flow distance-wall thickness ratios. The wall thicknesses in the test spiral tool can be varied between 1 mm and 5 mm (in 1 mm steps). A suitable tool or tool insert is needed to measure and run the tests. For tests with the carbon black-filled NEFA MB EL compounds in comparison to the reference, the framework conditions listed in Tab. 2 were applied.

The resulting flow distances of the two carbon black-filled compounds and the corresponding material reference (PP) are shown in figure 3.

Tab. 1: Comparison between test laboratory with HCR measurements and technical centre with injection moulding rheometer

Measuring device	High-pressure capillary rheometer (HCR)	Injection moulding machine (IMM) with injection moulding rheometer (IMR)
Common features	• Heated cylinder • Production of melt flow using the piston principle/piston movement • Multi-point measurement by varying the piston speed to determine shear rates • Pressure measurement to determine wall shear stress	
Differences	No thermally homogeneous melt	• Thermally homogeneous melt from screw rotation in IMM • Recording the influence of friction heat
	Ventilation through stuffing processes	Ventilation using the ram pressure in the injection unit of the IMM
Advantages	Small material quantities	Practical determination of viscosity taking account of all relevant processing factors

Designation	Parameter
Clamping force	1,000 kN
Volume flow	15 cm^3/s
Forward flow temperature of temperature control medium	40 °C
Cylinder temperature profile (nozzle → intake)	[230, 230, 220, 210, 70] °C
Material pre-drying	none

Tab. 2: Parameter settings for the determination of flow distances using the "Test spiral 3 mm" tool on the "Demag ergotech 100/420-310s" injection moulding machine

Fig. 6: Comparison of resultant flow distances in the same injection moulding conditions of NEFA MB EL 21845S. Left, standard, and right, with use of 2 % additive (NEFA MB A 19389)

As with the results with the injection moulding rheometer, once again the unfilled material shows the best flow behaviour with the longest achievable flow distances in mould filling the test spiral, followed by NEFA MB EL 23381S and NEFA MB EL 21854S. Generally speaking, it was also seen that all the materials can be used in the injection moulding process. This information could not have been concluded only using MFI measurement.
The visual impression was quantified by measuring the flow distance using a template (fig. 4).

The results are shown in figure 5, whereby the averages shown are each based on the measurement of 10 spirals per material batch.

A particular advantage of flow distance investigations in the test spiral tool is that the influence of process conditions and additives on usability in the injection moulding process can be examined very easily and in-process. In this specific example, the influence of a silicone-based processing additive (NEFA MB A 19389) on the usability of the carbon black-filled compound type NEFA MB EL 21845S was examined [4]. The additive was used in a ratio of two percent by weight and acted in the process as an external lubricant. Flow distance extensions of approx. 6 % were achieved (fig. 5). Using this additive increased fluidity roughly to the level of the type 23381S compound.

This example shows: Even at low concentrations, the use of additives can have a major impact on injection moulding processing and ultimately on product quality. The measurements were carried out in a very short time span and provided very practical information which could not have been identified in such way using laboratory testing techniques.

4 Added value for the user

The processing of highly filled compounds in the injection moulding process can present major challenges for both users and designers. Alongside classic methods for the characterisation of the rheological properties of compounds, processes have been presented that allow a rheological evaluation of unfilled and filled polymer melts directly at the injection moulding machines. In industrial practice, these processes can be used to determine rheological properties precisely in-process with a manageable increase in the apparatus required.

Using injection moulding rheology, flow curves can be recorded at the injection moulding machine that show a true rheological picture of materials. Alongside the development of formulae, injection moulding rheometers can also be used to answer questions about processing factors relating to dwell time, friction of melts and so on.

Measuring flow distances in the test spiral tool is a simple way of directly comparing and evaluating the suitability of polymers and compounds for processing. Using this test, for example, it is possible to show very easily and quickly what effect formula changes and additives have on processing in the injection moulding process.

5 References

[1] M. Hübner, I. Schaar: Innovative, carbon black-filled compounds and masterbatches at the interface of the plastics and dye industries. Applications and benefits of Caparol NEFA MB masterbatches for thermoplastic elastomers – part 1. TPE Magazine, vol.12, November 2020, p. 200-203.
[2] DIN EN ISO 1133.
[3] DIN 53014.
[4] M. Hübner: Tailored colour masterbatches for high-quality TPE tints. Applications and benefits of Caparol NEFA MB masterbatches for thermoplastic elastomers – part 1. TPE Magazine, vol.13, March 2021, p. 24-27.

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