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Flexible solutions for advanced material development

Maximize your knowledge about material characteristics and processing of new compounds

Application Compendium

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Flexible solutions for advanced material development

Welcome to the compendium on flexible solutions for advanced material development!

The challenges in modern material development are manifold: lightweight material for more fuel-efficient vehicles, conductive polymers for new appliances, optimized flow behavior for injection molding processes and many more.

Multiple applications are involved in developing new materials, from small-scale production to material characterization and optimization of manufacturing parameters. A flexible platform like the Thermo Scientific™ HAAKE™ PolyLab™ System can help you accomplish material development tasks with just one instrument – saving time and investment costs! On the HAAKE PolyLab System, interchangeable processing units can be attached in seconds to the proven drive and measuring unit. And it's all controlled by an open, intuitive software. This is the future of material processing, today!

The HAAKE PolyLab covers all these applications:
Small **batch mixers** help to characterize the material's response to shear energy and temperature to describe melting, degradation, plastification, flow and curing behavior. They can also be used to produce small batches of new material.

Twin-screw extruders are used to compound new formulations of a base matrix with multiple additives and fillers in a continuous manner. Precise liquid and solid dosing, as well as homogeneous mixing on a molecular level enable even the most challenging materials to be processed.

Sheets, films and thin fibers – final goods need to come in various shapes that can be produced using a **single screw extruder** and the appropriate **die** at the end of the instrument. Multiple **take-off devices** ensure the proper handling of the material.

Further processing of the new material requires extensive knowledge about its **rheology** for tasks such as designing new dies. Rod and slit capillary dies can be applied to insight into the material's behavior under real manufacturing conditions.

The applications listed in this compendium show a cross section of daily tasks that a material researcher may be confronted with and how to deal with them effectively. All applications in this compendium address needs in polymer research and other industries such as food/feed, cosmetics, and pharmaceuticals.

Table of contents

APPLICATION NOTE

No. LR-84

Measuring comparative electrical conductivity after mixing polyethylene pellets with carbon black

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Introduction

Conductive carbon black is used with a wide range of polymers to obtain permanently antistatic, dissipative or electro-conductive properties in plastics, rubber and paints. The carbon black impacts both electrical and thermal conductivity. It also influences the electromagnetic properties and coloration of paints and varnishes as well as the coloration of plastics and rubber. Typical application areas include extruded profiles, pipes, sheets, injection molded parts, and blown and cast films.

Carbon black types are available with different conductive properties to serve in various applications. Carbon black is also produced in batches and can vary from batch to batch. That is why it's important to have a reliable characterization method to quantify conductivity for different types and batches of carbon black.

Test equipment

High density polyethylene (HDPE) was melted in a laboratory mixer and blended with three different carbon black (CB) types in three consecutive experiments. The system used to prepare the three HDPE + CB samples was a Thermo Scientific™ HAAKE™ PolyLab™ OS Modular Torque Rheometer and an electrically heated Thermo Scientific™ HAAKE™ Rheomix Lab Mixer (600 OS version) with pneumatic ram, roller rotors and the option to measure comparative electrical conductivity. The sensor for measuring both temperature and conductivity (see Fig. 1) can penetrate the sample and is isolated from the mixing chamber. The system measures the resistance between the conductivity sensor and the mixing chamber for an output value of Siemens $S=\frac{1}{\Omega}$. The higher the comparative conductivity value in Siemens, the better the conductance in the final mixture.

Test conditions

33 g of HDPE pellets were put into the mixer chamber and mixed for 5 minutes at a rotor speed of 100 rpm and a mixer-temperature of 150 °C. During this period, the mixer torque and conductivity of the polymer was measured and displayed in a rheogram (Graphs 1, 2 and 3). After

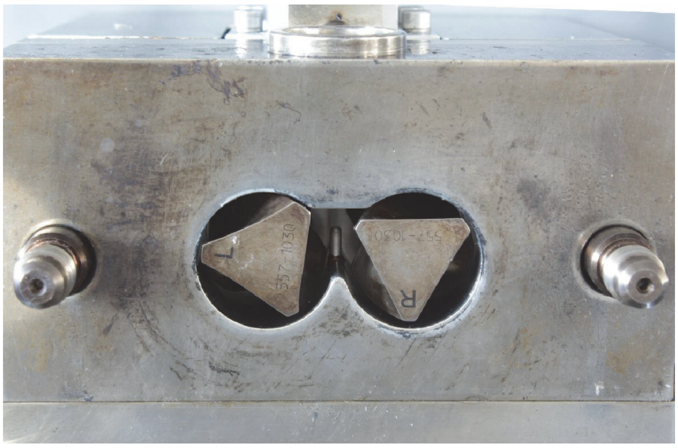


Figure 1: The chamber of the Rheomix Lab Mixer (600 OS version) with combined melt temperature and conductivity sensor.

the polymer was molten, the pneumatic ram was lifted up and 4 g of carbon back was added. The ram was lowered to close the mixer chamber. Mixing and measuring continued for another 10 minutes.

Materials and results

Three different samples were examined using the same grade of HDPE and 3 different types of carbon black (CB1, CB2 and CB3). For CB1, two manufacturing batches were tested to check for variation between batches.

The mixer results for the different samples and batches are shown in Table 1. The torque (left y-axis) and the electrical conductivity (right y-axis) of all tests are displayed with the same scaling for the y-axis in all rheograms.

To show the reproducibility of the test method, tests with carbon black type 1 batch 2 (sample numbers 2 and 3) were done twice (see Graph 1). Both test results showed the same comparative conductivity base line (red curves) of 230 mS, and the torque signal showed the typical loading peak and decreases to 13.4 Nm when the HDPE was completely molten.

Sample no.	Sample CB type	Specific Resistance [Ω*m] [1]	Electrical Conductivity [mS*m-1] [1]s	Comparative Conductivity [mS]
1	CB1-Batch1	max. 8000	max. 0.125	1,890 @ 15 min
2	CB1-Batch2	max. 8000	max. 0.125	620 @ 15 min
3	CB1-Batch2-Rep	max. 8000	max. 0.125	550 @ 15 min
4	CB2	max. 2000	max. 0.5	12,200 @ 15 min
5	CB3	∞	0	240 @ 15 min

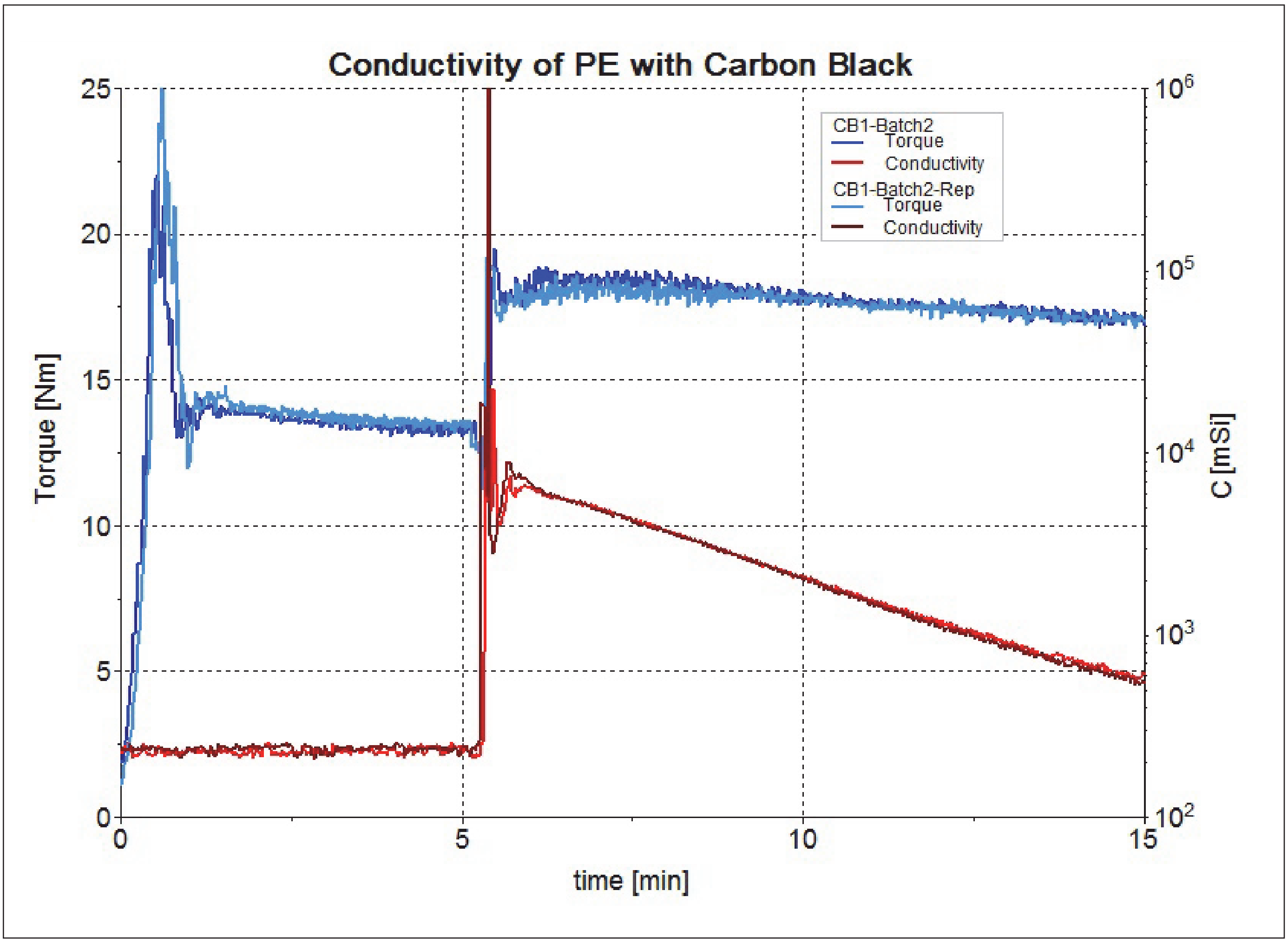
Table 1: HDPE + CB samples, their electrical resistance and productivity. Electrical conductivity obtained by van der Pauw method [1].

After 5 minutes, the carbon black was added. The measure of conductivity showed an immediate increase from the carbon black addition due to the conductivity sensor's location in the mixer chamber. After more thorough mixing, the comparative conductivity decreased again as the carbon black particles were better distributed within the polymer matrix. After 15 minutes, the output value was 620 mS and 550 mS respectively. Adding the carbon black resulted in a higher torque signal (blue curves) because it reinforced the polymer melt. It leveled out at the end of the mixing time at 17 Nm. The results show good repeatability for the test method.

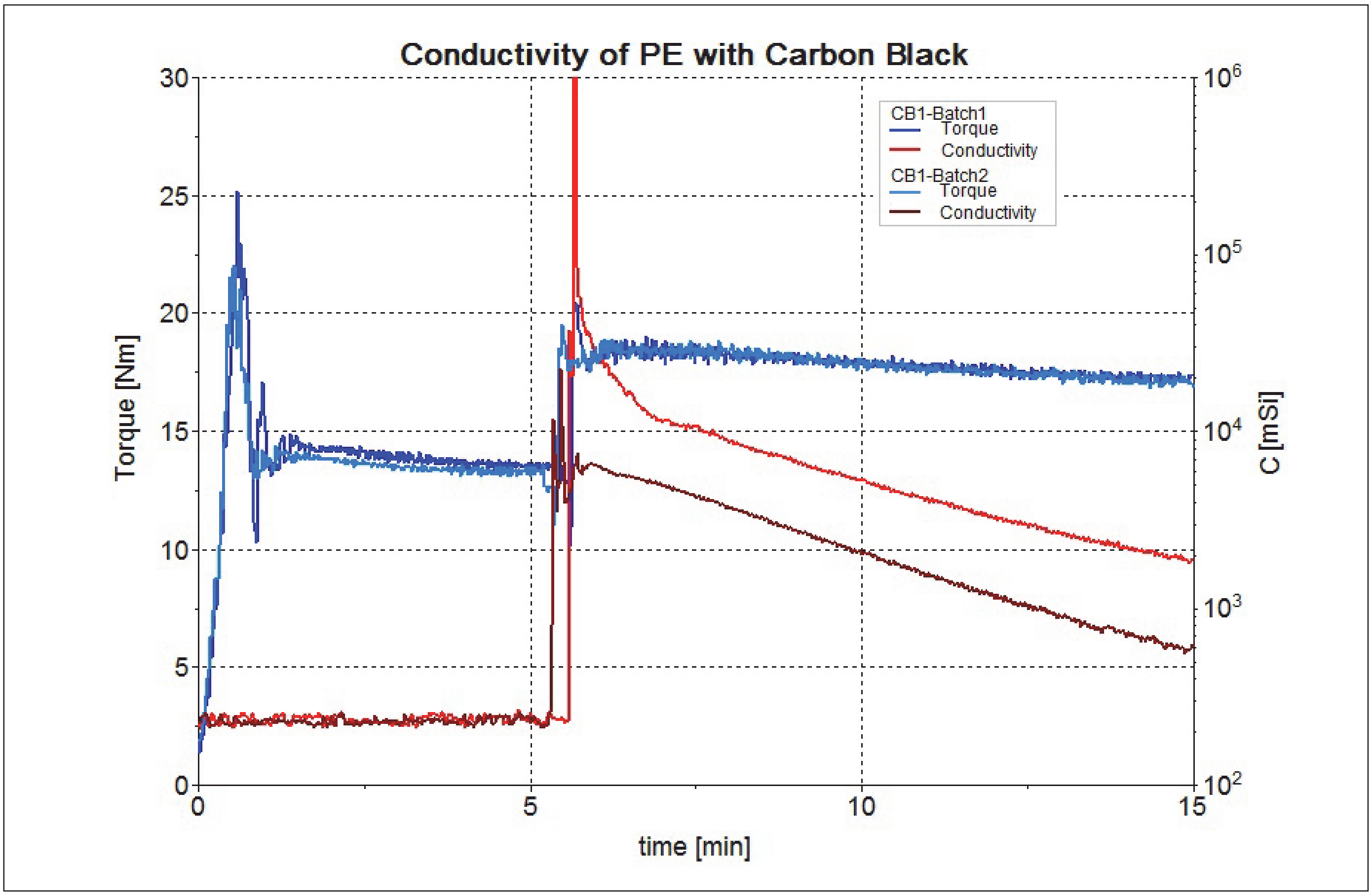
The differentiation between the two batches of carbon black type 1 (sample 1 and sample 2) is shown in Graph 2.

The readings of the comparative conductivity show a difference while the torque for both samples (blue curves) is equal with 17 Nm at the end of the test. After 15 minutes of mixing, batch 1 of carbon black type 1 (sample 1) has a value of 1890 mS (light red curve) compared to batch 2 of carbon black type 1 (sample 2) with only 620 mS (dark red line).

The comparison of all conducted tests (see Graph 3) shows good correlation with the electrical conductivity of the raw carbon blacks listed in Table 1.



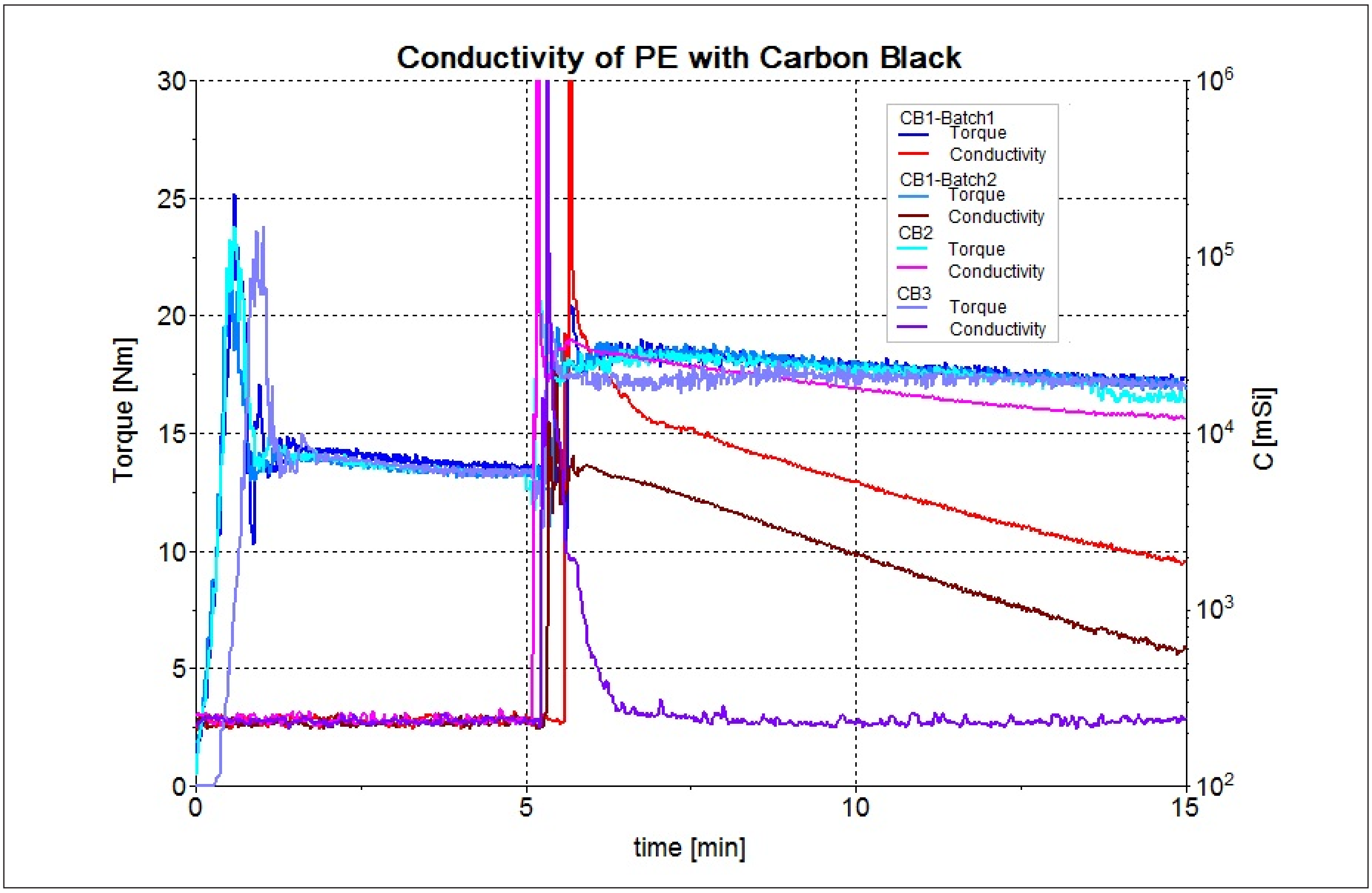
Graph 1: Repeatability of the mixer test with samples 2 and 3.



Graph 2: Variance of two batches of carbon black type 1 (sample 1 and sample 2).

Carbon black type 2 (pink line) shows the highest comparative conductivity at the end of the mixer test with 12,200 mS. Carbon black type 3 (violet line) with a base line value of 245 mS after 15 minutes of mixing time isn't conductive.

All conductive carbon blacks show similar torque curves. The torque curve of the nonconductive CB3 is slightly different after the carbon black is added to the polymer melt.



Graph 3: Rheograms of all four types of carbon black tested.

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Conclusion

Using the HAAKE PolyLab OS system with a batch mixer enables the researcher to obtain reproducible results of comparative conductivity data with minimal effort in a few minutes. This report shows how that can be done in an example using samples of HDPE with different carbon black types. Differences in batches and among various carbon black types can be reliably monitored. The measured results have good correlation with those values obtained by the van der Pauw method [1] for electrical conductivity (see Table 1). Beyond that, the comparative conductivity measurement allows for a more precise characterization of the value to help material researchers further optimize their formulations. This test method can also be used with rubber applications [2].

Literature

[1] A Method of Measuring Specific Resistivity and Hall Effect of Discs of Arbitrary Shapel. - J. van der Pauw: Philips Res. Reports 13 (1), 1958, p. 1-9.

[2] Macro- and microdispersion of carbon black in liquid silicone rubbers Le, H. H.; Ilisch, Sybill; Radusch, Hans-Joachim; Steinberger, H.; Plastics, rubber and composites. - London: IOM, Bd. 37.2008, 8, S. 367-375.

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LR-84 0518

APPLICATION NOTE

Influence of stabilizers on the flow and degradation properties of polyamide

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Introduction

Polyamide (PA), commonly known as nylon, is a popular engineered thermoplastic material. Automobile manufacturers often use it for engine parts such as air intake manifolds or engine covers because the material withstands high temperatures. It is crucial then to manage raw material quality and processing conditions, so the final material property of polyamide is suitable for such applications.

During the processing of polyamide, high temperatures and the presence of a nucleophile such as water lead to the degradation of the polymer chains. This causes a decrease in polymer molecular mass and an increase in polymer end-groups. That leads to a decline of the viscosity of the polymer melt and the mechanical properties of the final product.

It is possible to delay the onset of link decomposition by adding stabilizers. The Thermo Scientific™ HAAKE™ PolyLab™ system offers a quick, reliable method of examining the influence of stabilizers on material processing characteristics.

Test purpose

Test the effectiveness of a stabilizer in Polyamide PA6 processing.

Test equipment

- HAAKE PolyLab OS Torque Rheometer
- Thermo Scientific™ HAAKE™ Rheomix 600 electrically heated laboratory mixer
- Roller rotors
- Thermo Scientific™ HAAKE™ PolySoft Mixer Software

Test conditions

· Mixer temperature: 240 °C
· Rotor speed: 60 rpm
· Sample weight: 52 g

Test material

· Sample 1: PA6 without stabilizer
· Sample 2: PA6 with stabilizer

Test method

The mixer is heated to the desired testing temperature and the drive motor runs at the selected rotor speed.

Before the actual measurement, a calibration routine is conducted, to zero out any possible torque signal generated by the mixer gear box. Then the cold sample material is rapidly added into the heated, running mixer, and the mixer is closed by the feeding ram.

The torque and the melt temperature are recorded over the mixing time, to measure the melting and processing behavior of the sample.

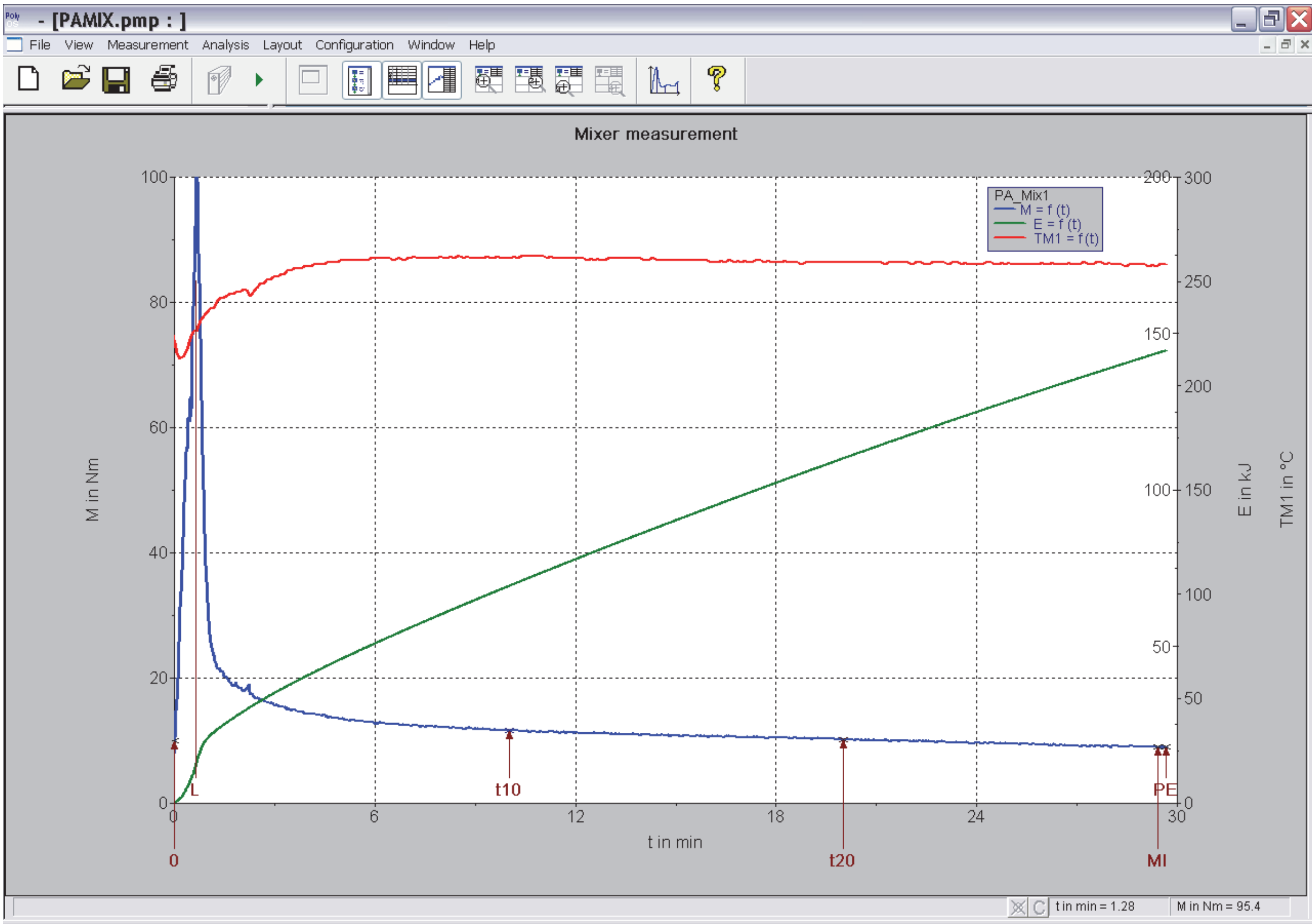
Test results

Figure 1 shows the torque-time curve of a polyamide without the addition of a stabilizer. The graph shows the torque (M, blue), the melt temperature (TM1, red) and the energy consumption (E, green) as a function of test time.

Basic curve discussion

The initial filling of the mixer with the rigid PA sample results in a significant rise in torque, the so-called Loading Peak (L). This peak serves as the starting time for the calculation of the substance's various characteristics.

After the sample material has become totally molten, the torque-time curve shows a continuous decrease in torque. This decrease in torque is caused by the reduction of the melt viscosity due to the degradation of the un-stabilized sample.



	L	L	MI	MI	t10	t10	t20	t20	PE	PE	Gradient t10/t20
	t in min	M in Nm	t in min	M in Nm	t in min	M in Nm	t in min	M in Nm	t in min	M in Nm	dM/dt in Nm/mir
PA_Mix1.pld	0.6445	111.9	29.42	8.950	10.01	11.62	20.01	10.15	29.66	8.878	-0.1347

Figure 1: Rheogram of mixer test without stabilizer.

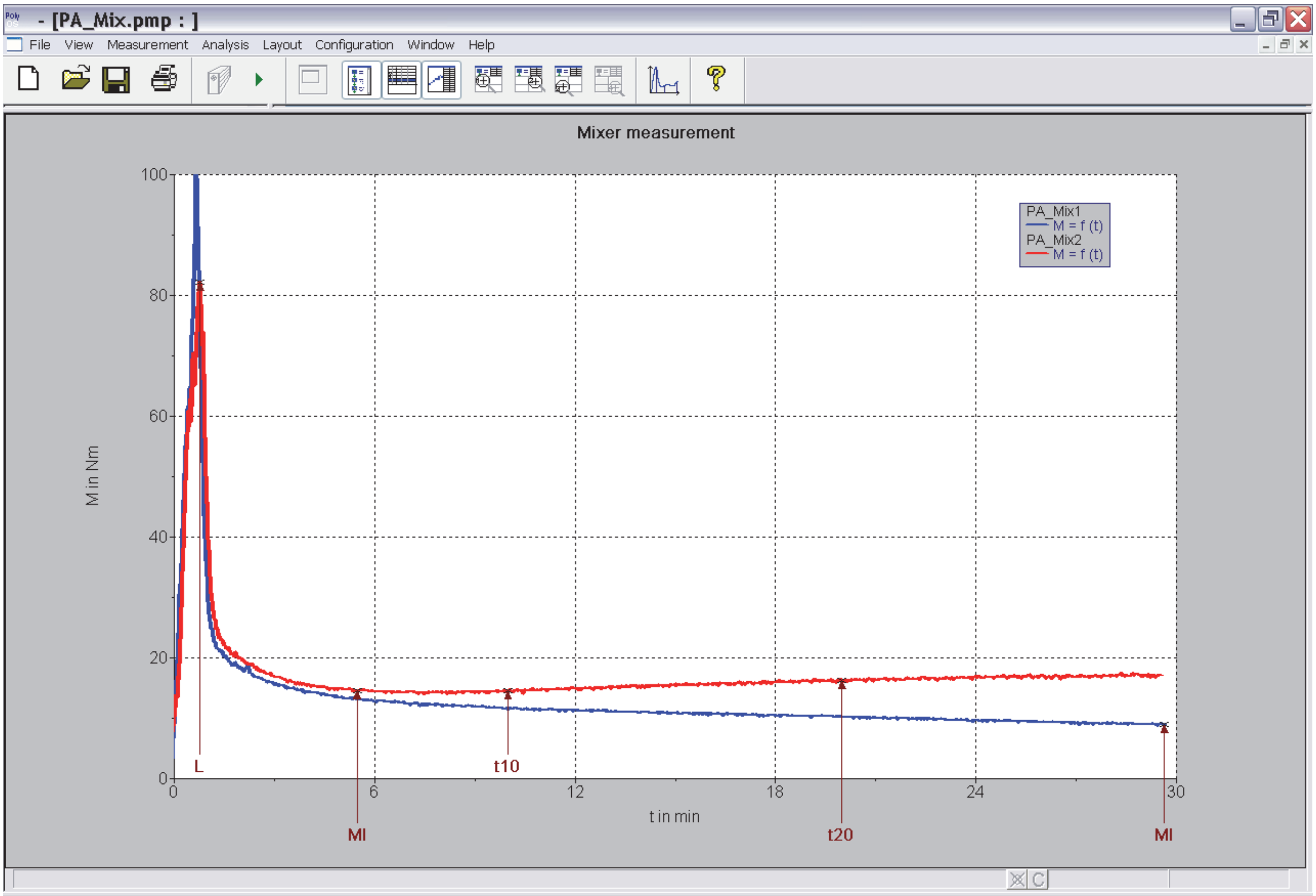
The evaluation of the characteristic curve points is done using the table shown below the graph in figure 2 . Apart from registering the time, torque, energy and melt temperature values, the gradient between the torque value after 10 minutes and 20 minutes was calculated as a measure of the degradation speed.

Another mixer test was carried out with sample 2, a PA6 polymer compound that contains stabilizer. The stabilizer helps to conserve the polymer end-groups under harsh temperature conditions and thus should result in an improved material stability. Therefore, with the second mixer test, a stable torque value is expected.

Comparison of test results

Figure 2 shows the torque curves of the mixer tests for the PA with and without stabilizer in one graph.

The stabilizer influence is clearly visible. The sample with added stabilizer (red curve) shows a higher torque value in the molten state. Also the torque does not decrease further over the course of the measurement. It can be concluded that the stabilizer prevents the breaking of the polymer chains and thus counteracts the degradation of the polyamide.



	L	L	MI	MI	t10	t10	t20	t20	PE	PE	Gradient t10/t20
	t in min	M in Nm	t in min	M in Nm	t in min	M in Nm	t in min	M in Nm	t in min	M in Nm	dM/dt in Nm/min
PA_Mix1.pld	0.6445	111.9	29.65	8.900	10.01	11.62	20.01	10.15	29.66	8.878	-0.1347
PA_Mix2.pld	0.7687	82.21	5.469	14.53	9.985	14.57	19.99	16.24	29.57	17.10	0.1776

Figure 2: Torque curves of mixer tests for PA with and without stabilizer.

Conclusion

The tests show that the HAAKE PolyLab Torque Rheometer with an attached laboratory mixer is ideal equipment to study the flow and processing behavior of polymer compounds. It can help to establish a QC routine for PA applications for easy, fast and reliable determination of final product quality attributes.

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LR-18 0518

APPLICATION NOTE

No. LR-68

Producing high-performance polymer-composites by embedding nanoparticles using twin screw extrusion

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Key words
Compounding, Carbon nanotubes, Composites, Twin screw extrusion

Introduction

Carbon nanotubes are graphite sheets rolled into seamless tubes, with diameters of just a few nanometers and lengths up to centimeters. Nanotubes have received much attention because of their unique mechanical, electrical and thermal properties.

There are a large number of potential applications for CNTs, especially in the field of polymer compounds, where they are used to improve mechanical and electrical properties. Polymer nanocomposites are frequently used in the automotive and aviation industries, as well as in construction materials for windmill blades.

Key to unleashing the unique properties of the polymer nanocomposites is dispersion of the CNTs thoroughly in the polymer matrix. Only when the CNT particles are dispersed homogeneously within the polymer and the formation of larger clusters is avoided, can the desired property improvements be achieved. The improved mechanical properties of the final compound can be tested by means of dynamic mechanical thermal analysis (DMTA) which can be performed, for instance, with a rotational rheometer [1].

One approach that can lead to a homogeneous distribution of the CNT particles within the polymer matrix is the use of CNT suspensions for the extrusion process. For this the CNTs are functionalized first (i.e. by amination) and dispersed afterwards in a carrier liquid like ethanol by means of high shear mixing or ultra sonic treatment. The obtained CNT suspension is then feed into the extrusion process. Using CNT suspensions in the extrusion process also avoids the formation of CNT dust in the laboratory environment.

The aim of this report is to demonstrate that CNT suspensions can be used to produce polymer nanocomposites by means of twin screw extrusion. With the described procedure a homogeneous distribution of the CNTs in the polymer matrix can be achieved in order to obtain the desired property improvements for the polymer nanocomposite.

Material and methods

Test material

- Base Polymer: Polypropylene Metocene HM562S (LyondellBasell)
- Two CNT-Ethanol suspensions with different functionalization (Rescoll/France)

Test equipment

- Torque rheometer system Thermo Scientific™ HAAKE™ PolyLab OS System
- Co-rotating twin screw extruder Thermo Scientific™ HAAKE™ Rheomex PTW16 OS System (L/D = 40)
- Gravimetric RotoTube feeder for pellets
- Liquid feeding pump for the suspensions
- Vacuum pump
- Strand line with Varicut pelletizer

Test conditions

- Screw speed: 250 rpm
- Temperature profile: 20°/230°/250°/250°/230°/220°/220°/200°/200°
- Feed rate PP: 0.919 kg/h
- Feed rate CNT-suspension: 0.114 kg/h (equivalent to 0.5 % CNT in PP)

Test procedure

The complete extruder and screw configuration is presented in Fig. 1. In the first stage (zone 1) the polypropylene was added and molten in the first mixing section (zone 2). The CNT suspension was dosed into the second feeding port (zone 3) into the polypropylene melt by means of a liquid feeding pump. The ethanol of the suspension was removed from the extruder using an atmospheric venting port in zone 4 and a vacuum venting in zone 9.

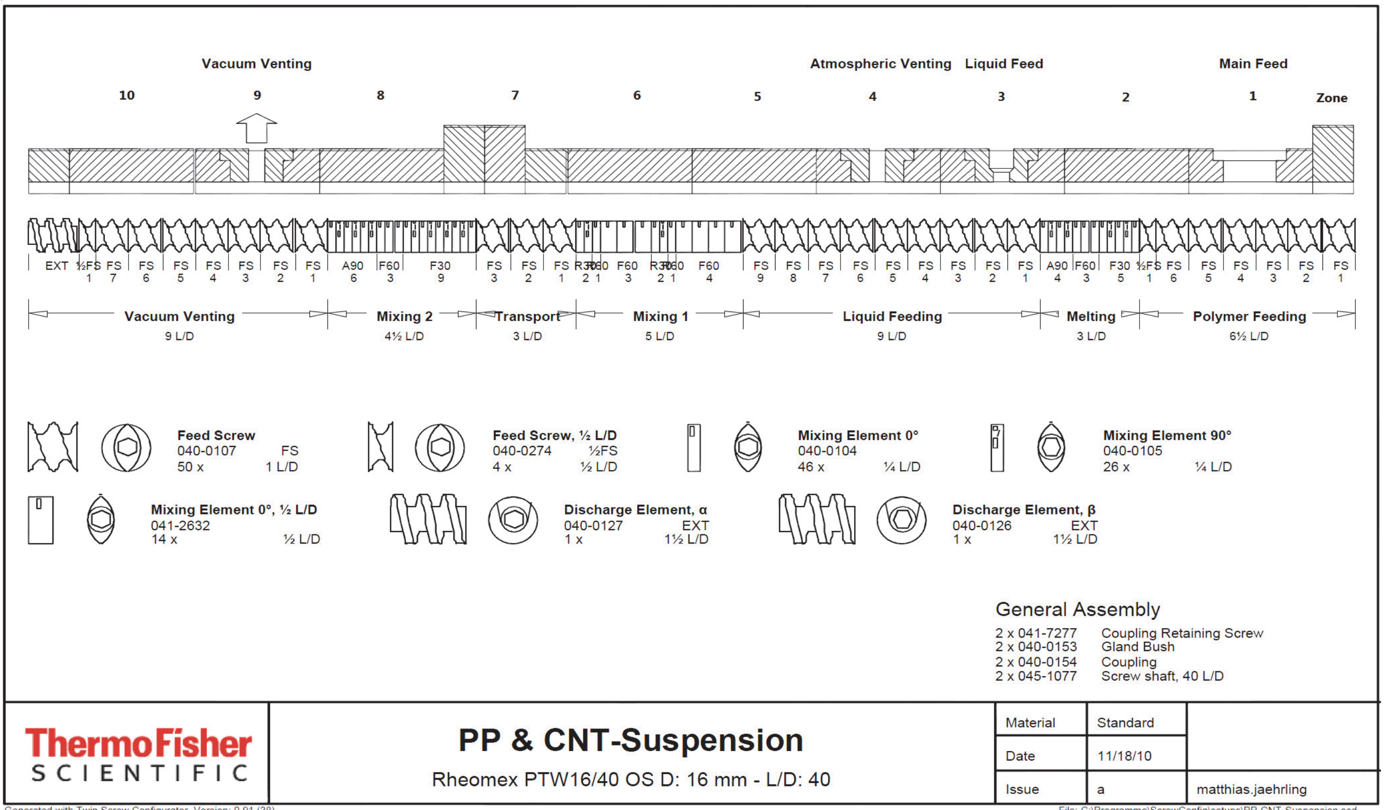

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Fig. 1: Extruder- and screw configuration.

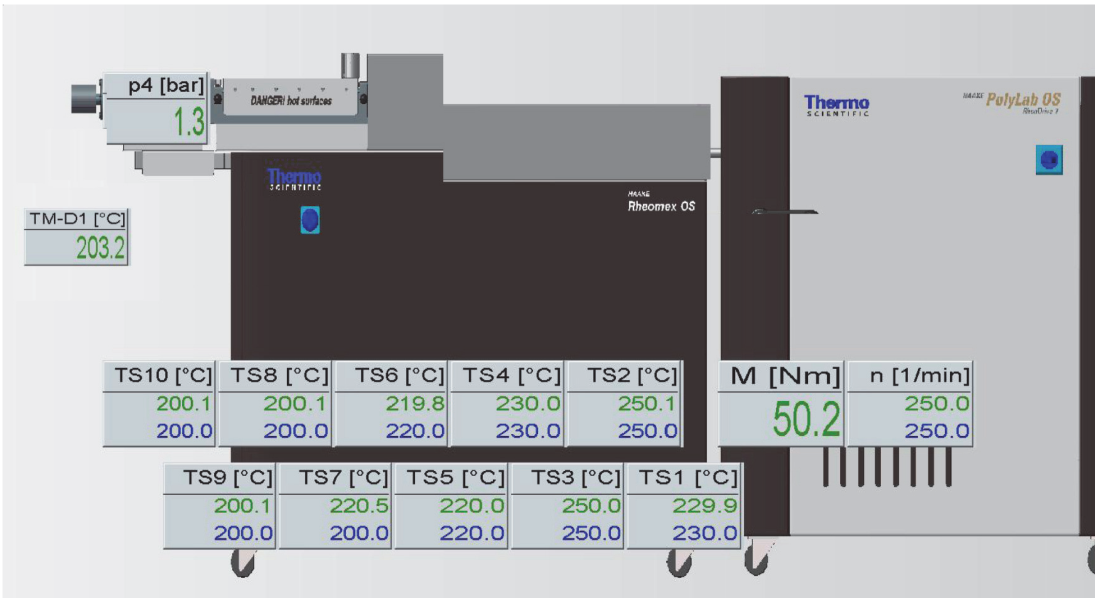

Fig. 2: Extrusion conditions.

The CNTs and the polypropylene were thoroughly mixed and sheared in two mixing sections in zones 5/6 and zone 8.

Results

During the test, the melt pressure at the die was measured. Fig. 3 shows this melt pressure as an overlay of three different extrusion tests. One test was done with the pure polypropylene, one test with the addition of CNT suspension "1" and one with CNT suspension "4".

It can be clearly seen that the pressure increased when a CNT suspension was added. The pressure difference between the two different suspen-sions itself was not significant. The extruded material was then formed into a strand, which was cooled down in a water bath and cut into pellets by a pelletizer.

Using our mini injection moulding machine, the Thermo Scientific™ HAAKE™ MiniJet System those pellets were injection moulded into specimens like disks and DMTA bars for further investigation.

Fig. 4 shows a microscopic picture taken from specimens made from the PP compound containing 0.5% CNT from suspension "1".

In this picture no agglomeration can be seen and the CNTs seem to be evenly distributed in the polymer matrix. Fig. 5 shows a microscopic picture taken from the PP compound containing 0.5% CNT from suspension "4". This picture shows a large amount of agglomerates. The dispersion seems to be much worse than the result we got from suspension "1".

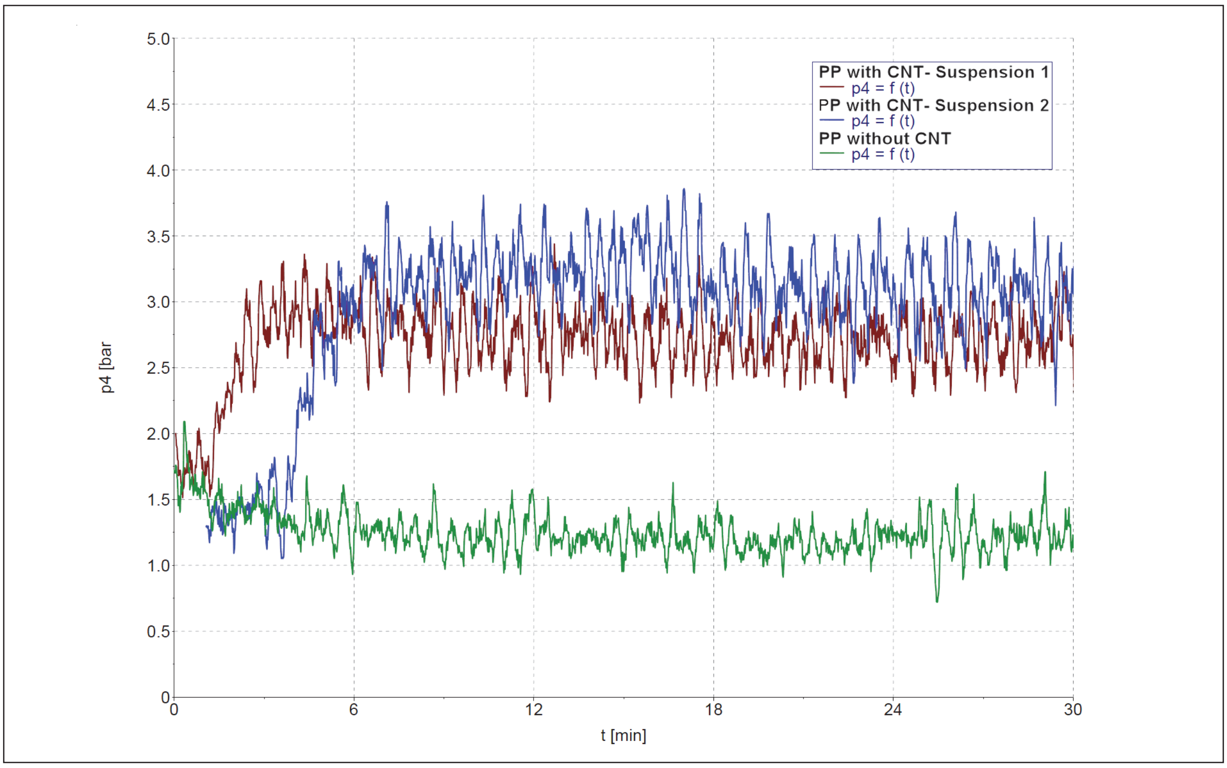

Fig. 3: Pressure at Die-Had.

Fig. 4: PP with 0.5% of CNT “1“.

Fig. 5: PP with 0.5% of CNT “2“.

Conclusion

The PolyLab System with the lab scale twin screw compounder, Rheomex PTW16, can be used to prepare compounds from polymers and CNTs using CNT suspensions.

The result of these tests shows significant differences between the compounds made with the differently functionalized CNTs.

Acknowledgement

We would like to thank the Fraunhofer Institute for Manufacturing Engineering and Automation IPA in Stuttgart, Germany for their input and the Research Company RESCOLL in Pessac, France for their kind co-operation and supplying the CNT-suspensions. We also thank Volker Räntzsch from the Karlsruhe Institute of Technology in Germany for providing the microscopic images.

Reference

[1] Thermo Scientific Application note V241 “Dynamic mechanical thermal analysis (DMTA) on polymer nanocomposites“ Fabian Meyer, Klaus Oldörp and Frits de Jong

Find out more at **thermofisher.com/extruders**

LR68 0617

APPLICATION NOTE

No. LR-56

Save production time and costs with powder injection molding manufacturing process

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Abstract

Powder Injection Molding is a manufacturing process that helps save time and decrease overall costs. A large number of mechanically complex products can be produced within shorter production times. The best base material for this process is fine ceramics or metal powder blended with a binder to form a free flowing feedstock for the injection molding. To obtain a high quality end product it's important to achieve a homogeneous dispersion of the ceramic powder within the polymer matrix. In the below application note we'll show you how.

Introduction

In test runs with small laboratory compounders we can prove feasibility of binder-powder compound. Binder systems are based on waxes or polymers (e.g. LDPE, PP, POM). Compared to color-masterbatch compounds the focus is on highest degree of filling of the powder, still obtaining a feedstock which can be used in a molding process. After molding the „green" parts undergo a heat treatment (sintering). End products are e.g. catalyst beads, turbine blades.

Usually laboratory development will check for compatibility of the binder/powder system and the maximum degree of filling. Moreover molding trials for feedstock formulations can easily be performed in order to optimize the composition of the various components. The Thermo Scientific™ HAAKE™ MiniJet Pro enables quick tests on process ability of the CIM feedstock. The samples can be sintered and used for mechanical testing.

Materials and methods

A polyethylene wax based binder was blended with Zirconium oxide. For the Thermo Scientific™ HAAKE™ PolyLab™ OS a Thermo Scientific™ HAAKE™ RheoDrive 16 and a Thermo Scientific™ HAAKE™ PTW16/25 XL parallel twin screw extruder with two HAAKE metering feeder (binder, ceramic powder) was used (Fig. 1) to compound the raw materials:

Fig. 1: Instrument setup, RheoDrive 16, PTW16/25, split feed with two metering feeders, die plate and conveyor belt.

- Feed method: split feed with two feeders first zone.
- Strand die 2.5 mm and conveyor belt was for take off.

In case of air bubbles, atmospheric venting is advised. Product was cooled on the conveyor belt, and then easily cut to pellets and manually fed to the HAAKE MiniJet Pro.

Fig. 1 shows the split feed with two metering feeders coupled by an adaptor. Split feed is essential as wax (brittle flakes) and the ceramic (fine powder) segregates when fed through the same hopper.

To setup the system with the feed of the wax in the first zone and the powder via the secondary feed port is shown in Fig. 2. For powder compounds with polymer grades with high Tg (melting temperatures) this way of feeding is advised to prevent higher wear on the barrel. As the pellets have higher melting point the lubrication is decreased compared to waxes. Also when looking for high output, feeding with separate ports is advised.

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Fig. 2: Separate feed of wax and powder.

Before starting the test with the volumetric feeders pretests for the output curve of the metering feeders were performed. Here the extruder was running the wax first, then subsequently adding the powder. Stable extrusion was achieved by the summarized set up:

Set values:
- Speed: 200 rpm
- TS1 (Feed): 30 °C
- TS2: 120 °C
- TS3: 160 °C
- TS4: 160 °C
- TS5: 160 °C
- T die: 160 °C

Measure values:
- Torque: 50 Nm
- Pressure die: 7 bar
- T (Melt): 170 °C

Fig. 3: The HAAKE MiniJet Pro.

For the MiniJet PRO (Fig. 3) the strand was broken to pellets and manually fed. The set values are as shown in table 1 resulting in e.g. a tensile bar (Fig. 4).

Table 1: Set values for HAAKE MiniJet Pro

Description	Values
Cylinder temperature	160 °C
Mold temperature	120 °C
Injection pressure	800 bar
Duration time	10 s
Post pressure	400 bar
Duration time	5 s

Fig. 4: Tensile bar in HAAKE MiniJet Pro mould.

Results and discussion

Compounding worked without problems all compounds produced showed excellent dispersion of the powders. The desired output of 6 kg/hr was reached with the given composition of powder and binder (85/15 % wt/wt). Neither the compounder nor feeding system was pushed to the limit. Fig. 5 shows the wax and powder, and the resulting compounds (disk, pellet, strand, tensile bar, sheet). Extruded strands were brittle and easy to break manually. Sheet extrusion was possible, but disks molded in the HAAKE MiniJet Pro showed higher surface quality, an indication of a very good dispersion. Injection molding by the HAAKE MiniJet Pro was easy with the parameters shown in the table 1.

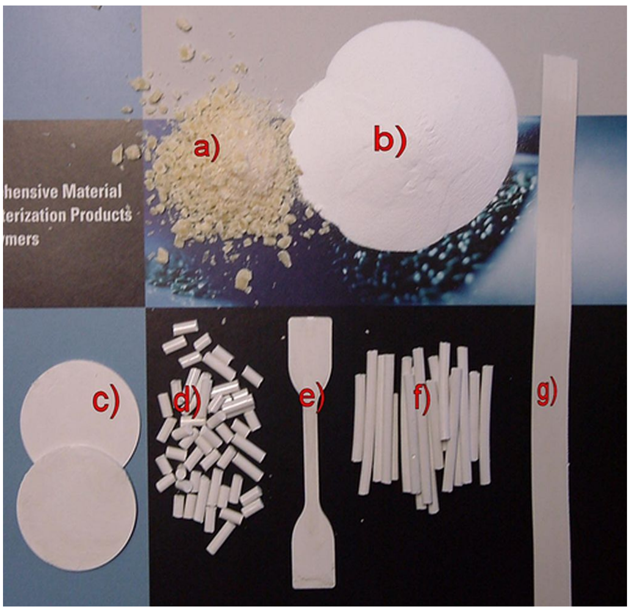

Fig. 5: Raw material (a, b) and product samples (c-g): a) wax (PE), b) ceramic powder (ZrO_2), c) disks, d) pellets, e) tensile bar, f) strands, g) sheet.

Conclusion

The HAAKE PolyLab OS system and a parallel twin-screw extruder is the ideal instrument for quick development of CIM feedstock. The compounding itself could also be performed with the Eurolab 16XL stand-alone compounder with similar parameters.

The good mechanical properties of the specimen produced with the HAAKE MiniJet Pro gives a clear indication of the excellent dispersive mixing achieved with the above mentioned twin-screw setup used. The CIM feedstock can be directly used for time and cost efficient mass production of ceramic parts.

Further to the compounding tests with a small batch mixer could be performed e.g. to evaluate minimum binder ratio or using single screw extruders to measure the viscosity of the feedstock.

Find out more at **thermofisher.com/extruders**

LR-56 1117

APPLICATION NOTE

The influence of carbon black types on the processability of Rubber Compounds in green tires

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Up to 15 percent of the gas in a car's tank is used to overcome the tires' resistance to the road. So with low-rolling-resistance (aka "green") tires, fuel economy can improve significantly.

To develop more fuel efficient tires, it is important to understand the processability of new rubber compound formulations. The perfect instrument to study this behavior is a torque rheometer with laboratory mixers and laboratory extruders, because it simulates the processing conditions in a small scale testing environment.

The following application note shows how to study the influence of three different types of carbon black on the processability of a rubber compound formulation for tire production.

Test samples

Rubber compound tire formulation, based on a branched cobalt butadiene rubber (Buna® CB 1220 from ARLANXEO), using three different types of carbon black:

- **N326** Rubber carbon black:
  Nitrogen surface area: 78 m2/g, Iodine adsorption: 82 g/kg
  Fine reinforcing carbon black with low-structure.
- **N234** Rubber carbon black:
  Nitrogen surface area: 118 m2/g, Iodine adsorption: 120 g/kg
  Fine reinforcing carbon black with increased structure.
- **N339** Rubber carbon black:
  Nitrogen surface area: 91 m^2/g, Iodine adsorption: 90 g/kg
  Fine reinforcing carbon black with increased structure.

Testing equipment

Thermo Scientific™ HAAKE™ PolyLab™ OS modular torque rheometer platform with:

- Drive unit: Thermo Scientific™ HAAKE™ RheoDrive™ 7 OS
- Single screw extruder: Thermo Scientific™ HAAKE™ Rheomex 19/10 OS rubber
  Screw diameter: 19 mm, length L/D 10, compression ratio 1:1
  Roll-Feeder system for rubber feeding

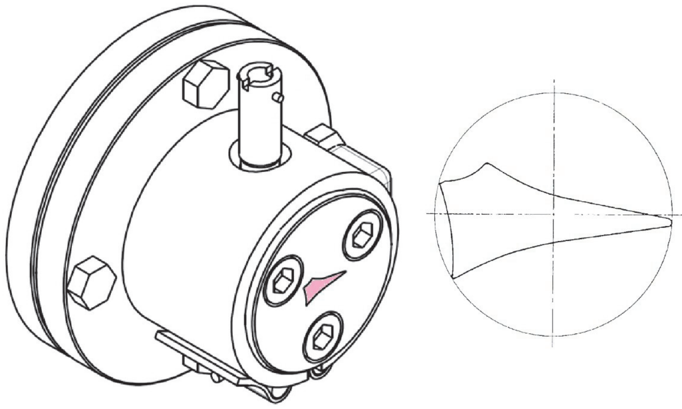


Fig. 1: Schematic drawing of a Garvey die and its profile.

Test method 1: Garvey Test

For this test, the extruder was equipped with an extrusion die with a Garvey profile according to ASTM D2230 (Figure 1) and a conveyor belt take-off.

The Garvey die produces a profile with four different angles, which looks somewhat like a scaled-down version of half of a tire tread. A well flowing rubber compound will give a smooth profile, with no defects even the smallest corners. A poor flowing rubber compound will show an uneven, ripped and swollen profile (Figure 2). The quality of an extruded profile is then ranked according to a ranking system described in the ASTM standard.

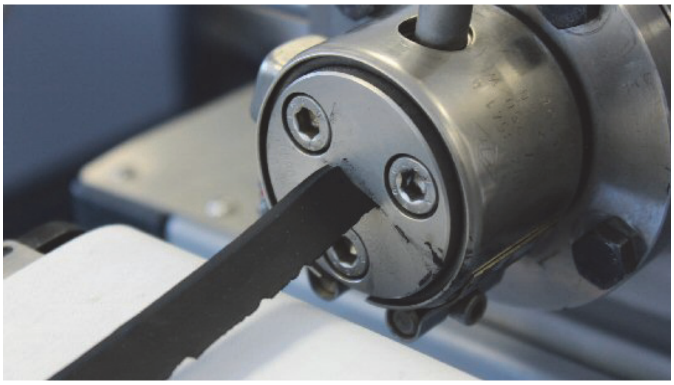


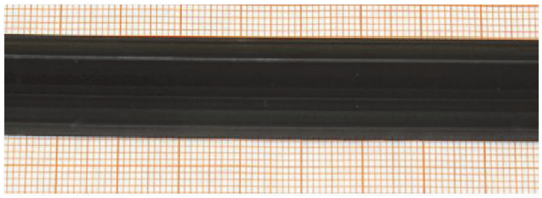
Fig. 2: Extruded Garvey die profile.

The results of the Garvey test with the three rubber compounds are shown in Figure 3.

CB N339:

	1	2	3	4
Swelling				x
Edge				x
Surface				x
Corners				x

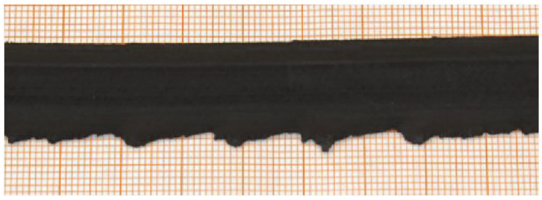
Edge:	10
Surface:	A



CB N326:

	1	2	3	4
Swelling			x	
Edge		x		
Surface			x	
Corners		x		

Edge:	4
Surface:	B



CB N234:

	1	2	3	4
Swelling				x
Edge			x	
Surface				x
Corners			x	

Edge:	8
Surface:	A

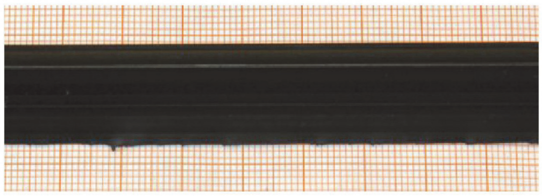


Fig. 3: Garvey profile examples of the 3 rubber formulations.

Figure 3 shows that the type of the carbon black has a significant influence on the profile quality. The carbon blacks with increased structure (CB N339, CB N234) give a much smoother profile compared to the sample with low-structure (CB N326).

Test method 2: Die-swell measurement

Die-swell (also known as the Barus effect) is a common phenomenon in polymer and rubber processing. It is where a polymer stream is compressed by entrance into a die, and then is followed by a partial recovery or “swell“ back to the former shape and volume of the polymer after exiting the die.

For this test, the extruder was equipped with a vertical rod die, a rod die nozzle D= 2mm, L/D= 0 and a laser die-swell tester.

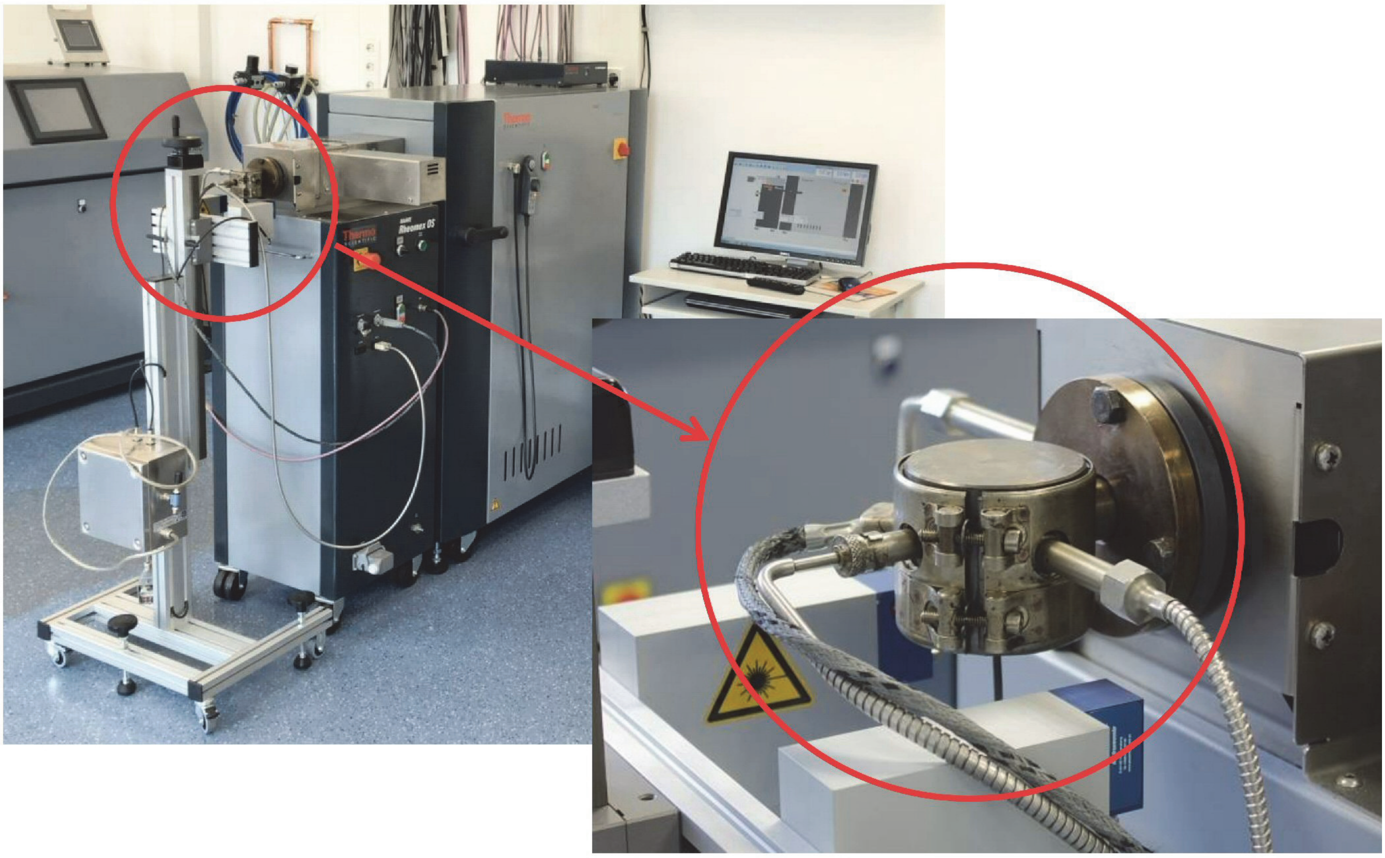


Fig. 4: HAAKE PolyLab OS setup with die-swell measurement.

The system continuously measures the diameter of the expanded strand. From the relation between the measured diameter and the actual diameter of the rod die nozzle, the die-swell is calculated.

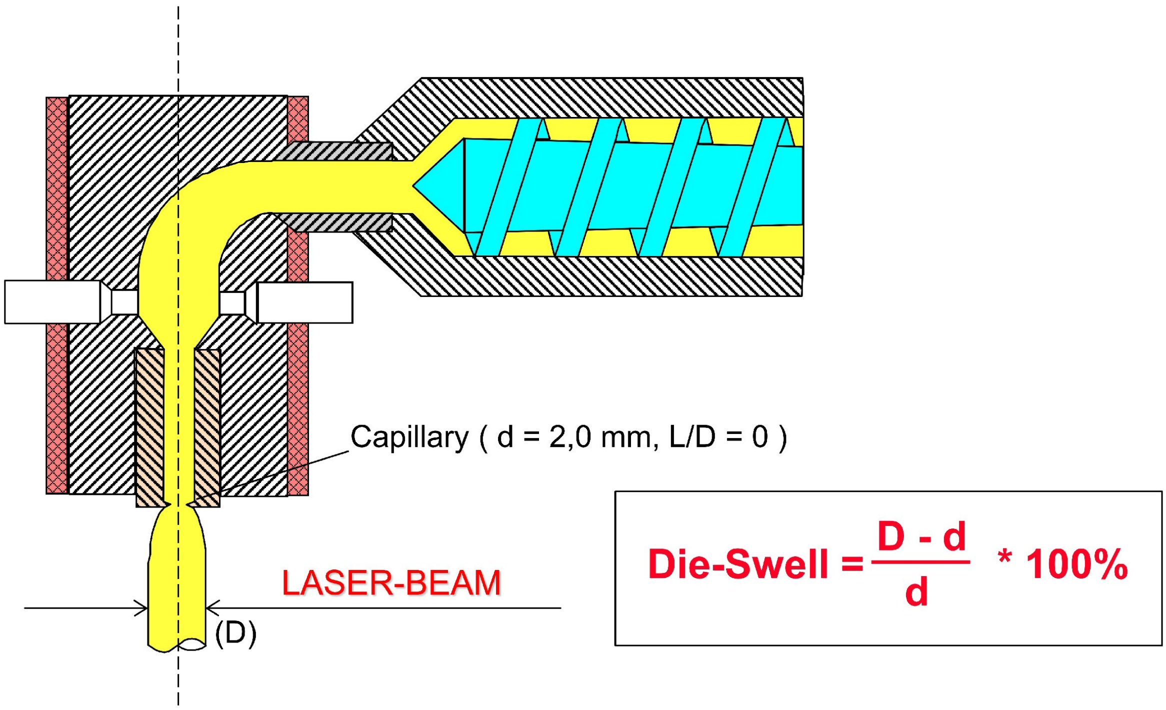


Fig. 5: Schematic and calculation of die-swell measurement.

The three samples were tested at three different screw speeds (20rpm, 40rpm and 60rpm).
The results of these tests are shown in Figure 6.

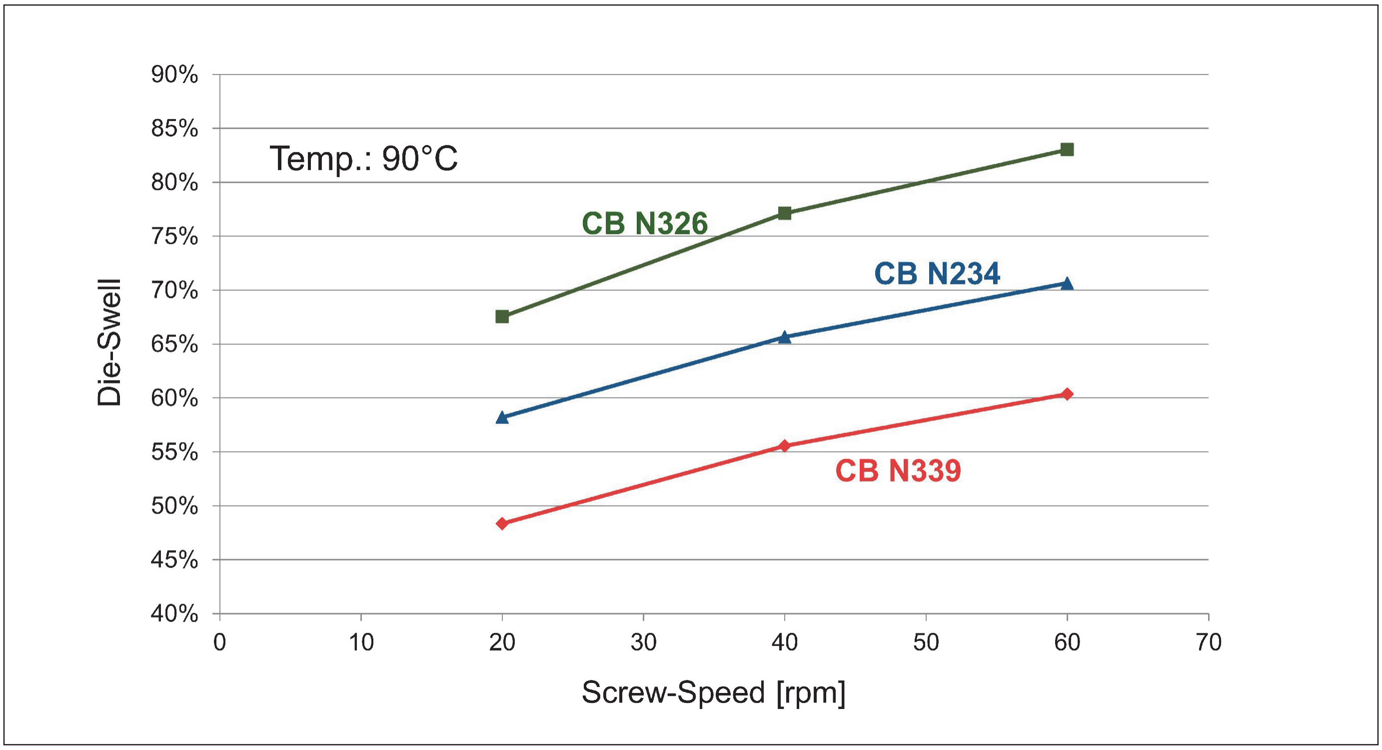


Fig. 6: Die-swelling phenomena for 3 rubber formulations.

Also in Figure 6 the significant influence of the type of the carbon black can be seen. The compounds with the carbon black with increased structure (CB N339, CB N234) show a much lower swelling behavior compared to the sample with the carbon black with low-structure (CB N326).
The die-swell test also more clearly shows differences between the compounds with the carbon blacks with the increased structure (CB N339, CB N234).

Test method 3: Extruder capillary rheology

To test the rheological properties of the rubber compounds, the extruder was equipped with a horizontal slit capillary die with a measuring geometry of W = 20 x H = 2.0 mm (Figure 7).

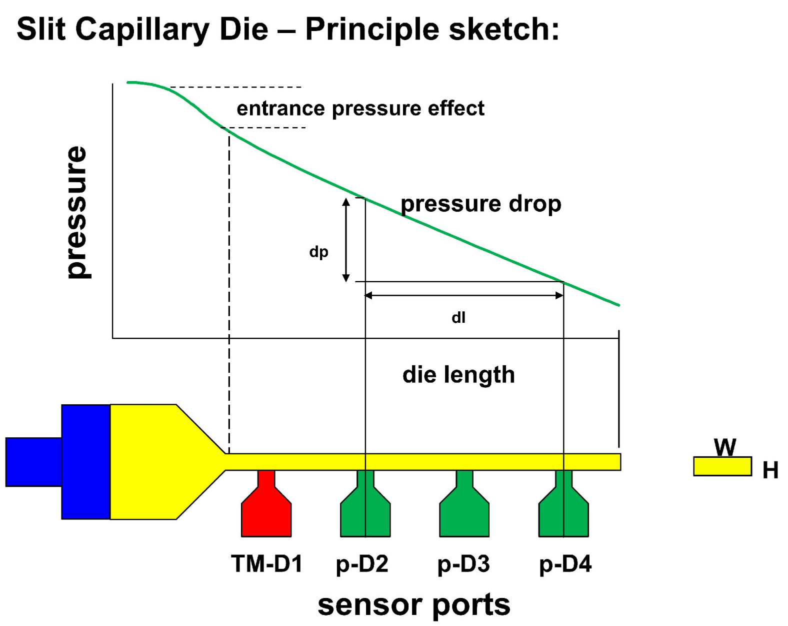


Fig. 7: Schematic of a horizontal slit capillary die.

To determine the output of the extruder, a balance connected to the HAAKE PolyLab system's control computer with an RS232 connection was used.

A test procedure was programmed using the PolySoft OS Capillary Rheometry software which executes the measurement sequence automatically after programming. The software runs the extruder at different speed steps. At each speed step it measures the pressure drop inside of the slit capillary, to calculate the shear stress, and than uses the output information from the balance to calculate the shear rate. From this measurement data the compound viscosity at different shear rates is calculated (Figure 8).

Slit Capillary Die - Calculations for Newtonian liquids:

Pressure Gradient: $p' = \frac{dp}{dl}$

Shear Rate: $\dot{\gamma} = \frac{6 \bullet Q}{W \bullet H^2}$

Volume flow: $Q = \frac{V}{t}$

Viscosity: $\eta = \frac{\tau}{\dot{\gamma}}$

Shear stress: $\tau = \frac{H}{2} \bullet p'$

Assumptions:
- Laminar, stationary and isothermal flow
- Wall sticking

Fig. 8: Viscosity calculation for 3 different rubber formulations.

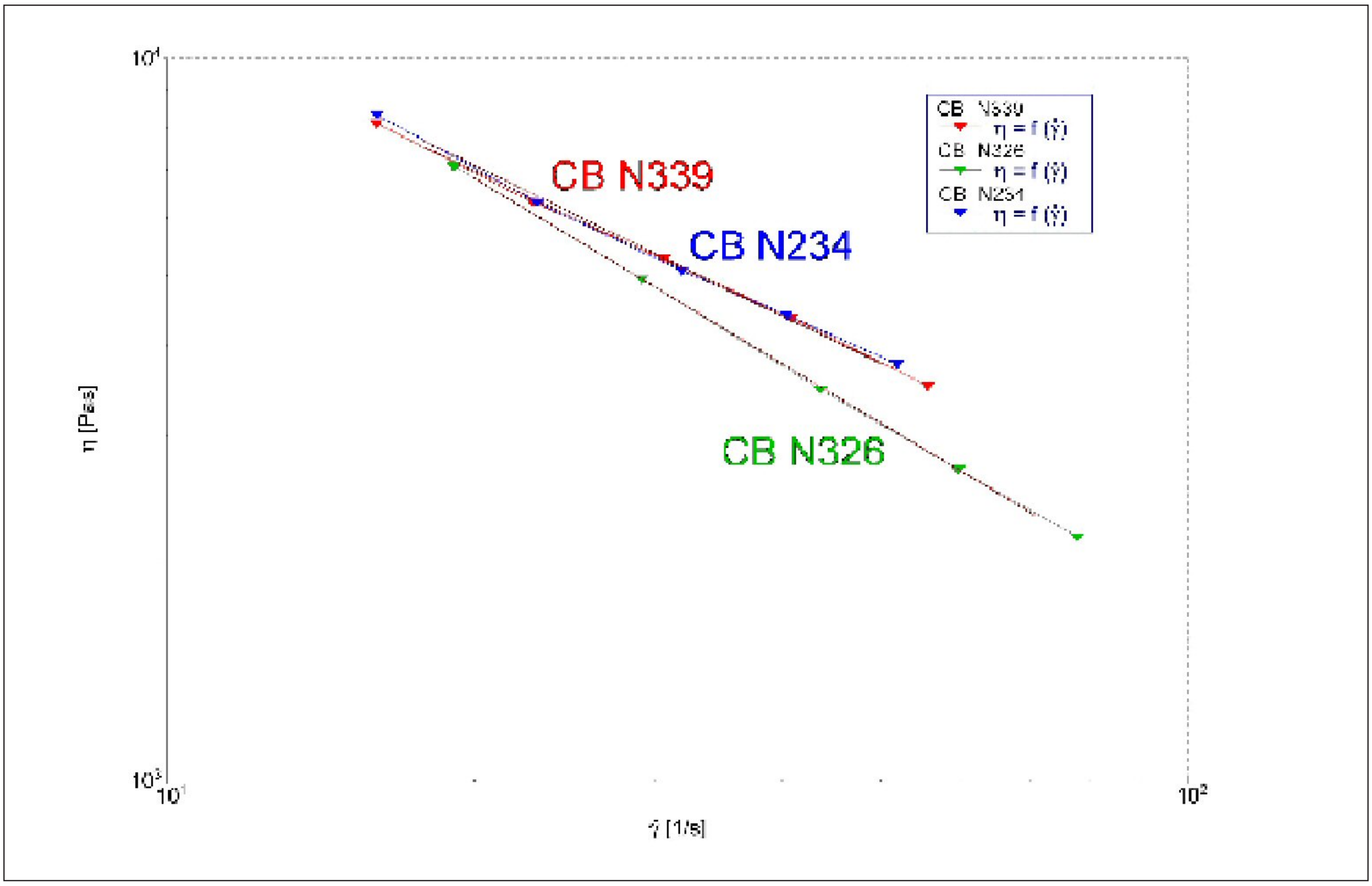


Fig. 9: The result of the viscosity measurements.

Again the significant influence of the type of the carbon black can be seen. The compounds with increased-structure carbon black (CB N339, CB N234) show a higher viscosity and a lower shear thinning effect. The rubber compound with low-structure carbon black (CB N326) shows a much lower viscosity, especially at higher shear rates.

Conclusion

The increasing demand for fuel-efficient tires at an affordable price increases the need for meaningful, accurate and simple test methods to develop and determine processability of new rubber compounds.

This application note shows how the HAAKE PolyLab OS torque rheometer system can be practically used to solve the above mentioned challenges. Three different test methods can be performed with one measuring system, and changeover time from one test to another is minimized due to the modular nature of the HAAKE PolyLab system. This time efficient workflow allows a high number of experiments to be performed in a short amount of time.

Linking test results and the real world production process is vital to success. As a scaled down production system, the HAAKE PolyLab OS system can achieve meaningful processing parameters on a laboratory laboratory scale that relate to the full scale manufacturing experience. The HAAKE PolyLab OS rheometer platform makes it possible to formulate compounds, produce test specimens, and characterize samples for processability all with one system.

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LR-82 0318

APPLICATION NOTE

No. LR-21

Testing the flow behavior of ceramic injection molding compounds

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Introduction

Powder injection molding (PIM), comprising metal injection molding (MIM) and ceramic injection molding (CIM), is an advanced manufacturing technology for complex, high-volume precision components. An example is the automobile industry's current evaluation of ceramic turbine blades with respect to engine heat for the development of more fuel-efficient automobiles.

CIM feedstocks are compounds of ceramic powder and a polymeric binder. In addition to the polymeric filler, molecular weight and the molecular weight distribution also influence the flow characteristics of the final feedstock. To achieve high-precision end products, manufacturers using PIM must determine the material characteristics of CIM feedstocks prior to processing.

Problem statement

A melt flow index (MFI) tester and a mixer sensor were used to characterize two different CIM feedstocks. Although this characterization showed no differences between the two batches, final parts made from these two feedstocks showed significant differences in mechanical properties. Obviously, there were differences between the two feedstocks.

The goal of this subsequent test was to differentiate between the two CIM compound samples using a torque rheometer with appropriate hardware and software accessories. The extruder capillary rheometer tests provide flow curves which can be examined to see what is different between the two samples.

Test equipment

Thermo Scientific™ HAAKE™ PolyLab™ OS Torque Rheometer system including:

- Thermo Scientific™ RheoDrive™ Software with Thermo Scientific™ Rheomex Single Screw Extruder 19/25
- Extruder screw with a compression ratio of 2:1
- Rod capillary die with a diameter of d=1.50 mm and length of l=30 mm
- Thermo Scientific™ PolySoft Capillary Rheology Software
- Circulator SC150-A10 to control temperature in feed zone of the extruder

The capillary rheometer is uniquely suited for the measurement of shear viscosity at process-relevant shear rates. The HAAKE PolyLab OS System can measure rheological characteristics under actual process conditions when used in conjunction with an extruder sensor and appropriate rheological capillary die. In addition, the PolySoft OS Capillary Rheometry software enables the process by helping users to pre-define test procedures, running measurements automatically, performing necessary corrections and allowing regression analysis for modeling of flow channels and molds.

Test conditions

Extruder temperatures:

- Feed zone: 20 °C
- 1st zone: 95 °C
- 2nd zone: 110 °C
- 3rd zone: 135 °C

Die temperature: 135 °C

Test method

To characterize the flow behavior of each CIM feedstock, a sample from each batch was plasticized in the extruder. Then it was transported to the die and pressed through the capillary. Different shear-rates were obtained by setting different extruder screw speeds.

The melt pressure in front of the capillary was measured using the pressure transducer. The connected balance automatically measured the corresponding melt output. After reaching constant pressure and melt throughput values, the data was recorded for calculation of rheological values. The software automatically triggered the subsequent drive speed that was set. Shear rate and viscosity were calculated from the measured data and displayed in a viscosity curve. The software automatically applied the necessary rheological corrections according to Bagley and Weissenberg/Rabinowitsch.

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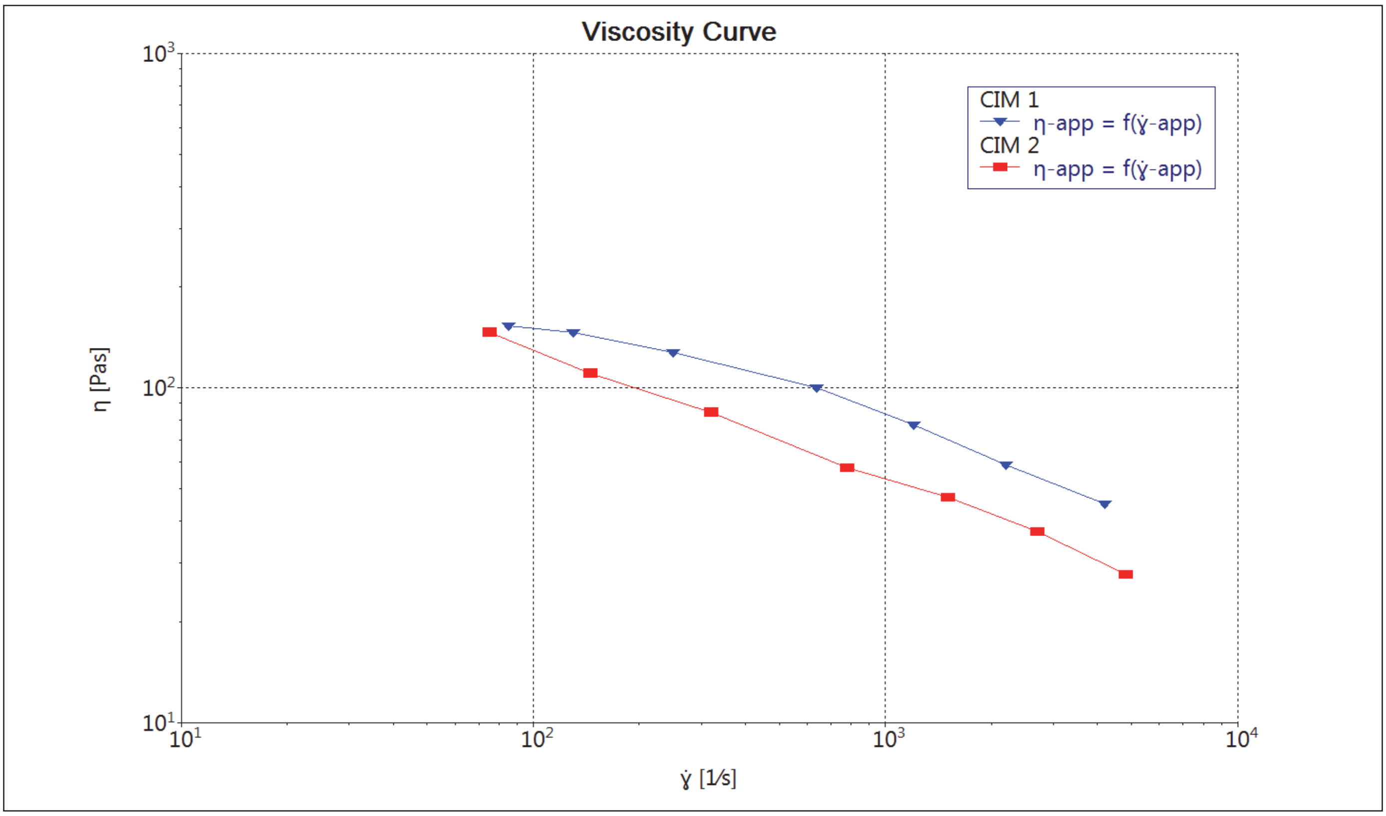

Graph 1: Viscosity curve of two different CIM feedstocks (CIM1 and CIM2).

Test results

The viscosity curve (Graph 1) shows the viscosity measurements of both batches of CIM feedstock. The graph displays the shear stress τ and the viscosity η above the shear rate γ. The binder for the two thermoplastic ceramic feedstocks was based on a polyolefin, so the curves show a shear thinning typical for polymers, i.e., a decreasing of viscosity at an increasing shear rate. Feedstock 2 (CIM2) exhibited more shear thinning than feedstock 1 (CIM1). The measured values are very similar at shear rates < 100 sec^{-1}, but they differ at higher shear rates. The viscosity value at 1000 sec^{-1} for feedstock 1, for example, is 42% higher than for feedstock 2.

Conclusion

The viscosity measurements explain why both feedstocks couldn't be differentiated with an MFI tester and a mixer sensor. Shear rates for that testing setup are normally below 100 sec^{-1} where both feedstocks looked similar. The extruder capillary rheology test allowed measurement at higher shear rates, so it was more comparable to what actually occurred in the extrusion process or during injection molding. The results show that feedstock 1 could exhibit problems and not fill the mold completely, or feedstock 2 (with too low viscosity) may not achieve the necessary form stability.

The extruder capillary rheology system delivered the right data needed to properly assess material properties for manufacturing complex high-volume precision components.

Summary

The HAAKE PolyLab OS system equipped with a capillary rheology measuring set-up provided fast, reliable testing for the flow properties of ceramic feedstock under conditions similar to those in manufacturing. Important material characteristics could be seen, which were not visible with simple MFI testing. That means the HAAKE PolyLab OS system can save time in manufacturing and ensure quality by establishing an automated, standardized test routine. The PolySoft Capillary Rheology Software can be tailored to run a test program suited for many different applications.

Find out more at thermofisher.com/extruders

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LR-21 0918

APPLICATION NOTE

No. LR-67

Innovative die design for a rapid rheological characterization of polymers

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Knowing the rheological properties of polymers in shear as well as in extensional flow are essential for their processing. However, their complete characterization in the laboratory requires the complementary use of sophisticated techniques which are time consuming and need great expertise. Therefore, quality control is mainly limited to the measurement of a melt flow index (MFI), a shear viscosity, and eventually a melt strength test to assess extensional properties. The on-line monitoring of material parameters would be very helpful but today is mostly restricted, whenever performed, to MFI or a capillary shear viscosity measurement.

The Thermo Scientific™ HAAKE™ X-die has been developed to cover the need for a quick characterization in shear and extension, with little or even no operator intervention. It can be mounted on a traditional torque rheometer or directly on-line with a melt pump feeding it. Data is obtained by this die with two batches of a standard PP (Polypropylen) with the same MFI but different performance in production by foaming the polymer. Oscillation tests with a rheometer correlate with this approach.

Industrial processes involving non-trivial polymer melt flows, such as injection moulding, extrusion, melt spinning and film blowing, a polymer melt is subjected to extensional deformation. This deformation makes predicting the polymer melt behavior difficult, potentially impacting the quality of the end product. The need for a fast and easy measurement of the extensional viscosity is therefore obvious. This die can be used off-line or on-line for process control determination of shear and extensional viscosity.

Experimental

Material

All measurements in this study were done with a done with two batches of commercial available PP. All experiments were conducted at 230 °C.

Methods

The measurements performed with the Thermo Scientific HAAKE X-die mounted on a Thermo Scientific™ HAAKE™ PolyLab™ OS torque rheometer with melt pump. For the oscillations tests a Thermo Scientific™ HAAKE™ RheoStress™ 6000 rheometer with 20 mm parallel plates was used.

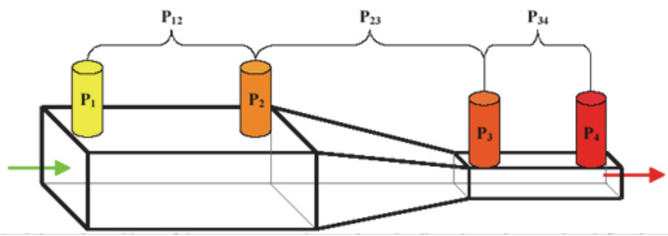

Figure 1: Superimposed test results for two TPU samples.

The HAAKE X-die consists of two slit dies linked by a defined contraction wedge, equipped with four pressure transducers located at the entrance and exit of each of the two slit dies sections (Fig. 1). The exact geometry of each part is defined so that the lubrication hypothesis can be applied (width at least ten times larger than the thickness). The contraction length and ratio have been chosen to enhance the extension and to minimize possible flow re-circulation. The two slit die geometries are such that the L/D ratio of both is the same. The change in cross-section results in a shear rate ratio of 1:64, and thus, in an expanded shear rate range.

The four pressure transducers (P1, P2, P3, P4) measure the pressure drop along the die. The volume flow is defined by the piston speed of the capillary rheometer or the r.p.m. of the melt pump when the die is mounted onto an extruder or by-pass rheometer. In the two slit sections of the die, the shear viscosity and the respective flow rates can be calculated using the well-known standard equations. With these two points of a flow curve, the power law coefficient **n** can be estimated for each flow rate. The calculation of the extensional viscosity is then performed in three steps:

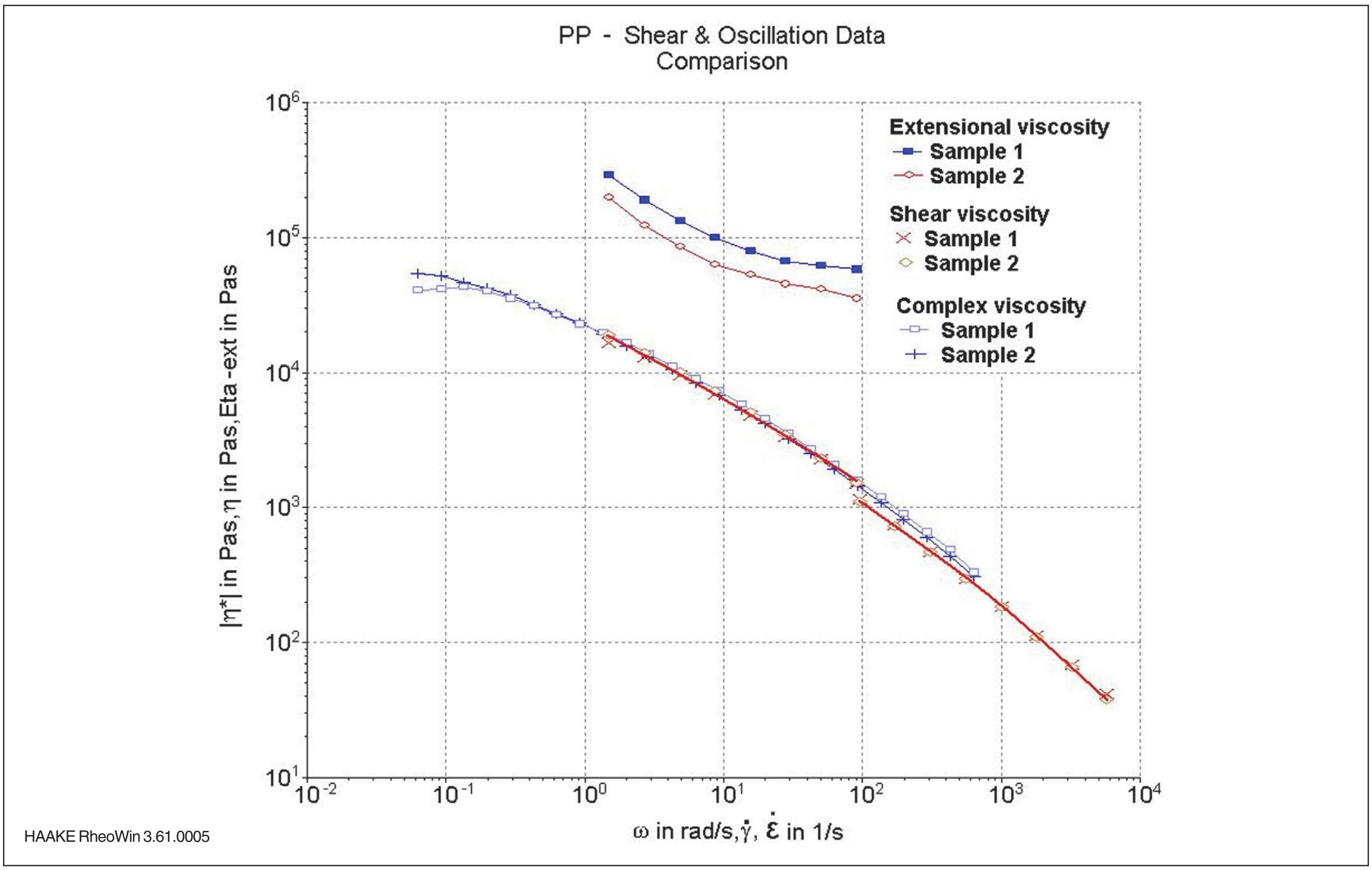

Figure 2: Viscosity data in shear, elongation and oscillation.

1. The pressure drop along the wedge is determined from measured pressures P2 and P3 extrapolated to the exact entrance and exit of the wedge.
2. The calculation of the viscous pressure drop in the wedge due to shear flow is based on the standard equations using known geometrical parameters and the estimated power law coefficient n.
3. The difference between the total and viscous pressure drop is the pressure drop due to non-shear or extensional component. From this difference and a mean extensional rate in the wedge, the extensional viscosity is calculated.

Results and discussion

Fig. 2 shows the results obtained done with the HAAKE X-die compared with the oscillation test with the HAAKE RheoStress 6000 rotational rheometer. With the HAAKE X-die a shear rate range from 10 to 10^4 s^{-1} can be covered, the complex viscosity data is identical and extend the shear rate range to 10^{-1} s^{-1}. The shear and complex viscosity data for both samples is identical. Only the extensional viscosity data shows a difference between the two samples and correlate with the performance in the foaming process.

Torque rheometer testing is similar to production conditions showing differences between the batches. Different samples can be tested in a reasonable time by purging. After the first encouraging results with a new type of extensional die presented earlier [1], this paper presents a comparison of batches to determine the extensional viscosity. For statistical control, further experiments have to be done with other types of polymers - however the results are a promising step towards the standard use of extensional data in polymer processing especially for on-line applications.

Reference

[1] G. Chaidron, J. Bouton, Study of extension and shear viscosities of polymer melts combining a specific contraction flow and an analytic numerical simulation, Proceedings of the 18th Processing Society, Guimarães, Portugal, 2002

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LR-67 1218 (v.1.1)

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