Application Note
LR-29

How to Relate Test Results of a Torque Rheometer to Problems in Elastomer Processing

Matthias Jährling, Thermo Fisher Scientific, Process Instruments, Karlsruhe, Germany

High quality standards of elastomers, elastomer compounds and their final products have to be realized at the lowest possible price, because the competitive situation and the requirements have increased extremely during the past eight to ten years. This leads to the necessity of optimizing the development process from the compound design to the presentation of the new product.
All activities surrounding compounding (design, mixing and extrusion) are very costly and time-consuming.

E.g. "How often do you have to run a compound on a production scale machine until it suits your specifications and processing capabilities?"

As a result, more and more manufacturers have started to bring compound-development and –processing closer together and are actively looking for methods of linking laboratory-scaled test results with production experience.
To meet these requirements test methods and development tools have to be meaningful and process-related. The documentation of test results and a comparison to accepted standards and tolerance levels is a must in order to meet the requirements stipulated by different quality standards like e.g. SPC, ISO 9000 ...
In the following technical report an overview of different test methods gives you an idea how torque rheometer test results can solve your production problems.

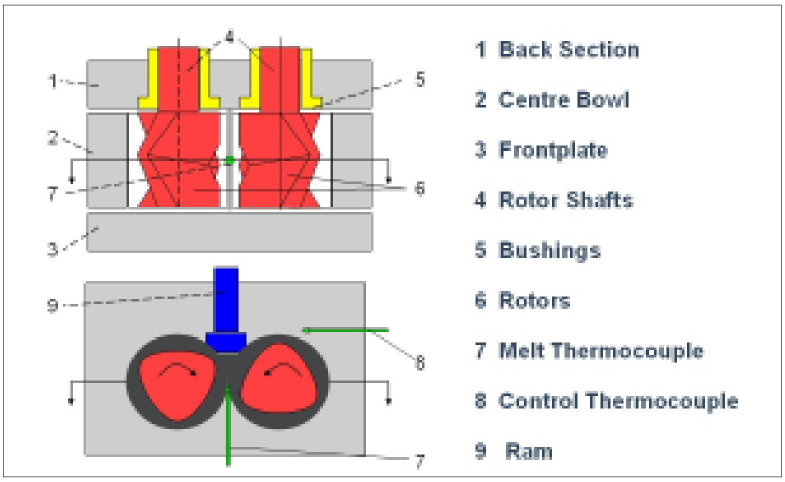

Fig.1: Principle sketch of an internal mixer

Laboratory-scaled internal mixers

Torque rheometers such as the Thermo Scientific HAAKE PolyLab System, equipped with laboratory-scaled internal mixers, have been in use in rubber industry for many decades with great success. They treat small rubber samples in a way similar to the mixing conditions encountered in internal production mixers. They allow the grading of polymers with respect to their behaviour during mastication and how compound ingredients change viscosity. Compounds with curing agents are tested for minimum viscosity, the onset of scorching and for the rate of cure.

The computerization of these instruments allows on one hand the developer to do detailed evaluations on the basis of the measuring results, on the other hand a fast batch control with easy-to-use evaluation and compare-routines.

Process simulation

Mastication is an important step in the mixing process. Rubber polymers such as NR require mastication to reduce their viscosity/elasticity and to even out variations between different polymer lots. This process can be simulated by torque rheometer tests.
These tests allow the assessment of the initial flow properties of the sample: the torque peak caused by the high resistance of polymer being sheared while still cold. Then one can evaluate the process of mastication.
Figure 2 combines two mastication test runs for an easy comparison:

a.) Mastication of a natural rubber ("NR") just under the influence of shear and temperature;
b.) Mastication as above but with the additional influence of a chemical additive called "Renacit 7" added to the polymer at a level of 0.5 %. This accelerates the breakdown of the molecular structure and greatly reduces the mixing energy.

The advantage of this test procedure can be easily seen.
The compound designer can determine the influence of different additives on the compound by using a small sample volume; the process engineer can optimize the mastication process with respect to the mixing energy and parameters. The biggest advantage attainable as an result of the above test procedure is extensive cost saving by reducing tests on productionscaled machines.

Batch differentiation

Rubber polymers are distinctly "non-Newtonian liquids" (i.e. liquids whose viscosity is strongly dependent on the shear rate). If polymers only differ e.g. by their molecular weight, they will still have equal viscosity levels at high shear. Differences between these polymers are shown more clearly at lower shear rates or rotor speeds.

Figure 3 illustrates the mastication of three NR-samples which originated from three different countries. At 70 rpm the curves of all three samples are too close to each other, thus preventing a differentiation. The torque rheometer can be programmed to reduce the rotor speed automatically after a certain time down to 5 rpm. At the end of this test after a total of fourteen minutes the three samples can be easily differentiated.

Flow-curing behavior

Rubber compounds containing all curing agents such as sulphur and accelerators vulcanize of course at a higher temperature. This vulcanization process can be monitored at best at its onset. It is of interest for the rubber technologist to determine how long a particular compound can still be mixed, extruded or injection-moulded at a given temperature and how fast viscosity will change once vulcanization has started. Figure 4 shows the original torque and stock temperature of a flow-curing test of an ethylene-propylene rubber compound (EPTYPE_A) and the corresponding evaluation of the test data.

This graph illustrates:

- The Loading Peak (L)
- The minimum torque (M), i.e. the viscosity before the onset of cure
- The time required (scorch time) to reach a torque limit expressed as a variable percentage higher than the minimum viscosity, e.g. 15 %
- The time required to reach a second torque limit of well advanced "cure" which may be perhaps 50 % higher than the minimum viscosity.
- The ratio of these two torque limits defines the rate of vulcanization.

A second ethylene-propylene rubber, yielding the same MOONEY-viscosity (EPTYPE_B), was tested under the same test conditions. The manufacturer of these two EP-compounds assumed that both would have the same flow properties. However, when the elastomers were processed, differences contradicting the results of the MOONEY test were observed.

The comparison of the two compounds is portrayed in Figure 5.

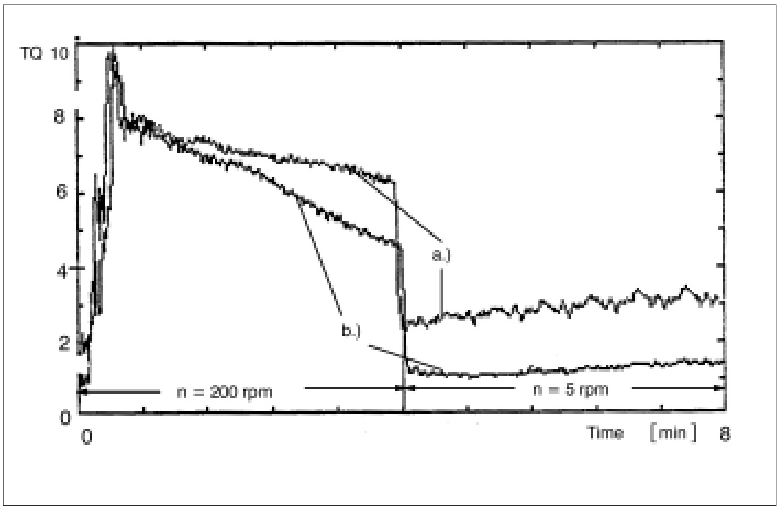

Fig. 2: Mastication test of a NR with and without "Renazit"

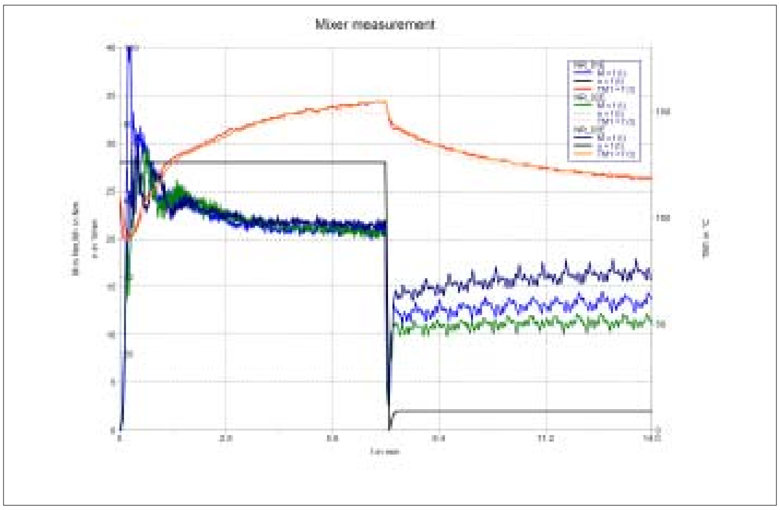

Fig. 3: Differentiation of 3 NR-polymers

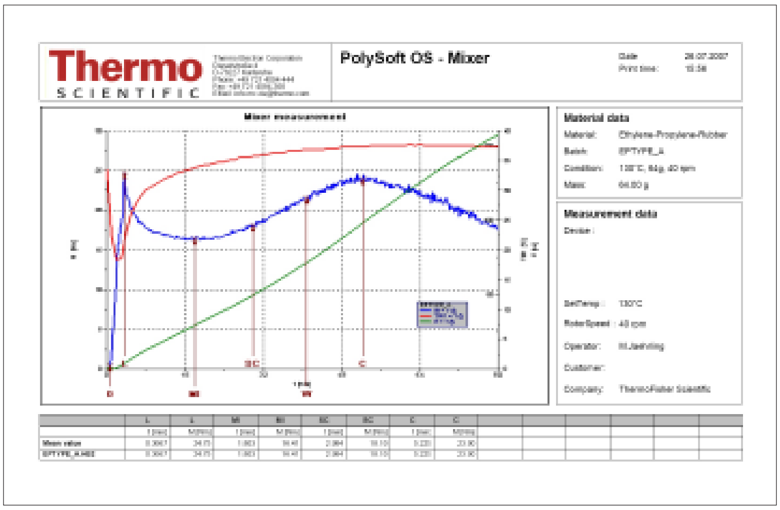

Fig. 4. Flow-curing behaviour of an EP-compound

During the mixer test the sample is sheared like in the production process. Because of this, the mixer test shows differences which couldn't be seen with the MOONEY rest.
The compound EPTYPE_A shows a lower torque level than sample EPTYPE_B. It therefore flows more easily, thus resulting in better processing properties. Additionally the time for cure is shorter.

Laboratory-scaled extruders

To widen the variety of process-relevant test methods for rubber applications, laboratory-scaled rubber extruders (with roll feeders) are available for torque rheometers. These measuring extruders are specially designed to simulate extrusion processes and simultaneously to control and evaluate the process parameters.

The measuring extruders can easily be equipped with a large number of dies which, according their geometry are suitable for a variety of applications.
Three different methods are presented below, which may be helpful in solving problems in the processing of un-vulcanized rubber.

1. Automatic extrusion-capillary measurement
Capillary measurements show their advantage where information about the flow behaviour of an un-vulcanized compound is required as an absolute value.
Injection moulding processes (e.g. for seals and O-rings) can be mentioned as an application, where rheological factors influence the success of the process to a great extent. Due to the narrow clearances and high rubber compound melt flow rate, extremely high shear rates can occur in the injection channels.
On the other hand, the final filling of the mould is slow and the applied shear is low.
As a rule, rubber compounds exhibit pseudo-plastic flow behaviour. As cited in the example above, various shear stresses are exerted on a rubber compound during processing. Because the viscosity is highly dependent on the shear rates, it is imperative that the viscosity be characterized as a function of the relevant shear rates.
The processing engineer’s main goal is the determination of these relationships for the injection moulding process.

Figure 6 shows the results of extrusion-capillary tests on two different rubber compounds.
In the case of extrusion capillary measurements the compound is forced through a slit capillary and a rod capillary die. The slit capillary die covers a shear rate range that usually accurse in extrusion process. The material flow in the smaller rod capillary reaches much higher shear rates, which correlate more with the injection moulding process.
The rheological factors are calculated from the differential pressure and the volumetric flow rate. The great advantage of extrusion-capillary measurements is that the sample is made to flow under process conditions.

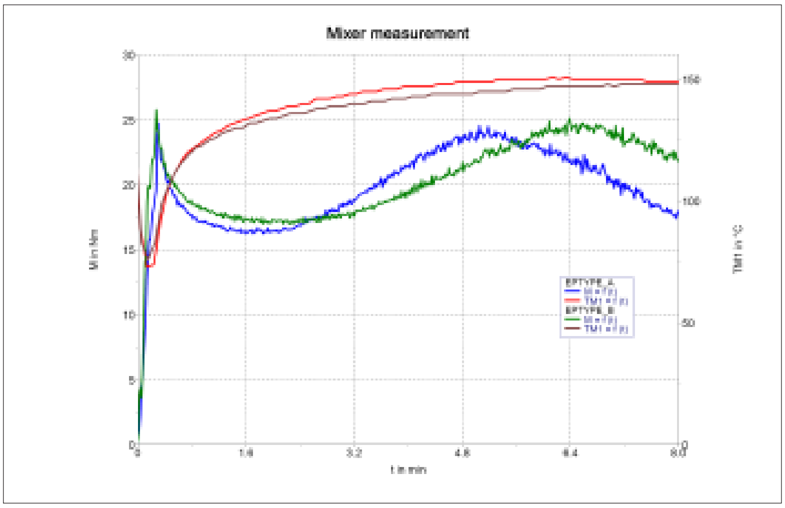

Fig. 5: Comparison of two EP-compounds, yielding the same MOONEY-viscosity

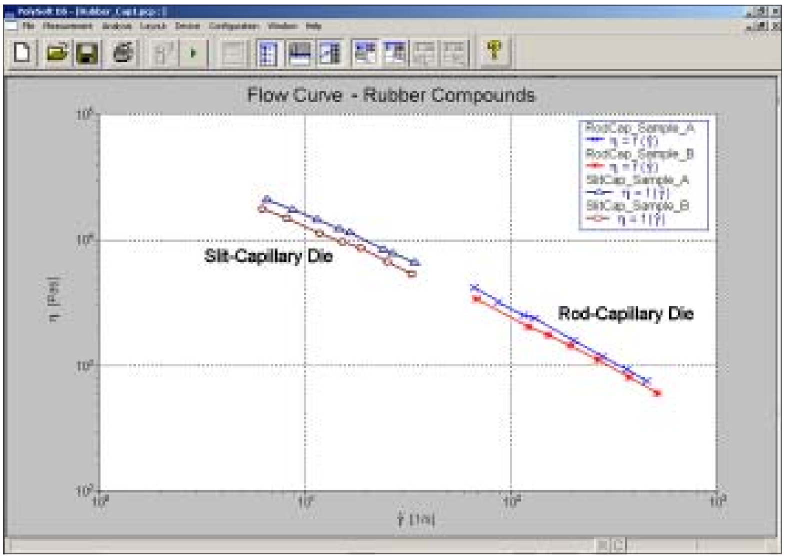

Fig. 6: Flow Curves Rubber

As this test can be run fully automatically, it is also suitable for fast and very accurate quality control differentiation of different batches.

2. Die swell behaviour
Apart from the viscosity, the elasticity of the polymer melt greatly influences the processing and the end product.
Tire components like tread profiles have to be extruded in very narrow tolerances. The success of this process depends on the evenness of the raw rubber polymer which is used for the compound. If this basic material dif-fers slightly in its elastic behaviour, the given tolerances for the end product, such uniformity, cannot be reached.
To ensure that your process does not run out of tolerance, the die-swell test can be a useful quality control instrument.

For this test, which can be directly linked to the above described capillary measurement, a laser sensor simultaneously measures the swell of the extruded strand. The viscosity and die-swell, which is a measure of the elasticity, is evaluated as a function of the applied shear rate (Figure 7).

The tests show very clearly, that the viscosity behaviour of both compounds show shear thinning and scarcely differ. On the other hand the elastic behaviour of both samples is extremely different. With this information, the processing of a compound can be easily optimized. Time- and money-consuming empirical tests for e.g. designing a new die on production-scaled machines can be minimized.

3. Qualitative testing

Extreme shapes like a tire tread with wings, a sidewall or an apex are very common in tire manufacturing. They require a great deal of experience in die-design and rubber extrusion to attain acceptable surfaces, sharp edges and equal dimensions for these complicated end products.

The Garvey test described in ASTM 2230 is an approved method which offers an easy alternative to test the extrudability of compounds according to the above mentioned parameters. For the Garvey test the measuring extruder is equipped with a standardized die, the shape of which is a much scaled-down version of half of a tire tread (see Fig. 8).

Problems concerning the extrudability of a compound can be found out very easily, without carrying out expensive empirical tests on production-scaled machines.

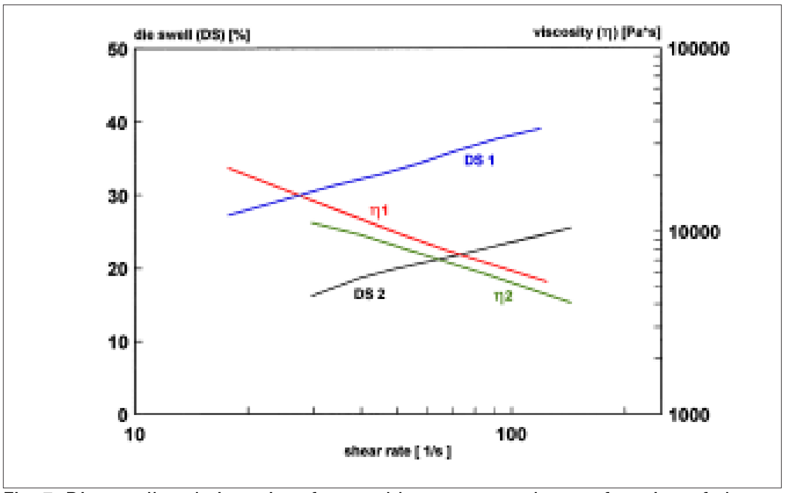

Fig. 7: Die-swell and viscosity of two rubber compounds as a function of shear rate

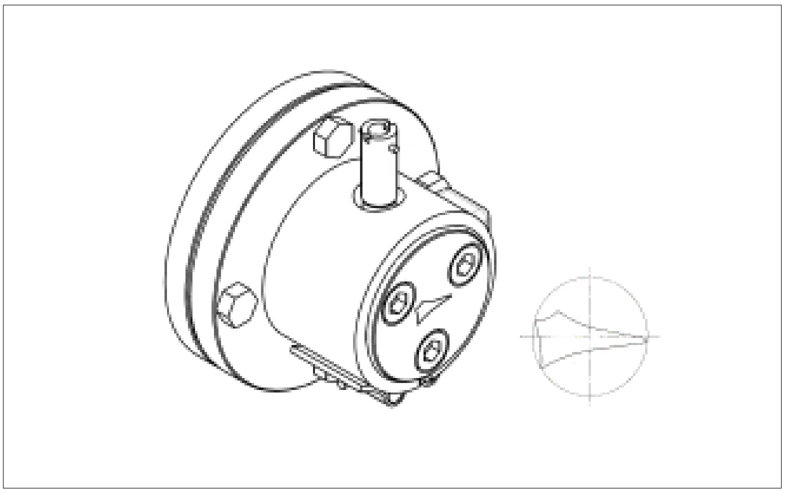
Fig. 8: Garvey Die and Cross Section


Fig. 9: Test result from a Garvey test with two rubber compounds

Conclusion

The increasing demand for high quality products at a low price level increases the need for meaningful, accurate and simple test methods as a development and quality control instrument. The importance of a linkage between the test results and the process experience is vital.

Based on practical test results, this report offers some different alternatives on how torque rheometers like the Thermo Scientific HAAKE PolyLab System can be practically used to solve the above mentioned problem.

The on-going computerization, easy-to-handle software and routine evaluation systems have established these systems more and more in routine use.

The great advantage of reducing time- and money-consuming empirical tests in the production plant can no longer be neglected.

Process Instruments

International/Germany
Dieselstr. 4,
76227 Karlsruhe
Tel. +49(0)721 40 94-444
info.mc.de@thermofisher.com

Benelux
Tel. +31 (0) 76 5 87 98 88
info.mc.nl@thermofisher.com

China
Tel. +86 (21) 68 65 45 88
info.mc.china@thermofisher.com

France
Tel. +33 (0) 1 60 92 48 00
info.mc.fr@thermofisher.com

India
Tel. +91 (22) 27 78 11 06
info.mc.in@thermofisher.com

United Kingdom
Tel. +44 (0) 1785 81 36 48
info.mc.uk@thermofisher.com

USA
Tel. 603 436 9444
info.mc.us@thermofisher.com

www.thermo.com/mc

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