Benchmark Tests for RheoPower Software Package

Synopsis

The assurance and capability of RheoPower software package [1] is evaluated by Benchmark testing. The aim of this report is to present illustratively strengths and limits of the software obtain molecular weight distribution (MWD) from viscoelastic data.

Introduction

The recent developments in rheology modeling, computer capacity, software programming tools and intent to solve ill-posed problems of the field can now offer robust software package to make polymer analyses and simulations.

Software customers have already carried years of field, laboratory and black-box tests with true data. No doubt RheoPower has assurance to model viscoelasticity: It has performed powerful public presentation with narrow MWD's, modeling viscosity flow curve and relaxation spectrum [2].

Problems are the reliability of polyolefin MWD measured by "wet methods" and the influence of other external errors. Here is carried out the first analytical step by benchmark testing with wide MWD's.

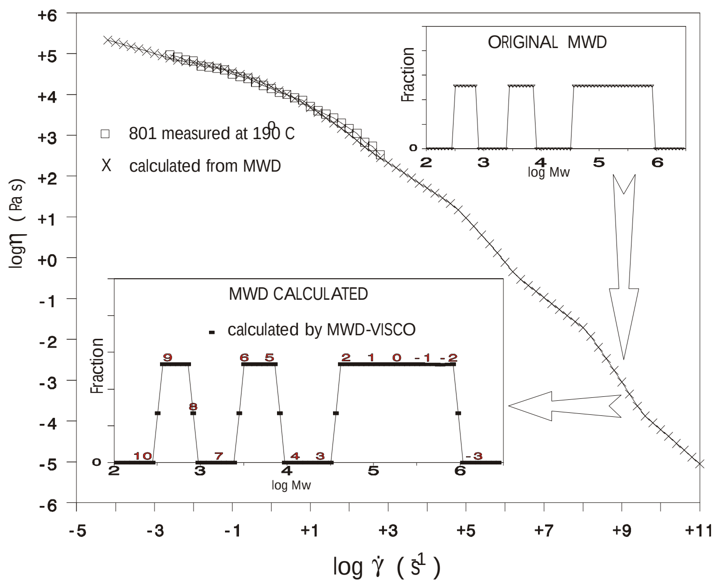

Figure 1. The test principle presented by two-box test at the software level of year 1995. The viscosity curve was generated by the RheoDeveloper (MWD-VIS) software starting from the data marked Orig. MWD. Using the generated viscosity curve the MWD results shown here were computed back by RheoAnalyzer (VIS-MWD).

Benchmark Testing

Benchmark testing examines the performance of the system, which cannot be affected by variables resulting from human involvement. One carrying aspect of the shown procedures is repeatability of test results by RheoPower version 2.04 or later.

Short Theory

The solutions of problem of field lead integral equations, where computation of MWD is known ill-posed problem. There is normally needed priori information of true results to get any solutions.

The new method [3-4] gives an accurate piece of MWD curve of respective viscosity data range. The computation of MWD's both sides at out of measured data range may have still some uncertain solutions coming from general inverse problems.

Generating of Data

In RheoDeveloper (MWD-VIS) software is drawn MWD, from which is generated complex viscosity flow curve $\eta*(\omega)$. Viscosity data η is copied on databases or an ASCII file.

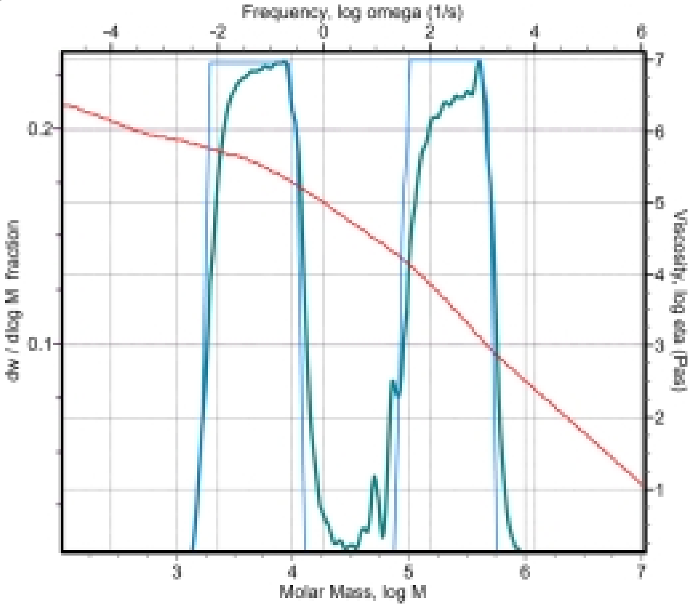

Figure 2. The two-box test in the year 2001. Optimization for true data generates some distortions.

Setting of RheoAnalyzer

All settings are default after starting to run RheoAnalyzer. The data range in use is limited according testing procedure. All presented frequencies are in logarithm scale. Every test run was started by importing over again data to eliminate influences of earlier computations. The follow presets are in use:

Go mode level: 5
Smoothing level: 5 (50%)

If there is given priori information and only in the case there are used parameters for respective values:

Regularization level of Mw: 5 (50%)
Regularization level of MwR: 5 (50%)
Regularization level of η_o: 5 (50%)

Possible exceptions are told in the text.

Linearity of the Model and Software

To simulate transformations from the MWD to the viscosity flow curve and vice versa the two-box test suggested by Malkin [5] is used. At first two cubic boxes were drawn by the RheoDeveloper (MWD-VIS) software simulating bimodal MWD's. The generated viscosity curve was used for RheoAnalyzer (VIS-MWD) software. The result level achieved in 1995 can be seen in **Fig. 1.** Unfortunately this very linear relation was very sensitive to the noise and errors.

The recent results in 2001 can be seen in **Fig. 2** MWD–η–MWD made by version 2.0. We can attain some distortions of MWD boxes generated from optimising procedures of true data, but still the procedure is rather linear.

Wide data range

The used η viscosity flow data range is –2.8<ω<+2.8 in logarithm scale or in respective decades 5.6. The results of RheoAnalyzer can be seen in **Fig 3**. This type data can be generated by master curve measured at different temperatures.

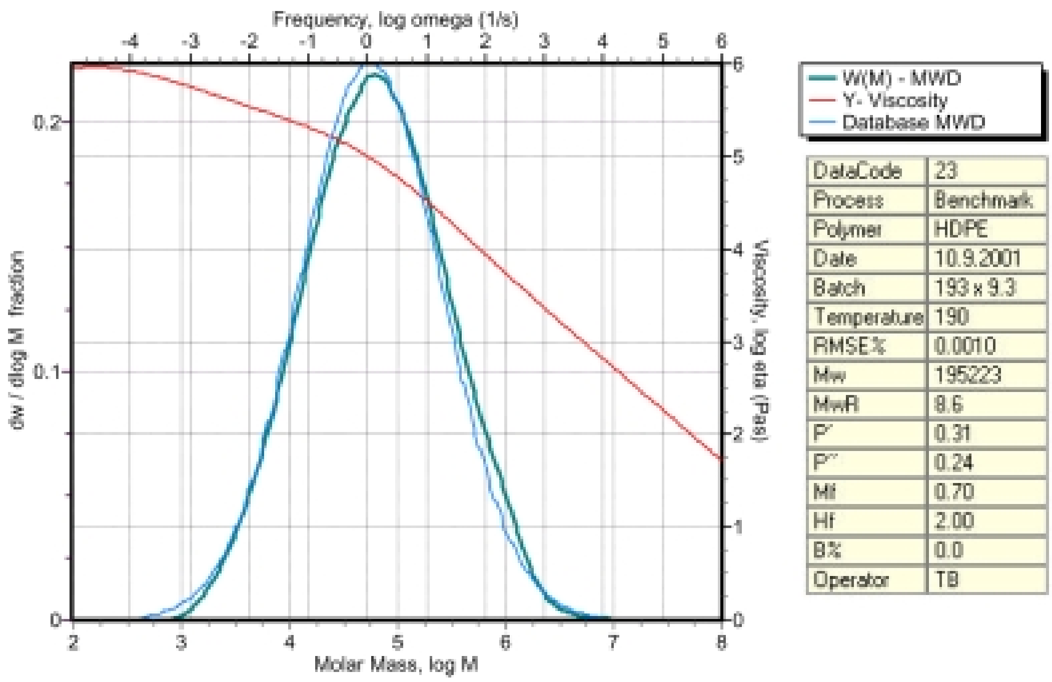

Figure 3. MWD of wide 5.6 data range. Blue thin is original source MWD used in RheoDeveloper (MWD-VIS) to get viscosity and thicker green MWD is recomputed backwards.

The error between generated or "measured" and modelled viscosity is in range RMSE%=0.0010 as it is normally with other models in range RMSE%=0.6. Also source and modelled MWD's are very close each other.

Data ranges with priori information of Mw and MwR

Normally can be measured dynamic properties at one temperature at three rate decades or for example in frequencies 0.01/s<ω<1/s in logarithm scale –2<ω<+1. In the notation **of Fig 4** has written used logarithm rate ranges for viscosity data.

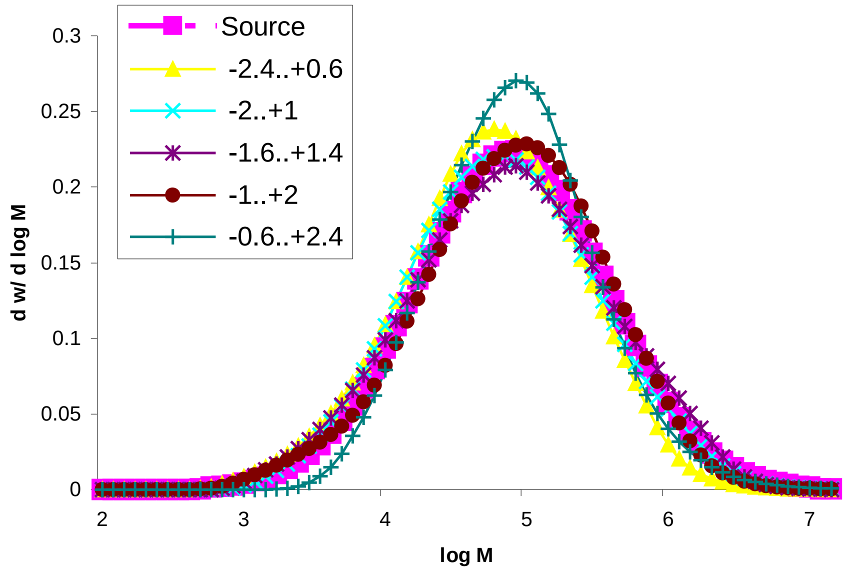

Figure 4. MWD computed from 3.0 decades of data range. Find, all other results are in line except MWD from range frequencies –0.6<ω<+2.4 in logarithm scale.

Data with priori information of η_o

Constant three decades of frequencies –1<ω<+2 in logarithm scale has been used. In the notation **of Fig 5** has written used viscosity data ranges and other priori information if used with zero shear rate η_o information.

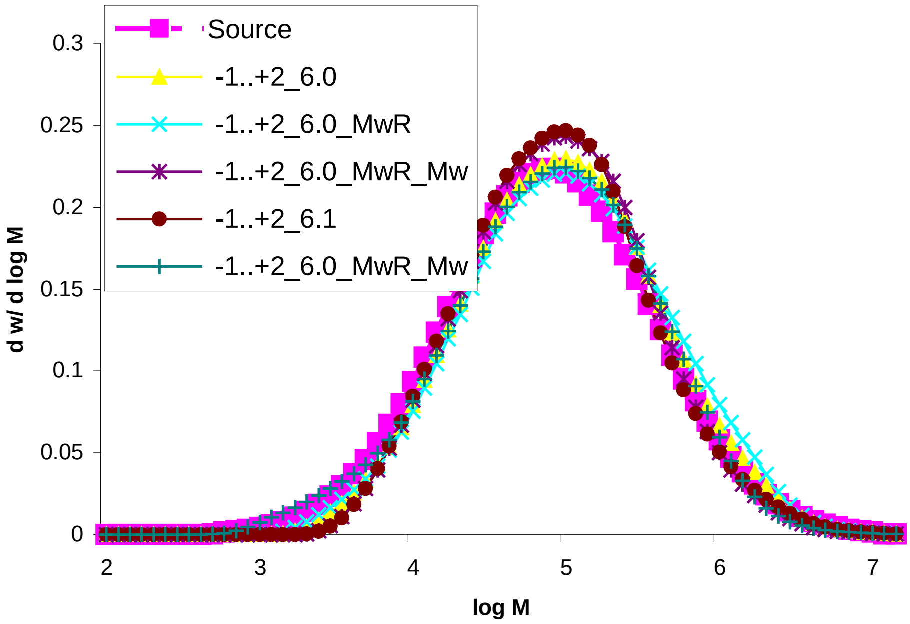

Figure 5. MWD computed from constant 3.0 decades of data range and zero shear rate η_o is used as priori information. We find that zero viscosity is good priori information.

Data ranges without priori information

A variable range in three decades of frequencies in logarithm scale has been used. We did not get bad results during this type of benchmark testing shown in **Fig 6**, but with true data results can escape during computation without giving directions by priori information.

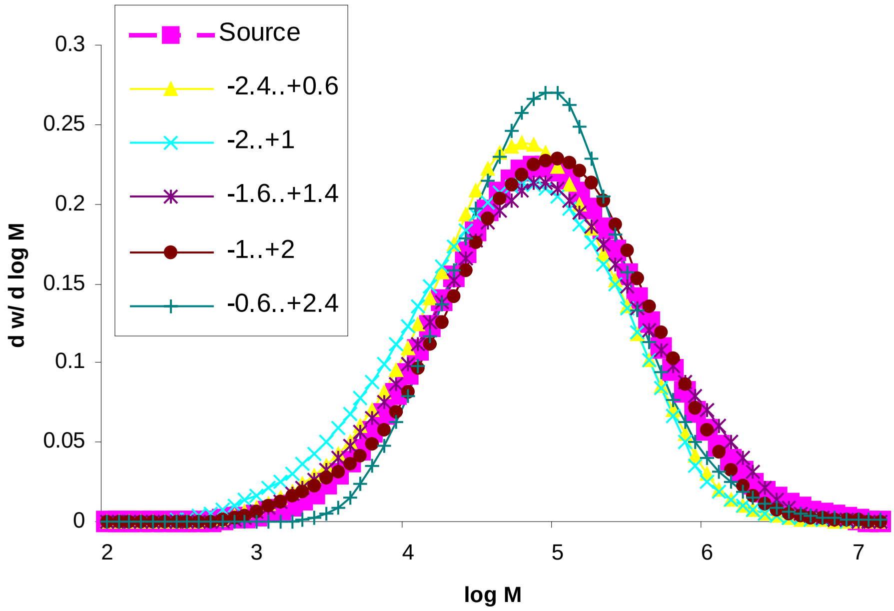

Figure 6. MWD computed from 3.0 decades of different data ranges without priori information. This time the results were rater stabile without escaping to the false results during long period computing.

Narrow data range with priori information of Mw, MwR and η_o

One-decade data with priori information of Mw, MwR and η_o may work. But in this case RheoDeveloper software is the better tool.

Mw	MwR
174355	9.06
175792	8.86
192836	10.52
121028	7.86
173869	5.51
189878	6.1
213098	7.26
230425	8.05
177329	5.63
179233	9.17
183134	6.7
195223	8.39
195374	8.92

Short Error Analyses

The error of average Mw with original source is -4.5% and polydispersity MwR error –15.6%. The major source for MWD errors is the cutting of MWD tails to simulate true procedures related to the other methods such as GPC and SEC.

The %RMSE was in the range 0.0010 in most computations. In table is shown Mw and MwR values.

With well-measured true data the error is many times less in the range RMSE%=0.0005, which is in close numerical round-off range. Benchmark test had twice as high error compared with the best true analysis. We first integrated with RheoDeveloper to develop the viscosity flow curve and another time during RheoAnalyzer procedure.

Conclusion

The wider is data range the better RheoPower works. Unfortunately is impossible to measure at such wide data ranges. Another route is to give some priori information. True zero shear viscosity turned to be good priori information. If there is available other similar constants, they are easily added to the analysing procedure.

References

[1] T. Borg, RheoPower software trial version, http://www.tomcoat.com
[2] T. Borg, 2nd Workshop on Inverse Problems in Rheology and Related Experimental Techniques, 9th - 11th May 2001, Black Forest, Germany.
[3] T. Borg, E. J. Pääkkönen, "Determining the Molecular Weight Distribution form Viscosity Measurements", (to be published, 2002).
[4] T. Borg, E. J. Pääkkönen, The general model of viscoelasticity and relaxation modulus of polymers", (to be published., 2002).
[5] Malkin A. Ya., Some inverse problems in rheology leading to integral equations, Rheol Acta **29** (1990) 512-518.