RHEOLOGY AS A QUALITY CONTROL INSTRUMENT

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ABSTRACT

Quality control in polymer production is a decisive success factor today, growing in importance with the steadily increasing demands regarding the performance of polymeric materials. Rheological methods are ideal for application in quality control, as they allow to draw conclusions regarding both molecular structure and processability from their results. This is especially true for the linear viscoelastic parameters of a polymer melt. Using several examples from industrial practice, the capacity of rheological measurements to clarify quality problems like degradation effects or non-homogeneity is demonstrated. The question of precision and reliability is finally addressed, based on the results of two round-robin tests.

INTRODUCTION

In the last few decades, rheology has attained a status in polymer research which makes it an indispensable tool in the development and production of polymer materials. Regardless of whether the problems in question con-

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cern the analysis and characterization of new or unknown materials, production or quality control or the design of molding processes [1], the determination of rheological parameters is a significant element.

With increasing demands regarding the processability of polymers on the one hand and new materials with often significantly different properties pushing into the market on the other hand, a quick and meaningful characterization of a polymeric material is often required. Rheological parameters can be used to simulate processing steps not only in injection molding [2], but also in single- and multilayer extrusion [3, 4], as well as other more complex technologies. Time-consuming and cost-intensive trials to find the ideal processing parameters can thereby be eliminated, or at least strongly reduced to a kind of final optimization.

Parameter Determination

Rheological parameters of polymers, i.e. the material functions describing the viscoelastic behavior in the molten or also in the solid state, have a central role in polymer research. They both reflect the molecular structure and determine the processing and application behavior (Figure 1). Traditionally, polymer
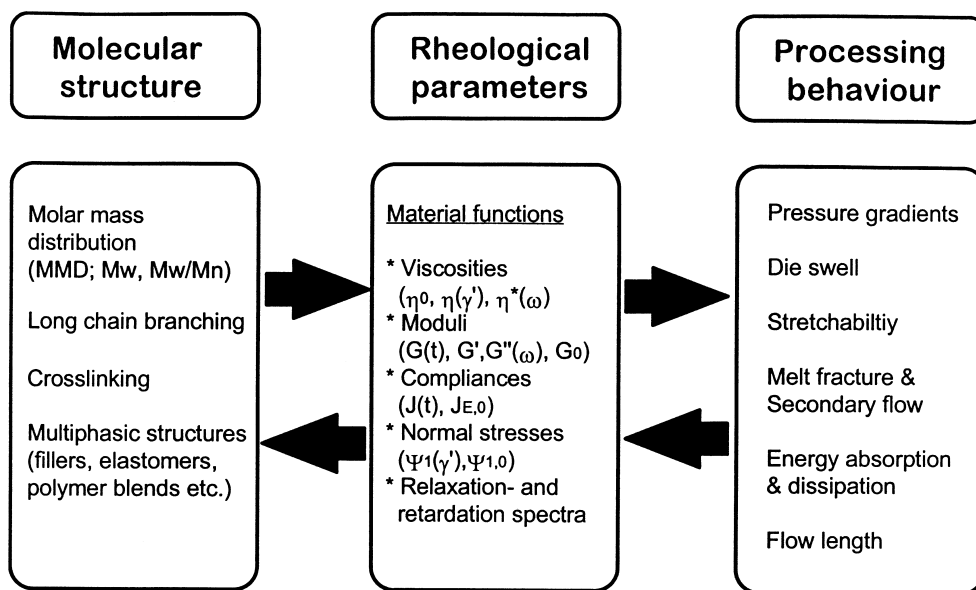

Figure 1. Rheological parameters acting as a "link" between molecular structure and final properties of a polymer.

melts were mainly investigated in capillary setups to determine flow or viscosity curves (viscosity η or stress σ as a function of shear rate γ′) for simple processing predictions. This technique, however, has several drawbacks ranging from material and time demand to the possibilities of data analysis. Therefore, the determination of the linear viscoelastic material behavior in the oscillatory test is preferred nowadays, yielding the storage and loss modulus of the material as a function of frequency (G′, G′′(ω)). The advantages of this method result from its relative simplicity as well as in the information content of the result, which separates viscous (G′′) and elastic (G′) components of the material behaviour. Moreover, the conversion to other linear viscoelastic parameters, as well as a connection to the molar mass distribution is possible via a spectral analysis of the data [5-7]. This way, also the material behavior under creep or relaxation conditions is accessible.

Quality Control

Several examples for the importance of rheology as a quality control tool can be given here. Common to all these is the fact that the problems adressed here, even if gathered for the case of polypropylene, may appear in everyday practice of polymer production for other polymers as well.

Generally, each quality problem has three aspects:
- Technical reason for the problem (e.g. temperature deviation in reactor, degradation problems in extrusion, ...)
- Molecular background of the problem (e.g. variation of the molar mass distribution, partial crosslinking and gel formation, ...)
- Consequences for product quality (e.g. reduced mechanical performance, increased yellowness index, ...)

As a consequence, detecting a quality problem in a measureable parameter (like a viscosity curve) as a result of a customer complaint is only the first step. The advantage rheology offers lies in the possibility to correlate such a change to the material structure and sometimes even to the underlying reason. The following examples should illustrate various possible problems and their detection with rheological means.

Degradation and Crosslinking Effects

The production of "Controlled Rheology" (CR)-PP, the peroxide-induced degradation of polypropylene (PP), is a widely applied technology for the adaption to specific applications. Especially the processability can be adjust-
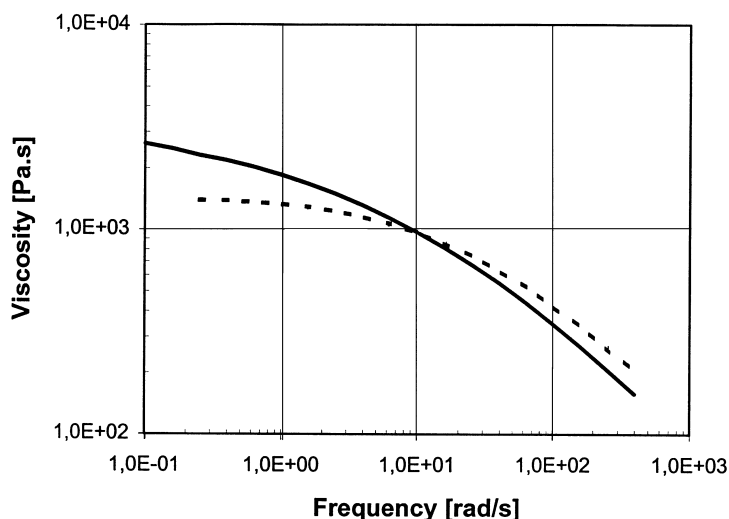
Figure 2. Effect of degradation on viscosity curve of PP homopolymers ($\eta^*(\omega)$ as calculated from plate/plate measurement at 230°C); both materials at MFR (230°C/2,16kg) of 8 g/10min, reactor grade (———) has a flexural modulus of 1600 MPa and CR-grade (- - - - , from MFR = 0.5) of 1200 MPa.

ed in this process, which results in an increase of the flowability with a parallel reduction of the width of the molar mass distribution (Figure 2). Apart from this degradation on purpose, however, PP is generally rather susceptible to chain scission resulting from radical generators in the environment like oxygen, chemicals or radiation. This inherent instability, which is in contrast to the behavior of other polyolefins, results from the chain structure with tertiary H-atoms at the base of each methyl side group.

With PP-impact-copolymers (HECO's), the situation is more complex - mechanics are mainly determined by their morphology (particle size and distribution). Through the different reaction of the matrix (PP) and the elastomer phase (EPR/PE) to radical reactions, the ratio between the molar mass of the matrix and the disperse phase will change, causing aggregation effects and loss in toughness

Both rheology and mechanics are affected in this process, pointing to the strong interaction between these two factors [8, 9]. Degradation reduces the polydispersity of the molar mass distribution (MMD) leading to a decrease in impact strength because of the reduced number of tie-molecules and in stiffness as well because of the reduced number of crystallization nuclei [10].
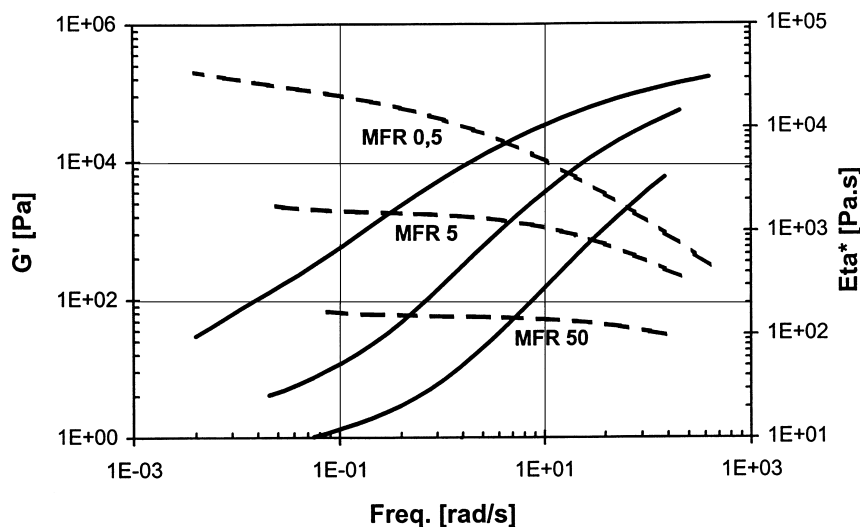
Figure 3. Evolution of rheological behavior in the degradation series of a heterophasic EP-copolymer (impact type); increase of elasticity at long relaxation times with increasing MFR.

[11]. This effect is strongly reflected in the rheology, where a secondary plateau in G' is developed at low frequencies reflecting a contribution of long relaxation times of the elastomer phase (Figure 3) [12]. This can even lead to a solid-like behavior of high-MFR grades at low shear stresses like in rotomolding.

As a second consequence, the mechanical and optical properties of the resulting material are strongly deteriorated by the bigger elastomer particles (Figure 4). This way, a degradation over two decades in the MFR leads to an impact strenght reduction by 85% for the heterophasic copolymer in Figures 3 and 4. With the same increase in flowability, a hompolymer only loses about 60% of its toughness.

Homogeneity of Bimodal Grades

One of the most important developments in the field of polymer design in recent years was the production of polymers with a bimodal MMD. Mainly produced by operating two polymerization reactors under different conditions in series, these materials consist of two "fractions" with average molar masses which differ significantly, i.e., by at least one decade. As a result of this MMD,
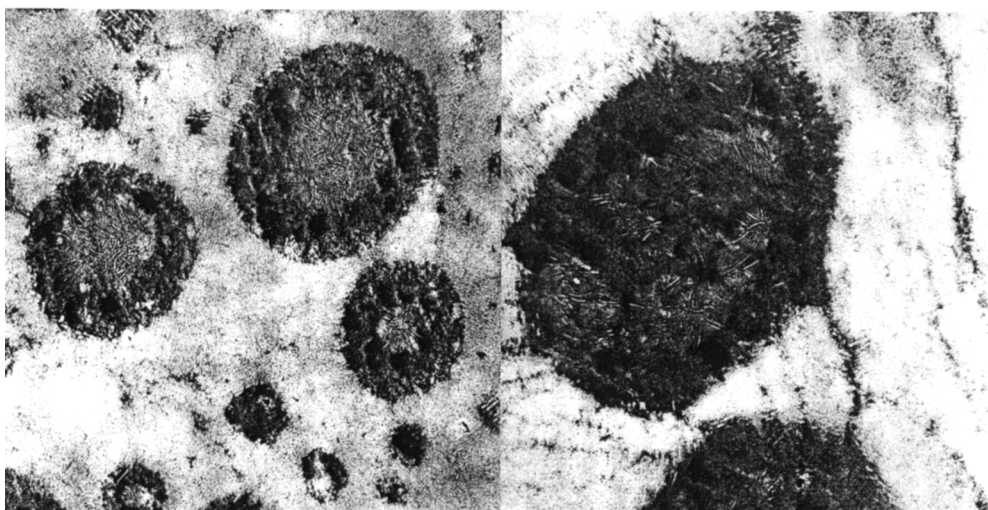
Figure 4.   Phase morphology of heterophasic EP-copolymer from Figure 3, left sample MFR (230°C/2,16kg) = 0.5 g/10 min, right sample MFR = 50; transmission electron micrographs after staining with RuO_4, magnification. 22.300x

bimodal grades have a series of advantages both in processing and in application [13, 14].

   The combination of high molar masses providing mechanical strength and lower molar masses supporting processability has opened some completely new fields for application and facilitated applicability in others. However, one of the preconditions for application of such grades in critical fields is the homogenous distribution of the high molar mass component. This is not only critical in optically challenging applications like thin films, where agglomerates of long molecules form gels.

   Rheology has proven to be a very sensitive tool for checking homogeneity of bimodal PE- and PP-grades, as in the case of a non-homogeneous distribution, the rheological as well as mechanical behavior is dominated by the low molar mass component. The well documented strengthening a toughening effect of tie molecules from the high molar mass fraction [15] will then be largely suppressed. Figure 5 shows the effect of melt homogenization on the reactor powder of a bimodal product in a twin screw extruder with intensive mixing. In this
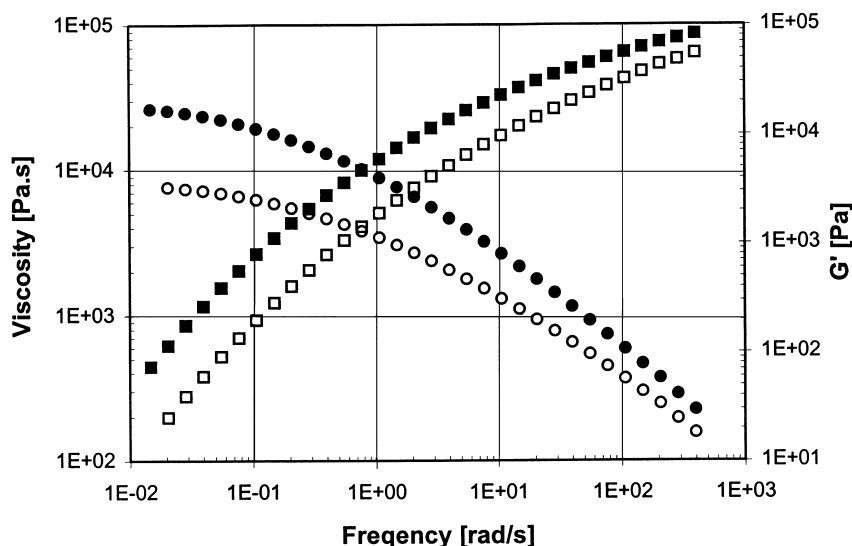
Figure 5. Homogenization effect on storage modulus G' (□) and complex viscosity η* (〇), both from plate/plate geometry at 230°C, of bimodal PP-homopolymer grade; open symbols refer to compressed powder sample, filled symbols to compounded sample.

case, also another effect was obvious: The crystallization temperature of the compounded sample was about 5°C higher, documenting the better distribution of the longest molecules in the sample which act as inherent nucleants [10].

Mineral-Filled Compounds

Another class of materials where homogeneity problems can play an important role are compounds with mineral fillers. Even if hydrophobic fillers like talc are used, the polarity is still much higher than for polyolefins and the compatibility is therefore poor.

Here, again, rheology can assist in judging the quality of a material. Compounds of thermoplastics with a high volume content of mineral fillers show a viscoelastic behavior which is significantly different from homogeneous systems [16, 17]. A strong nonlinearity is combined with the development of a second plateau region of the dynamic moduli at lower frequencies (again leading to a nearly solid-like behavior at low stresses). These effects are determined by particle size, loading, and dispersion quality, all of which also define mechanical properties (Figure 6, 7). The determination of the linear viscoelastic properties of
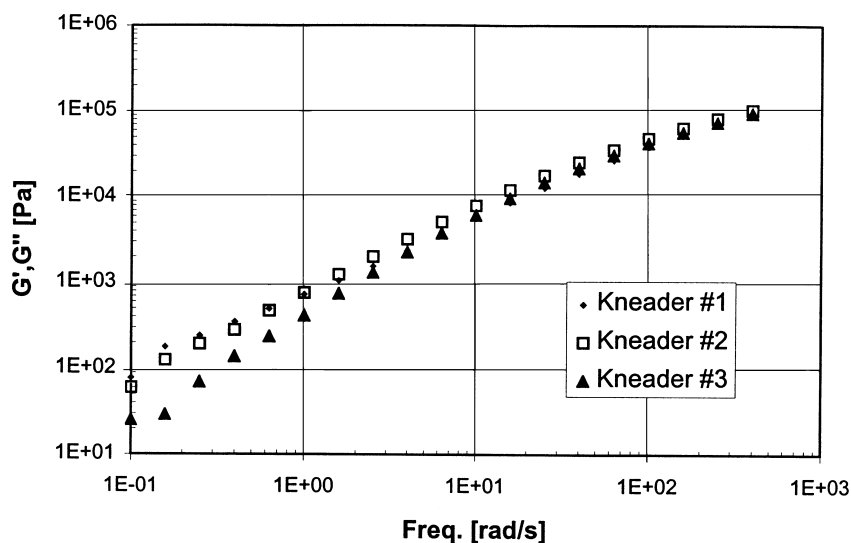
Figure 6. Effect of dispersion quality on the rheology of a 30 wt% PP compound produced on three different compounding machines homopolymers (G'(ω) as calculated from plate/plate measurement at 230°C); better dispersion leads to elasticity at long relaxation times and also improves mechanical properties.

a mineral filled thermoplastic material in the melt can provide a quick and reliable way to investigate filler properties and dispersion quality [18, 19], even if severe limitations exist and a certain reliability can only be attained based on experience.

Precision

A central issue for test methods applied in quality control is the precision, which can be separated into three requirements. For quality control, test results on a material should be:

- repeatable over time,
- comparable between different laboratories and,
- meaningful regarding material structure.

Over the last years, our rheology laboratory participated in two round-robin tests. The first test was organized by PCD in 1994 [21]; the primary scope was to check the comparability and reliability of oscillatory measurements on
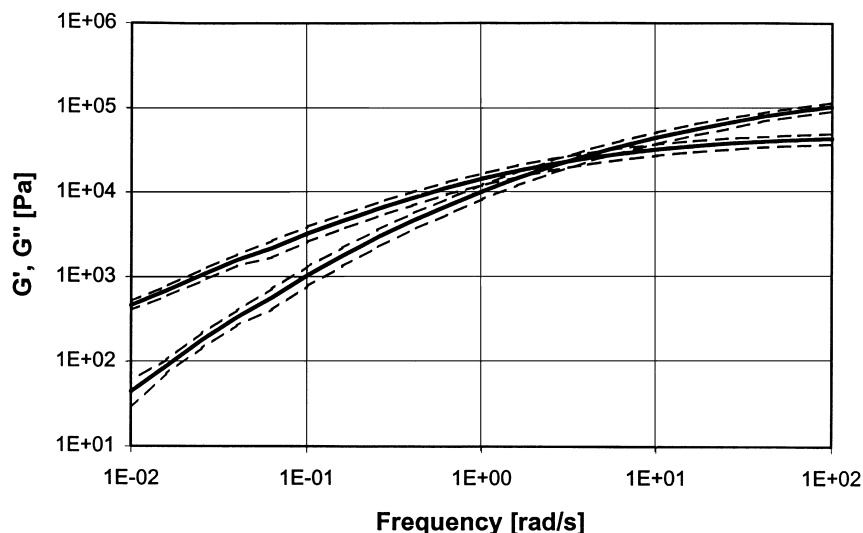
Figure 7. Results of round-robin test for PS 168 N at 200°C; average values and 95% confidence interval.

different polymer melts. Eleven laboratories in four European states took part in the test; three polymer systems were included: Polystyrol PS 168N (BASF AG), Daplen FSC 1012 (heterophasic EP-copolymer) and Daplen FSC 65 T 30 (talc-compound on copolymer-base), the latter two being products of PCD Polymere GmbH. The tests to be carried out were in the dynamic mode (including a strain sweep - G', G" (γ) at $\omega = 1$ and 100 rad/s - to determine the linearity region (γ_{crit}) of deformation) and a steady shear measurement of $\eta(\gamma)$ at the same tempera-ture; all of these in cone/plate- or plate/plate-geometry, as well as under nitrogen to avoid degradation at 230°C for PP and 200°C for PS. Each measurement was to be carried out twice and, in case the difference in the two results exceeded 5%, a third time.

The results (Figure 5), show a good coincidence between the different laboratories' results for the two unfilled systems at least. The standard deviation varies with both frequency and temperature, being highest (i.e., 15-25%) for low and lowest (i.e., 5-8%) for high frequencies; the reason being the lower modulus values at these frequencies (especially for G'). Temperature induced deviations are observed for the PS-sample only. The variation was significantly stronger for

the compound sample [19], maybe because of the inability to reach a truely linear viscoelastic regime in this case.

The second test was organized by the British NPL, one year later [22]. Here, oscillatory measurements in plate/plate geometry (10 labs, 2 materials, 1 temperature) were carried out, as well as steady shear capillary measurements (20 labs, 2 materials, 1 temperature). Repeatability and reproducibility prove to be in the same range for both methods, the former one being between 8 and 12%. No systematic difference between stress- and strain-controlled instruments can be found.

Similar results have been obtained in other studies [23], so the reliability of results obtained in dynamic mode can be assumed to be rather high with deviations in the <10%-range.

CONCLUSION

Using practical examples from the polymer industry, it can be shown that melt rheology is not only an important tool in polymer research, but also an useful instrument for quality control in production. The fact that viscoelastic parameters allow to draw conclusions regarding both molecular structure and processability is of prime importance here.

Using the full capacity of these methods will however require to go from single point measurements to a more complete characterization of materials in quality control investigations. Again, rheology or more specifically the determination of linear viscoelastic properties has some advantages to offer: With a minimum of sample preparation and a short measuring time a lot of information allowing also subsequent calculations can be gathered.

Furthermore, the statistical certainty of rheological results is rather high, eliminating the necessity for time-consuming multiple measurements.

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