Rheol Acta 35:186–193 (1996)
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ORIGINAL CONTRIBUTION

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New ill-posed problems in rheology

Received: 12 October 1995
Accepted: 11 December 1995

Dedicated to Prof. Dr. J. Meissner on the occasion of his retirement from the chair of Polymer Physics at the Eidgenössische Technische Hochschule (ETH) Zürich, Switzerland

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Abstract Many methods of material characterization by rheological methods lead to ill-posed problems. The nature of ill-posedness is discussed. In this light, some such new problems appearing in molecular weight characterization of homopolymers as well as in the characterization of size distribution of dispersed phases in polymer blends by rheological techniques are analyzed. The working capability of a nonlinear regularization method is demonstrated with examples of blend rheology. The role of Professor Meissner in motivating the research in the field of ill-posed problems as well as his important contribution to rheology of polymer blends is outlined.

Key words Ill-posed problem – nonlinear regularization – viscoelasticity – polymer blend

Introduction

In 1987, as one of the authors (J.H.) got to know Professor Meissner, first at a rheology meeting, later on a visit to Zürich, he still though as a theoretical physicist does: theoreticians should develop mathematical models and compare their consequences with experimental data. The meetings with Prof. Meissner were, however, the starting point for a new way of thinking about what else the task of a theoretician could be. Such a new task was arising because of a problem, which at the first glance appeared incidental, namely the critical analysis of the determination of a relaxation time spectrum from experimentally given moduli. However, contemplation about this led to the recognition of an interesting, nearly ubiquitous problem, the ill-posed problem.

Methods were already well developed for the treatment of such a problem (Groetsch, 1984; Morozov, 1984). That there is a problem with the usual least-squares method was already discovered by Tanner (1968) some basic papers treating the ill-posedness were given in the rheology literature also (Wiff et al., 1975; Wiff, 1978; Friedrich et al., 1983). The way from the mathematical formulation of the proposed methods to the adaptation to rheological problems was however in no way obvious. This way demanded knowledge of stochastic as well as numerical methods and also familiarity with rheological experiments.

The problem soon proved as so general that one recognized it also as an important question in many different areas, in NMR-spectroscopy, NMR-tomography, light-scattering and pharmacokinetics. The problem was even recognized as a special case of a more general question which appears in almost all sciences, namely, how can one infer not only parameters but functions from experimental data, in order to characterize the system under investigation?

The basic situation is everywhere the same. That what you want to know, cannot be measured directly. However, there always exists a nontrivial relationship between the unknown function – this may be a particle size distribution, a relaxation time spectrum, a tissue density or a stochastic process – and an experimentally accessible quantity, for example, the dynamic modulus. Furthermore, which is also very important, all experimental data are noisy.

The basic relationship between experimental data $Y(t_i)$ and the function $X(\tau)$ to be determined is called observation equation and can be formulated in the following way:

$$Y(t_i) = \int K(t_i, \tau) X(\tau) d\tau + \varepsilon(t_i) \tag{1}$$

where $\varepsilon(t_i)$ represents the experimental noise. The kernel function $K(t_i, \tau)$ may be given completely by the special problem as in the case of rheology or light-scattering. It may contain some parameters yet to be determined by the data as in NMR-spectroscopy or rheology (see later on). There are also problems outside the polymer science, where the kernel function is unknown and at first an estimate of it has to be established on the basis of a calibration procedure. The analysis of sensor array data is such an example. Finally, in analyzing some complex systems one may encounter problems of the type (1) where the kernel function is unknown and can also not be estimated by a calibration; only some information about the experimental noise is given.

The observation equation (1) is therefore a general pattern and the problems connceted with it differ in the information which is given for the quantities on the right-hand side.

Coming back to rheology the question arises of whether the knowledge of the kernel function is sufficient to determine function $X(\tau)$ from the data $\{Y(t_i) i = 1, M\}$. The answer is that this is not sufficient. This is because the kernel function $K(t_i, \tau)$ in rheology is a singular operator. The manifest consequence of this can be seen if one tries to estimate the function $X(\tau)$ on a lattice of points $\{\tau_j, j = 1, N\}$ with the normal least-squares method. The estimated error become larger, the larger one chooses the number N of these points, for $N \to \infty$ the estimated error even tends to infinity, too (see e.g. Hlavacek et al., 1975; Honerkamp and Weese, 1989). This demonstrates that the better one wants to resolve the function $X(\tau)$ with increasing N, the more sets $\{X(\tau_j) j = 1, N\}$ can be found which are compatible with the data. That means, that there are many functions fulfilling Eq. (1) and the information from the experimental data is not sufficient to separate a special one.

This is the reason to call such a problem ill-posed. The introduction of further information, to find out a unique solution of the problem, is called a regularization method.

In this paper, we introduce some new ill-posed problems which arise in rheological material characterization, present an especially robust regularization method and demonstrate its capabilities with an example taken from polymer blend rheology.

Ill-posed problems in rheology

Now, some of the most important ill-posed problems in rheology will be presented and their peculiarities will be discussed. The authors are aware that not all ill-posed problems will be addressed. This is merely an attempt to show the complexity and variety of the different problems. The problems that will be discussed can be attributed to two fields in rheology: firstly the field of rheometry and secondly the field of rheological constitutive equations.

Let us start with the rheometry. Representative for a group of similar problems, we will follow the question of how the deformation rate distribution $\dot{\gamma}(r)$ in a rotational rheometer depends on the gap-radius r. We assume that the outer cylinder of radius R_o is at rest, the inner of radius R_i rotates with the angular speed Ω_i and the ratio of both radii $K = R_i/R_o$ is smaller than 0.99 (wide gap). Substituting the radius r by the shear stress τ, the unknown function $\dot{\gamma}(\tau)$ depends on the experimentally detected quantity Ω_i in the following way:

$$\Omega_i = \int_{\tau_o}^{\tau_i} \frac{\dot{\gamma}(\tau)}{2\tau} d\tau \ . \tag{2}$$

The actual important value $\dot{\gamma}(\tau_i) = \dot{\gamma}_i$ (τ_i is the shear stress at the inner cylinder) can be estimated as the boundary value of the distribution to be determined. The peculiarity of this problem is, that the corresponding variable t_i (see Eq. (1)) is missing in the kernel, but it appears as the upper boundary of the integral. This allows to resolve the integral by differentiation and to transfer it into the equivalent differential equation. To determine the unknown function, we have to carry out numerical differentiation of noisy experimental data. This is also an ill-posed problem and requires the use of a suitable algorithm. Approximate solutions are well-known (see e.g. Yang et al., 1978). A direct solution is possible on the basis of a regularization method to be discussed.

Similar problems are to be solved in the case of the determination of the distribution of the first normal stress difference in a Couette viscometer from the pressure-difference between outer and inner cylinder or in the case of determination of the deformation rate distribution in a capillary experiment (Macosko, 1994).

In the field of rheological constitutive equations the variety of ill-posed problems is even larger. Therefore, it turns out that one has to analyze different ill-posed problems of different complexity.

We begin with one of the oldest tasks which attracted the attention of rheologists for a long time: the determination of the relaxation time spectrum from measured material functions. Here we would like to analyze how the logarithmic relaxation time spectrum $H(\lambda)$ can be inferred from the storage module $G'(\omega)$ and the loss-module $G''(\omega)$ of the complex shear module $G^*(\omega) = G' + iG''$. The relationship between these functions is given by the following integral relations (see e.g. Tschoegl, 1989):

$$G'(\omega) - G_e = \int_{-\infty}^{\infty} H(\lambda) \frac{(\omega\lambda)^2}{1+(\omega\lambda)^2} d\ln\lambda \ , \tag{3a}$$

$$G''(\omega) = \int_{-\infty}^{\infty} H(\lambda) \frac{(\omega\lambda)^1}{1+(\omega\lambda)^2} d\ln\lambda \ . \tag{3b}$$

In this case as well as some other cases, also material parameters have to be adapted. Another example is the determination of the retardation time spectrum from measured creep function under adaptation of the spontaneous creep compliance and the Newtonian viscosity.

It is characteristic for rheological measurements that the measuring points are given over many decades and, therefore, they should be presented logarithmically. Spectra spreading over many decades are the consequence. That is why the transformed function $\tilde{H} = \log H$ must be determined instead of the function H itself. The nonlinear relationship that must be solved instead of Eq. (3) then reads:

$$G'(\omega) - G_e = \int_{-\infty}^{\infty} 10^{\tilde{H}} \frac{(\omega\lambda)^2}{1+(\omega\lambda)^2} d\ln\lambda \ , \tag{4a}$$

$$G''(\omega) = \int_{-\infty}^{\infty} 10^{\tilde{H}} \frac{(\omega\lambda)^1}{1+(\omega\lambda)^2} d\ln\lambda \ . \tag{4b}$$

At the first moment the difference between a linear and nonlinear variant of this problem seems to be unimportant. From the point of view of a numerical method to be implemented it represents a considerable difference.

A further problem is related to the interconversion of different material functions given within the theory of linear viscoelasticity. If the function $G^*(\omega)$ is given, for example, and you are interested in the relaxation function $G(t)$, an inverse Fourier transform has to be performed:

$$G^*(\omega) = i\omega \int_0^{\infty} G(t)\, e^{-i\omega t} dt \ . \tag{5}$$

This is also an ill-posed problem (see Morozov, 1984) whose direct solution can be avoided by the calculation of the relaxation time spectrum and the subsequent recalculation of the relaxation function. In other words, instead of solving Eq. (5), Eq. (4) has to be solved an knowing the relaxation time spectrum, the relaxation function $G(t) = \int_{-\infty}^{\infty} \mathrm{H}(\lambda) \exp(-t/\lambda)\, d\ln\lambda$ can be calculated straightforwardly. At any rate, an ill-posed problem has to be solved.

Another group of ill-posed problems in rheology that was advanced in recent years is the calculation of the molecular weight distribution from rheological data. At the moment there is no generally accepted model which relates the rheological material function (e.g. the dynamic module G^*) to the molecular weight distribution $w(M)$. Therefore, special rheological constitutive equations are used which quantitatively correctly describe the rheological behavior of blends of monodisperse polymer fractions or of polydisperse polymers. The double reptation model of deCloizeaux (1990) and the model of Tsenoglou (1987) belong to the first category. In principal, these models are mixing rules for the relaxation function $G(t)$ and can be presented in the following way:

$$\Phi_{\mathrm{eff}}(t) = \left[\int_0^{\infty} w(M)\, g_1(t,M)\, dM \right]^2 \quad \text{with}$$

$$\Phi_{\mathrm{eff}} = \left[\frac{G(t)}{G_0} \right] \ . \tag{6}$$

G_0 is the plateau modulus and the Ansatz $g_1 = \exp[-t/\lambda_0(M)]$ is often used to describe the kernel function. The dependence of the terminal relaxation time λ_0 of the molecular mass follows the well-known scaling relation $\lambda_0 \propto M^{3.4}$. Other empirical relations can also be used to describe the integral kernel. They have no influence on the ill-posedness of the problem and little influence on the solution (Wasserman, 1995). In the case of Eq. (6), we have to solve a non-linear problem, because the right-hand side of this equation is quadratic.

The second category of constitutive equation problems is even more complicated. As an example, we give the constitutive equation, which was developed by McLeish (1992) for polydisperse polymers. Its agreement with experimental results has not yet been checked. The model reads as follows:

$$\Phi_{\mathrm{eff}}(t) = \left[\int_0^{\infty} w(M)\, e^{-\left(\int_0^t \Phi_{\mathrm{eff}}^{1/2}(t')\, dt'\right)/M^3} dM \right]^2 \ . \tag{7}$$

Additional to the nonlinearity known from Eq. (6), the experimental data appear now in the kernel function, too. Up to now we assumed that the kernel is given independent of the data.

A further class of ill-posed problems belongs to the group of rheological constitutive equations of emulsions or suspensions with spherical inclusions. In this case, the experimentally determined material function depends crucially on the amount and the size distribution of dispersed material. Introducing the size distribution function $v(R)$ fulfilling the condition $\int v(R)\,dR = \Phi$ (= volume fraction of disperse polymer), the Palierne model (1990) – at the moment the best model – reads as follows:

$$G_b^*(\omega) = G_m^*(\omega)\,\frac{1+3\int\limits_0^\infty P[G_m^*(\omega), G_d^*(\omega), R, p]\,v(R)\,dR}{1-2\int\limits_0^\infty P[G_m^*(\omega), G_d^*(\omega), R, p]\,v(R)\,dR}\,. \tag{8}$$

In this relationship, $G_b^*(\omega)$ is the complex shear modulus of the blend, $G_m^*(\omega)$ that of the matrix, $G_d^*(\omega)$ that of dispersed material, and P represents the integral kernel of Palierne's model. The peculiarity of this ill-posed problem consists in the fact that P depends on unknown parameters p (this may be the interfacial tension α, or an interfacial shear modulus β) which have to be determined during the solution procedure. Friedrich et al. (1995) showed that in the case where only the interfacial tension is unknown the problem can be transformed to a problem with an exactly given kernel.

Certainly, the list of ill-posed problems in rheology is not complete. But to the best of our knowledge, these are the most important tasks at the moment. In the following we will show principally, how these problems can be solved.

A special regularization method

The application of regularization methods in rheology was discussed and tested in different papers: Wiff et al. (1975), Wiff (1978), Friedrich and Hoffmann (1983). Some improvements and the generalization to the case where the experimental quantity depends nonlinearely on the spectral function has been given by Honerkamp and Weese (1989, 1990) and Weese (1993). As an example, we will solve Eq. (4) using a special Tikhonov regularization method and infer $\tilde{H}$ from the experimentally given G' and G''. The solution of this problem can be found by minimization of the following functional:

$$\begin{aligned} V(\lambda_R) = {} & \sum_{i=1}^{n} \frac{1}{\sigma_i'^2}\left(G_i'^\sigma - G_i'(\tilde{H},\omega_i)\right)^2 \\ & + \sum_{i=1}^{n} \frac{1}{\sigma_i''^2}\left(G_i''^\sigma - G_i''(\tilde{H},\omega_i)\right)^2 \\ & + \lambda_R \int\limits_{-\infty}^{\infty} \left(\frac{d^2\tilde{H}}{d\lambda^2}\right)^2 d\ln\lambda\,. \end{aligned} \tag{9}$$

$G_1'^\sigma, \ldots, G_n'^\sigma, G_1''^\sigma, \ldots, G_n''^\sigma$ are the measured values for the dynamic module $G'(\omega)$ and $G''(\omega)$ respectively, which are characterized by the relative error σ via the equation $\sigma_i' = \sigma G_i'^\sigma$ and $\sigma_i'' = \sigma G_i''^\sigma$. $G_i'(\tilde{H},\omega_i)$ and $G_i''(\tilde{H},\omega_i)$ are the values of the model at the frequency ω_i which can be calculated using $\tilde{H}$. The first two terms on the right-hand side of Eq. (9) insure that the result is consistent with the data. They correspond to a functional that has to be minimized using a least square method. The third term, which is a result of application of regularization theory, stabilizes the inverse and prevents experimental errors from having an inordinately large effect on the result. This term is weighted by the so-called "regularization-parameter" λ_R, which has essentially the same effect as the band width of a filter used in smoothing noisy data. When this parameter is too small, the results include artifacts caused by experimental error and when this parameter is too large, the results are smoothed to an excessive degree. The optimal value of this parameter can be determined using the SC method developed by Honerkamp and Weese (1990).

The relaxation time range $\lambda \in [\lambda_{\min}, \lambda_{\max}]$ in which the solution is valid can be inferred from the frequency range in which the experimental data were measured: $\lambda_{\min} = 1/\omega_{\max}$ and $\lambda_{\max} = 1/\omega_{\min}$. However, the numerical calculation demand to enlarge the interval by two decades on both sides. By this, the accuracy of the spectra points close to the interval boundary is increased. The number of points of the spectrum can be varied largely without having any effect on the accuracy of the numerical method. The algorithm was published by Weese (1993) and is implemented in the computer program NLREG.

In many cases it is meaningful to consider further conditions for the solution and to use them for numerical calculations. NLREG also contains this option, which can be activated if desired. The numerical method for determining the spectrum will not be considered here due to its complexity. However, the examples discussed in the following section were calculated using this computer program.

Before switching to the next section, we will compare the different methods for solving ill-posed problems in rheology. Methods that are based on the numerical realization of approximation formulas for the solution of Eq. (4) e.g. will be excluded from the considerations.

There are two large groups of methods to solve that problem adequately. The first group deals with the ill-posedness and uses regularization methods to determine the distribution functions. To this group belong the computer programs developed by Provencher (1982), Weese (1993), Mead (1994), and Wasserman (1995). The second group avoids the problem of ill-posedness by determining a sparse discrete distribution function. In this case, not more than three points per decade can be calculated using the conventional methods of linear algebra. Two representatives of this group are Baumgaertel and Winter (1989), as well as Laun (1978). The difference between the two groups consists in the fact that by the help of the methods of the first group a continuous distribution function is estimated (100 and more points per decade is no principal problem), whereas the methods of the second group provide discrete spectra.

Among the programs dealing with the ill-posedness of the problem, Tikhonov regularization is the widely used procedure. Starting with Provencher (1982) who used at first this idea for inferring diffusion time distributions from dynamic light scattering data, all the following methods minimize the same functional equation (9). Mead's program is even based on Provencher's program CONTIN. The differences between the procedures used within this group come mainly from the method used for the determination of the regularization parameter. Provencher uses the old discrepancy principle (see e.g. Morozov, 1984) whereas Weese uses a more modern, very robust procedure that leads to the optimum regularization parameter depending on the error level of the primary data. Wasserman (1995) determines the regularization parameter in an empirical way that brings in to the solution some arbitrariness. It is worth mentioning that Weese's program, NLREG, is the only one available that solves nonlinear ill-posed problems, too.

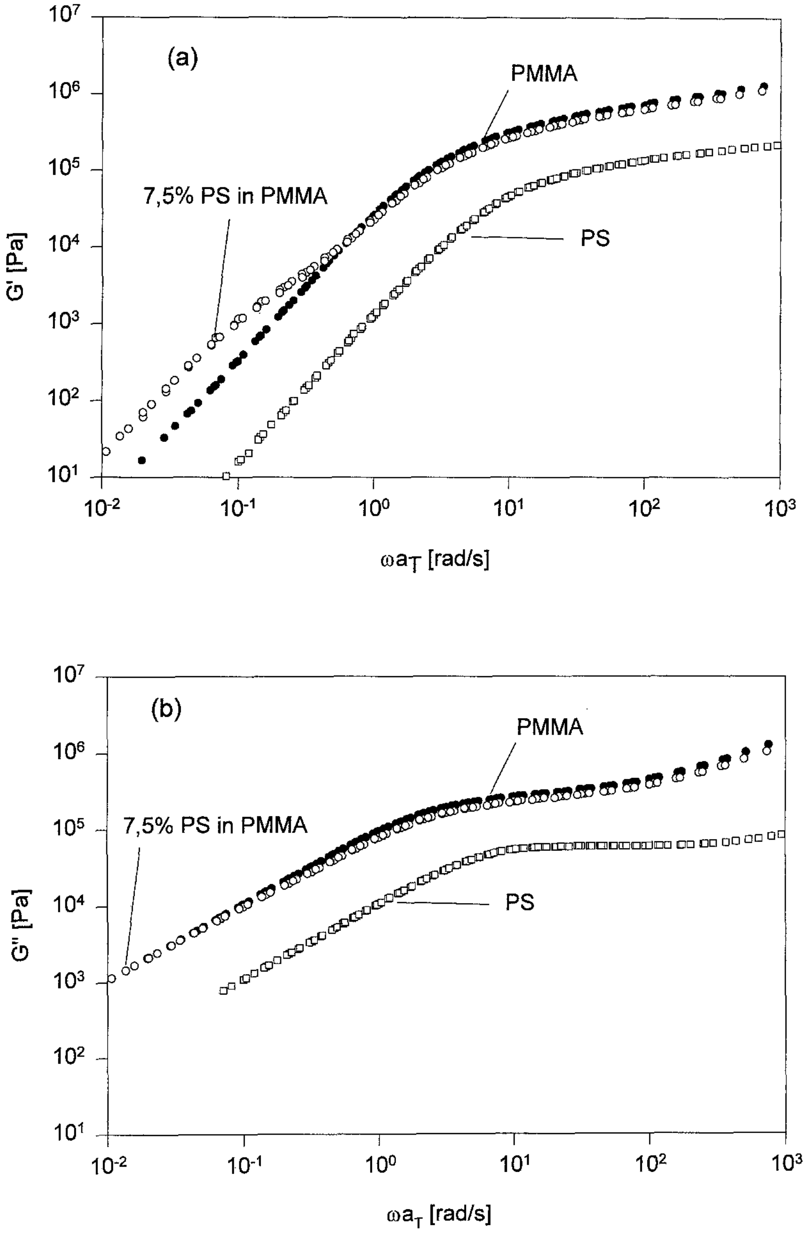

Fig. 1 Master curves of the storage moduli (a) and loss moduli (b) of the polymer blend (7.5% PS in PMMA), the matrix polymer (PMMA) and the dispersed polymer (PS)

Results of certain problems

The rheology of polymer blends offers a lot of different ill-posed problems. With the example of a blend containing 92.5 wt% PMMA ($M_w = 31$ kg/mol, $M_w/M_n = 1.19$, Newtonian viscosity $\eta_0 = 92$ kPas) and 7.5 wt% PS ($M_w = 100$ kg/mol, $M_w/M_n = 1.03$, $\eta_0 = 9.45$ kPas), we will discuss this variety. Using a modified variant of Eq. (8), we will show that besides the particle size distribution function the interfacial tension of both polymers can be determined. Let us start with the rheology of the blend and blend's components.

Figure 1 shows the master curves of the storage modules G' and the loss modules G'' of the matrix polymer (PMMA), of the dispersed polymer (PS) and of the blend at a reference temperature $T_0 = 190\,°\mathrm{C}$. Expecially the storage module of the blend (Fig. 1a) shows the relaxation shoulder at small frequencies that corresponds to the form relaxation time λ_F of the spherical inclusions. The exact determination of this characteristic time is possible using the relaxation time spectrum of the blend as given in Fig. 2. Professor Meissner (see e.g. Gramespacher and Meissner, 1992 and Meissner, 1992) appears to be the first who referred to the importance of the relaxation time spectrum for the determination of that time. They showed that the knowledge of this characteristic time together with a simple rheological model and the knowledge of a mean particle diameter is sufficient to determine the interfacial tension. Certainly, the use of one Maxwell mode for the description of the interfacial rheological properties of a polydisperse blend represents a strong simplification. Nevertheless, Graebling et al. (1992) could show that the volume averaged radius is a sufficient morphological characteristic value in the case of narrow particle size distribution. Using the Gramespacher-Meissner procedure, in our case (volume averaged radius $R_V = 102$ nm, $\lambda_F = 6.5$ s) an interfacial tension $\alpha = 2.52$ mN/m can be determined for our PMMA/PS blend.

This procedure demonstrates clearly that morphological information is necessary to determine interfacial tension. However, the Laplace pressure – the ratio of interfacial tension and a characteristic radius – can be estimated through rheological measurements only. Then the independent determination of particle dimensions allows the calculation of α from the Laplace pressure. This situation is also prescribed by the structure of the emulsion models.

Using Eq. (8) for the case that only the isotropic interfacial tension determines the interfacial properties ($p = \alpha$), the Palierne model can be written in the following form:

$$G_b^*(\omega) = G_m^*(\omega) \, \frac{1 + 3 \int\limits_{-\infty}^{\infty} P[G_m^*(\omega), G_d^*(\omega), R'] \, u(R') \, d \ln R'}{1 - 2 \int\limits_{-\infty}^{\infty} P[G_m^*(\omega), G_d^*(\omega), R'] \, u(R') \, d \ln R'} \, . \tag{10}$$

In this equation, $R' (= R/\alpha)$ is a transformed radius (in principle, the inverse Laplace pressure) and $u(R')$ is a new size distribution function that can be inferred from the size distribution $v(R)$ by

$$u(R') = \alpha \, v(\alpha R') \, . \tag{11}$$

The result of the calculation of the corresponding distribution function is given in Fig. 3.

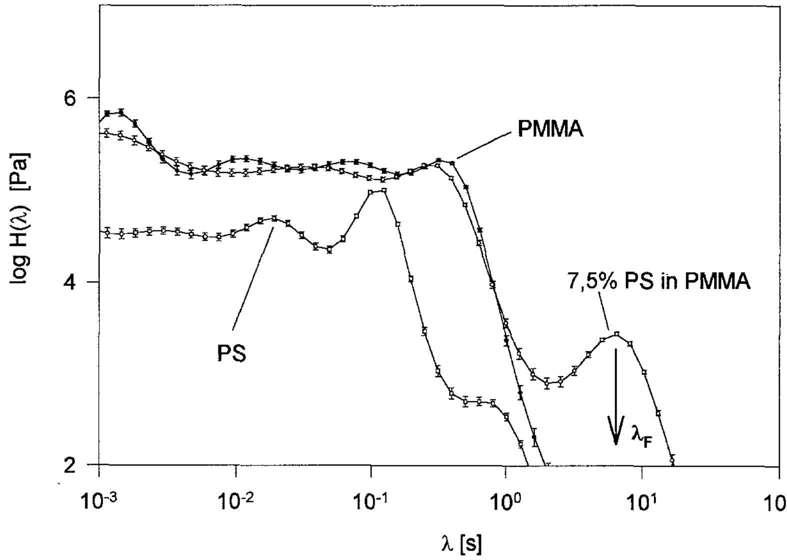

Fig. 2 Relaxation time spectrum of the polymers given in Fig. 1. The spectra are determined solving Eq. (4) by a nonlinear regularization method (Weese, 1993)

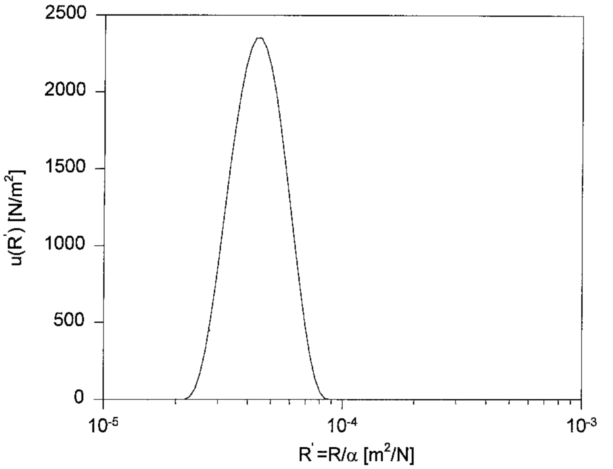

Fig. 3 Modified sphere size distribution function $u(R')$ as determined from Eq. (10) by a nonlinear regularization method (Weese, 1993)

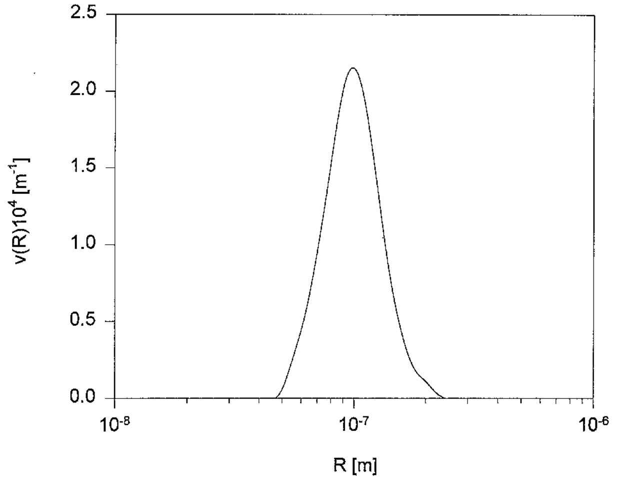

Fig. 4 Sphere size distribution function $v(R)$ as determined from solving the "tomato salad problem" (see Gleinser et al. 1993) by a nonlinear regularization method (Weese, 1993)

Now we will discuss two cases. First, if the interfacial tension is known, the particle size distribution can be determined from rheological data directly. Knowing the material functions of the blend and blend's components and using Eq. (11), the unknown particle size distribution $v(R)$ can be estimated. In this case, rheology appears to be a tool for a morphological characterization.

In the second case we will assume that the distribution of profile radii is known from TEM pictures. Then, by solving another ill-posed problem, called tomato salad problem (how large is the tomato knowing only some slices?), the volume weighted size distribution of inclusions can be estimated as shown by Gleinser et al. (1993). Here, we dispense with mathematical presentations of this problem and refer to Gleinser's paper. Their solution of our problem for the blend system under consideration – the distribution function $v(R)$ – is given in Fig. 4. Now, the morphological information is given independently and we can try to determine the interfacial tension by "shifting" the distribution $u(R')$ on $v(R)$. Choosing the coincidence of the first moment of both distributions as criterion of agreement, the interfacial tension is given by the following equation:

$$\alpha = \frac{\int_0^\infty R\, v(R)\, dR}{\int_0^\infty R'\, u(R')\, dR'} \tag{12}$$

Using this equation, a value of $\alpha = 2.2$ mN/m is determined which is in good agreement with the Gramespacher-Meissner procedure. Our method is more complicated but leads to interfacial or to morphological information from rheology depending on what else is known.

Outlook

The number of inverse problems alone in rheology is impressive. Actually one can assume that whenever one is interested in a function that cannot be measured directly, an inverse problem arises, and in most cases it is ill-posed. This is the case as we have shown for the determination of the deformation rate distribution, for the determination of relaxation time spectra, the molecular weight distribution and the distribution of sphere radii. The formulation of the problem starts always with the precise statement for the observation equation of the form (1) or its nonlinear version.

It requires not much fantasy to imagine further, even higher dimensional inverse problems in material science. One can think about a position and time-resolved material characterization. The time variable in Eq. (1) may stand for any series of measuring points, be it a single frequency or a single position or be it position and time. At all such applications, some new considerations are necessary to find a robust estimate of the function $X(\tau)$.

At Freiburg now a cooperation with scientists from other disciplines is planned to solve higher dimensional inverse problems. Experience made in rheology will be very helpful in this respect.

It can be seen that the development in this field is still strongly growing and becomes more interdisciplinary. For us, the starting point is associated with Professor Meissner.

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