

Correlations Between Rheological and Mechanical Properties of Mineral Filled Polypropylene Compounds

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SYNOPSIS

A comparative study of rheological and mechanical properties of Polypropylene compounds with talc as a mineral filler is presented. It turns out that the main factors determining the mechanical behavior, namely (a) filler concentration, (b) filler particle size, and (c) degree of dispersion, influence the linear viscoelastic properties as well. Thus, a quick method for estimating compound properties from melt rheology is established. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

One of the most important reasons for the increasing use of Polypropylene in technical applications is the possibility to vary its properties by a wide scale of copolymerization, compounding, and blending techniques.¹ Among other substances used here, mineral fillers are often able to improve the performance of PP, at the same time reducing the cost of the material.² The rheological behavior of such compounds has, therefore, gained widespread attention,³⁻¹¹ as generally the rheology of polymer/filler systems.¹²⁻²¹

Compounds of polymers with mineral fillers or reinforcements like talc, calcium carbonate, or mica exhibit a rheological behavior that is significantly different from the base polymer. Factors influencing the change in the viscoelastic behavior are grain size, shape and concentration of the filler, dispersion quality and the interface adhesion in the molten state.^{3,4,15,17,19,20} As the latter factors, which are difficult to determine separately, are also important for the mechanical properties of the compound in solid state, rheological measurements can be interesting here for predicting the possibilities of a filler/resin combination as well as for production control. This is facilitated by the fact that especially in the case of fine fillers in the μm and sub- μm range, which

appears to be most interesting for major improvements in the mechanical behavior, the rheological effects are quite drastic. A review of these effects has been given by White,²⁰ but also the recent work by Adams and Walters¹⁰ points out the sensitivity of viscoelastic effects to changes in the compound structure.

The measurements on which this work is based were aimed at finding a quick and at the same time reliable method for determining the structure of Polypropylene compounds, mainly with respect to filler particle size and degree of dispersion. The rheometrical technique used was the determination of the linear viscoelastic properties, namely the storage and loss moduli G' , $G''(\omega)$. To be able to separate the rheological properties of both components, filler and matrix, the relaxation time spectra of the systems were calculated and compared with those of the base polymers.²² The results turned out to correlate quite well to the mechanical properties of the compounds, namely the impact strength.

THEORETICAL BACKGROUND

It is widely accepted that the linear viscoelastic behavior of a polymer melt can be described using a discrete relaxation time spectrum.³⁰ Starting with the equation of state of linear viscoelasticity,

$$\underline{\sigma}(t) = \int_{-\infty}^t m(t-t') \underline{\underline{C}}^{-1}(t') dt',$$

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the memory function for the time dependent part of the material behavior can be expressed by a discrete spectrum of N pairs of relaxation times τ_i and relaxation strengths g_i according to

$$m(t-t') = \sum_{i=1}^N g_i \exp\left(-\frac{t-t'}{\tau_i}\right).$$

The linear viscoelastic material functions, namely the relaxation modulus $G(t)$, the transient viscosity at low shear rates $\eta_0(t)$, and the dynamic moduli $G', G''(\omega)$ can then be calculated from the spectrum, for example

$$G'(\omega) = \sum_{i=1}^N g_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2}$$

$$G''(\omega) = \sum_{i=1}^N g_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2}$$

The precision of this method can be increased by applying the BSW (Baumgaertel/Schausberger/Winter) model,^{31,32} which was derived from results with polymers having a very narrow MMD (nearly monodisperse samples), where it turned out that for an exact representation of the plateau region of the dynamic moduli a row of "upper frequencies" had to be added to the leading relaxation time τ_i . Thus, the Maxwell model equations for storage and loss moduli of each element are modified as follows:

$$G'(\omega) = \sum_{i=1}^N g_i \sum_{k=1}^{10} c_s^{k-1} \frac{(\tau_i c_\tau^{k-1})^2 \omega^2}{1 + (\tau_i c_\tau^{k-1})^2 \omega^2}$$

$$G''(\omega) = \sum_{i=1}^N \sum_{k=1}^{10} c_s^{k-1} \frac{(\tau_i c_\tau^{k-1}) \omega}{1 + (\tau_i c_\tau^{k-1})^2 \omega^2}$$

The determination of the spectrum can be carried out using a predefined or variable set of relaxation times (about 1–2 per decade between $1/\omega_{\max}$ and $1/\omega_{\min}$) and minimizing the sum of deviation squares between experimental and calculated moduli by variation of the g_i values.^{33–36} For the BSW extension, a number of 10 relaxation times turns out to be sufficient in any case, accepting $c_s = 0.6$ and $c_\tau = 0.1$ to be model constants.

The correlation between this relaxation time spectrum and the molar mass distribution of the polymer has been investigated intensively.^{23–28} When this method is extended to multiphase systems like immiscible polymer blends^{29,37} it turns out that the contributions of the two phases are not sufficient

for the description of the system, but an interaction term defined by the particle size of the disperse phase and the surface tension between the phases has to be added.

Similarly, we consider the contribution of a mineral filler to the viscoelastic behavior of the compound to be defined not only by the volume fraction, but also by the particle shape and particle–particle or particle–matrix interactions. The relaxation time spectrum of compounds seems to be an appropriate tool for investigating these effects. A concept for the change in relaxation time distribution was developed before by Matsumoto,¹³ assuming a box type distribution for the relaxation times added by the filler to the spectrum of the matrix polymer. This effect, which seems quite comparable to the development of yield stress behavior in steady-state flow,¹⁴ can be explained by particle–particle interactions in the fluid. As practically all factors mentioned above influence the average interparticle distance as well,³⁸ an increase of the effect by (a) increasing the volume fraction of the filler, (b) reducing the average particle size, and (c) improving the dispersion quality of the filler can be expected. All three factors were, therefore, checked in the presented investigation program.

EXPERIMENTAL WORK

Several compounds prepared in developing new PP compounds with different types of talc were investigated together with their base polymers. Two heterophasic EP copolymers were used as matrix materials: EP 1 is a high-impact, medium molecular weight type ($M^w = 260.000$ g/mol) and EP 2 is a standard medium molecular weight type ($M^w = 380.000$ g/mol). Fillers and their key properties are listed in Table I. The compounds had been prepared by melt mixing in twin screw extruders (W&P ZSK 53 and Berstorff ZE 25) at 250°C.

The storage and loss moduli were measured on a Rheometrics RDS II in cone/plate geometry at 230°C. To avoid influences of different sample preparation techniques, all samples for the rheological investigations were cut from injection molded pieces prepared for the mechanical testing of the compounds. As it turned out to be impossible to find a strain region where the compounds with higher filler loadings showed a linear behavior through the whole frequency scale (10^{-2} to 10^3 rad/s), a strain of 5% was used in all measurements. This practice seems justified from experiences in the literature.⁶

Table I Filler Types and Their Properties

Filler Type	TX 1	TX 2	TX 3	TX 4
Bulk density DIN 52110 [g/cm ³]	0.12	0.14	0.20	0.42
Specific surface BET [m ² /g]	13.30	7.00	4.20	2.50
Oil absorption DIN ISO 787/5 [g/100 g]	56.00	48.00	42.00	31.00
Average grain size [μm]	0.90	2.20	4.00	14.00

The frequency range was, in any case, scanned from lower to higher frequencies, and the results of the first scan were used for the evaluation, because a second run always showed much less pronounced influences of the filler. This observation is in accordance with the literature.¹⁰

To account for degradation of the polymer matrix during the mixing process, which is influenced not only by the kneader type and processing temperature, but also by the volume fraction and grain size of the filler, which influences the amount of air introduced during the mixing process, all modulus curves used for the following comparison and spectrum calculation were normalized to the crossover parameters,

$$G_C = G'(\omega_C) = G''(\omega_C) \text{ and } \omega_C,$$

according to G'/G_C , G''/G_C , and ω/ω_C . As these normalization parameters are proportional to the parameters of the molecular mass distribution, M_w

and M_w/M_n ,²⁷ this procedure should improve the comparability significantly. Figures 1 to 3 show the results of the three different variations further described in the following section, together with the results for the base polymer.

The relaxation time spectrum was subsequently calculated from the normalized moduli as described in section 2, keeping the number of relaxation times per decade constant. A plot of $\log(g_i\tau_i)$ vs. $\log(\tau_i)$, which is in the case of pure polymer melts roughly proportional to the MWD was used to visualize the results (see Figs. 4 to 6).

The mechanical properties of the compounds were determined from injection moulded specimens in three-point bending according to DIN 53457 (flexural modulus) and impact testing according to ISO 179 1c at 23°C (Charpy impact strength, U-notch). The results are summarized in Table II, showing the strong influence of filler particle size, filler concentration, and degree of dispersion, especially on the impact strength.

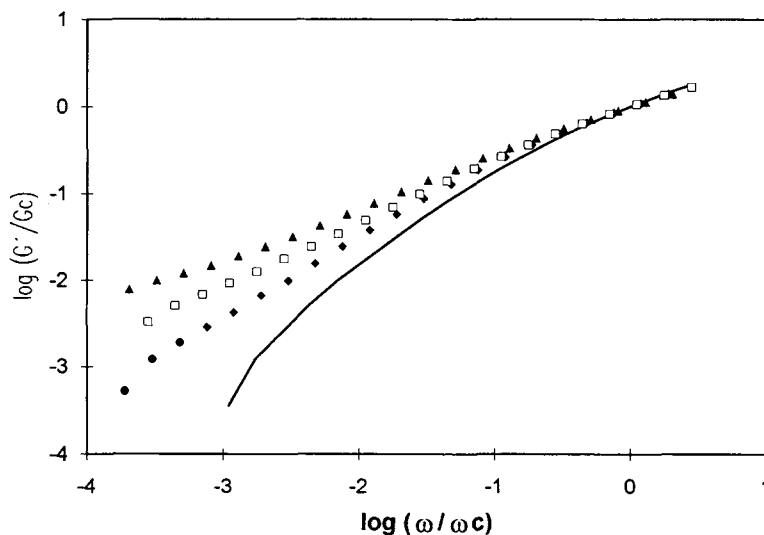


Figure 1 Influence of filler concentration on rheological properties of PP compounds—Normalized storage modulus for: —: EP 1; ◆: EP 1 + 20% TX 2; □: EP 1 + 30% TX 2; ▲: EP 1 + 40% TX 2.

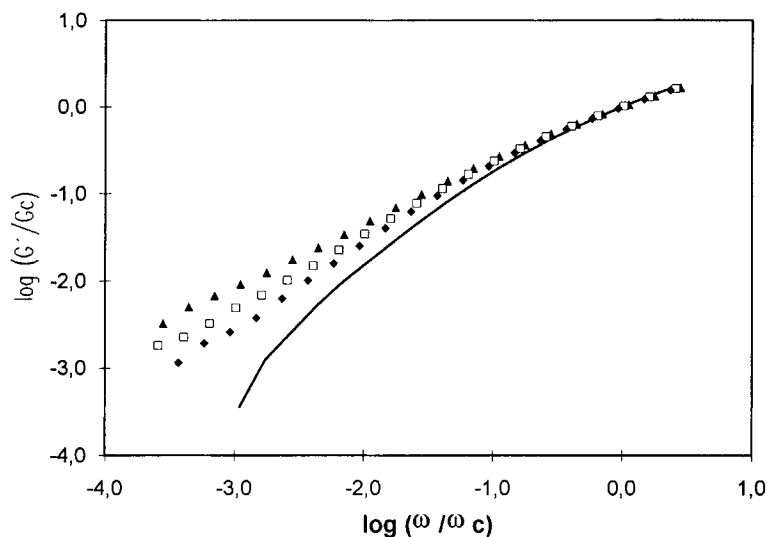


Figure 2 Influence of filler particle size on rheological properties of PP compounds—Normalized storage modulus for: —: EP 1, \blacktriangle : EP 1 + 30% TX 2; \square : EP 1 + 30% TX 3; \blacklozenge : EP 1 + 30% TX 4.

RESULTS AND DISCUSSION

When considering the literature accumulated until now in the field of the rheology of particle-filled polymers (or viscoelastic suspensions in general), one can easily see that the investigation of the dynamic-mechanical properties^{6-8,10,12-14} has significantly assisted in creating theoretical concepts for these systems. Especially in the case of the notorious

“yield stress discussion,”^{6,15-17,19,20} low-amplitude dynamical measurements turned out to be very helpful. This way it could be shown by Matsomoto, Hitomi, and Onogi¹³ as well as by Lobe and White,¹⁴ that the “yield stress” behavior detected in steady-state measurements and also turning up in the dynamical behavior can be attributed to a “pseudogel” produced by particle-particle interactions, which does not only disappear at extremely low fre-

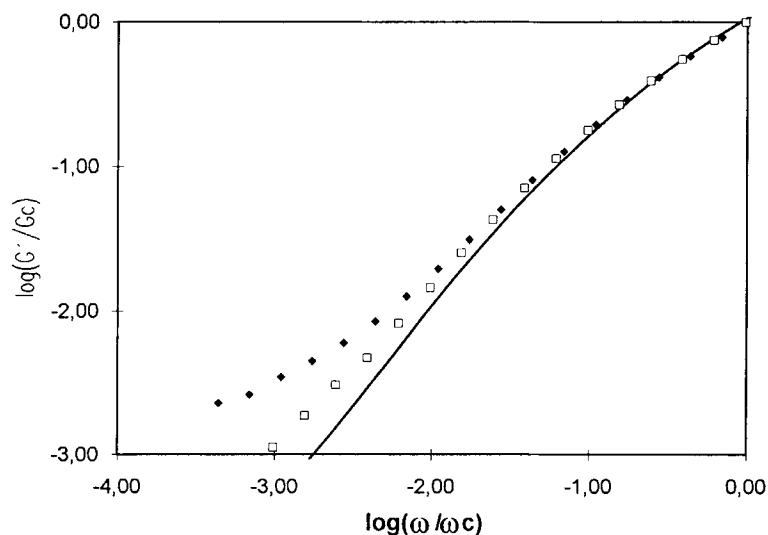


Figure 3 Influence of filler dispersion on rheological properties of PP compounds—Normalized storage modulus for: —: EP 2; \square : EP 2 + 30% TX 1/short kneader; \blacklozenge : EP 2 + 30% TX 1/long kneader.

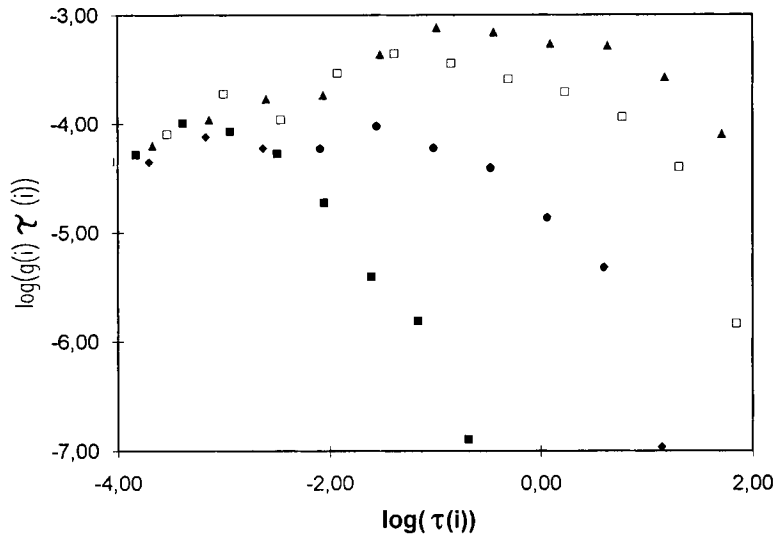


Figure 4 Influence of filler concentration on rheological properties of PP compounds—Relaxation time spectrum for: ■: EP 1; ◆: EP 1 + 20% TX 2; □: EP 1 + 30% TX 2; ▲: EP 1 + 40% TX 2.

quencies, but is also extremely strain dependent. In connection with this, it also turned out to be possible to correlate high-strain dynamical measurements and steady-state measurements of highly filled systems via the usual Cox/Merz relation

$$\dot{\eta}(\omega) = \eta(\dot{\gamma}) \text{ for } \omega = \dot{\gamma},$$

which is usually considered to be impossible.^{8,10,20}

From these results, it appears that dynamic-mechanical testing is a rather powerful technique for

the investigation of such systems. In our case, three major influences on the system behavior were investigated:

Concentration of the Filler

A variation of the filler concentration is usually the simplest way to influence the mechanical behavior of a compound. In our case, weight concentrations of 20, 30, and 40% of filler type TX 2 were used, equivalent to 7.64, 12.42, and 18.07 vol %. If the

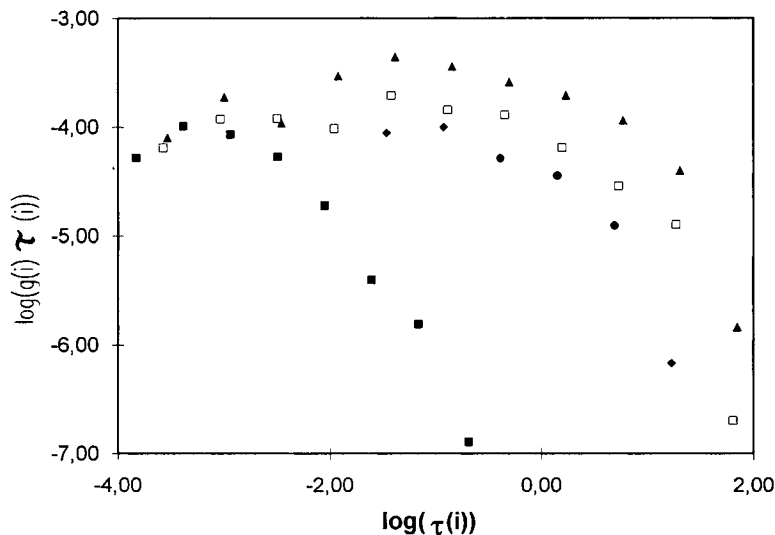


Figure 5 Influence of filler particle size on rheological properties of PP compounds—Relaxation time spectrum for: ■: EP 1; ▲: EP 1 + 30% TX 2; □: EP 1 + 30% TX 3; ◆: EP 1 + 30% TX 4.

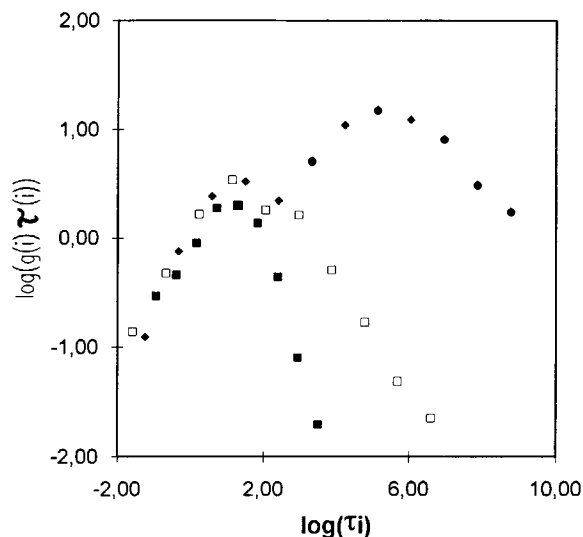


Figure 6 Influence of filler dispersion on rheological properties of PP compounds—Relaxation time spectrum for: ■: EP 2; □: EP 2 + 30% TX 1/short kneader; ◆: EP 2 + 30% TX 1/long kneader.

filler particles are approximated by spherical shape, taking the average particle size as diameter, and the formulations developed by Wu³⁸ are used, one arrives at average interparticle distances of 1.98, 1.35, and 0.94 μm for the three concentrations. At the same time, the particle/matrix interface is significantly increased. If complete dispersion and wetting is assumed (which is also one of the assumptions for the former calculation), interface areas of 1.34, 1.84, and 2.25 m^2/cm^3 are obtained.

These changes are well reflected in the rheological behavior (see Fig. 1). When the relaxation time spectrum is calculated (see Fig. 4), it turns out that the second contribution attributed to the filler increases in the maximum strength reached as well as in the terminal relaxation time. For the comparison in Table II, the maximum strength $g_i\tau_{i,\max}$, was used. It turns out that the values correlate quite well with the flexural modulus, but show an inverse correlation

to the impact strength. Obviously, the interaction effect is here overcompensated by the pure volume effect of the filler leading to an increasing brittleness with increasing filler content.

Particle Size of the Filler

One possible way to overcome the problem of brittleness in PP compounds is the use of fillers with smaller particles. A filler variation between TX 2, TX 3, and TX 4 at 30 wt % loading leads to massive changes in the rheological (see Fig. 2) and mechanical behavior again. The reason for these changes can be seen in the variation of the average particle distance (calculated with the same assumptions as above, values of 1.35, 2.46, and 8.62 μm are obtained) as well as the interface area (1.84, 1.11, and 0.66 m^2/cm^3) for the three filler types.

The correlation between the relaxation time spectrum (Fig. 5) and the mechanical properties is different in this case. As the filler loading is constant, the increasing interaction improves both flexural and impact properties of the compounds.

Degree of Dispersion

One of the difficulties connected to the use of extremely fine-grained fillers is the dispersion quality. Only highly intensive mixing kneaders are appropriate to obtain effective particle sizes in the compound that are close to the primary particle size of the filler. To investigate the effect of different degrees of dispersion, the same composition was compounded on a Berstorff ZE 25 kneader in a “short” ($L/d = 38$) and a “long” ($L/d = 48$) version with otherwise similar screw configurations. The resulting differences in the rheological (see Figs. 3 and 6) and the mechanical behavior are obvious. The fact, that the flexural modulus of the compound with higher impact strength is somewhat lower can be attributed to a higher extent of matrix degradation due to the more intense mixing process. We assume

Table II. Mechanical and Rheological Parameters of the Compounds

Compound	Kneader	Flexural Modulus [MPa]	Impact Strength [kJ/m ²]	$g_i\tau_{i,\max}$ [Pa.s]
EP 1 + 20% TX 2	ZSK 53	2450	10.10	9.70E-05
EP 1 + 30% TX 2	ZSK 53	3350	9.10	4.40E-04
EP 1 + 40% TX 2	ZSK 53	4020	5.00	7.70E-04
EP 1 + 30% TX 3	ZSK 53	2980	6.70	1.90E-04
EP 1 + 30% TX 4	ZSK 53	2780	5.70	1.00E-04
EP 2 + 30% TX 1	ZE 25 short	2973	8.80	3.50E+00
EP 2 + 30% TX 1	ZE 25 long	2564	9.80	1.50E+01

that these differences can be explained by different effective particle sizes in the compound which, in turn, influence interparticle distance and interface area.

CONCLUSIONS

The determination of the linear viscoelastic properties of a mineral filled thermoplastic material in the melt appears to provide a quick and reliable way to investigate filler properties and dispersion quality. While the filler loading and particle size can be determined by other routine techniques (i.e., ashing and light scattering methods), only qualitative estimation of the degree of dispersion from microscopic investigations seems possible otherwise. As all three parameters are important for the mechanical properties of the compound, the possibility to get an at least qualitative information from rheological measurements seems very interesting for industrial practice.

Apart from the results presented in this work, investigations have been carried out on various matrix, filler, and kneader systems showing a broad applicability of the method. However, as long as no quantitative relation between the rheological results and mechanical parameters has been established, the method remains a comparative one and experiences gained in the field of compound rheology are indispensable for successful application.

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