

## Rheological Properties of Calcium Carbonate-Filled Polypropylene Melts

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### Synopsis

An experimental study was carried out to investigate the viscoelastic behavior of calcium carbonate-filled polypropylene melts, using the Han slit rheometer. In the analysis of the experimental data, the pressure gradient was used to determine the wall shear stress, and the exit pressure to determine the elasticity of the filled polymers. The study shows that the materials studied follow a power law in viscous behavior over the range of shear rates investigated and that the viscosity increases and elasticity decreases as filler concentration is increased. Also investigated was the effect of temperature on the viscoelastic properties of filled polypropylene melts.

### INTRODUCTION

The rheological characterization of polymeric materials is one of the most important steps in studying the various problems encountered in polymer processing. There are two fundamental rheological properties which are of primary concern in this context; they are the viscous and the elastic properties.

In recent years, intensive activity has been reported in the literature<sup>1-4</sup> concerned with developing filled polymers, for instance, by adding mineral fillers, in order to improve such properties as hardness, high-temperature creep resistance, stiffness, and optical properties, etc., of the finished product. In the plastics industry, fillers are used, in general, to make reinforced plastics. On the other hand, in the rubber industry, the use of fillers (e.g., carbon black) has been the practice for a long time, for reasons somewhat different from those in the plastic industry.

Whatever the purpose of the use of fillers might be, it has long been recognized that an addition of fillers to either thermoplastics or elastomers brings a change in processing conditions. For instance, it is known that an addition of fillers increases the pressure drop across the die, due to the increase in melt viscosity, whereas it gives rise to less die swell, indicating that elasticity of the melt is decreased. The decrease in melt elasticity can raise the critical shear rate at which melt fracture starts to occur, and therefore an increase in throughput may be brought about.

Unfortunately, however, there have been only a few quantitative studies reported<sup>5-7</sup> which attempted to explain the role fillers play in the flow behavior of viscoelastic polymer melts.

The purpose of this paper is to present our recent measurements of the viscoelastic properties of calcium carbonate-filled polypropylene melts.

## EXPERIMENTAL

For the measurement of rheological properties, use was made of the Han slit rheometer, which was constructed in connection with the earlier research programs of the author.<sup>8</sup> The slit die used is 3.28 in. long, and it has a slot opening of 0.1 in. by 1.0 in. Details of the die design and operating procedure of the rheometer are given in a previous paper.<sup>8</sup>

Briefly mentioned, measurements were taken of wall normal stresses of a filled polymer melt flowing through a slit die, which was maintained at a constant temperature by means of an automatic temperature controller. The measurements of wall normal stress permit one to determine both the viscous and elastic properties of the materials investigated. Methods for analyzing experimental data are given in earlier papers by Han.<sup>8,9</sup>

Polypropylene (Enjay Chemical, Resin E115) and calcium carbonate (Camel-Wite from H. T. Campbell & Sons) were melt blended by means of a twin-screw compounding machine (ZSK 53/L, Werner & Pfleiderer Corp.). The filler concentrations chosen were 10, 20, 40, and 70 wt-%. The ZSK twin-screw extruder is a convertible design based on the building block principle, consisting of two screw shafts arranged side by side. The homogenizing of the material is achieved by conveying and kneading with screw bushings and kneading elements assembled. The material is discharged through a die plate and into a water bath. The strands quenched in the water bath are then cut into pellets.

Measurements were taken at three temperatures (180°C, 200°C, and 220°C) for four composite materials of different filler concentrations. Measurements were taken, also, for two base polypropylenes, one as received from the manufacturer and the others as extruded in a twin-screw compounding machine. This was done in order to investigate the extent of shear degradation, if any, of the material which had gone through the twin-screw compounding machine.

## RESULTS AND DISCUSSION

### Viscous Behavior of Filled Polymers

Figure 1 gives representative pressure profiles of the 10% CaCO<sub>3</sub>-filled polypropylene at 200°C. Similar pressure profiles were also obtained for samples with higher filler concentrations, but space limitation here does not permit us to present those results. It is seen from Figure 1 that, at a given rate, a constant pressure gradient ( $-\partial p/\partial x$ ) is obtained along the die axis,

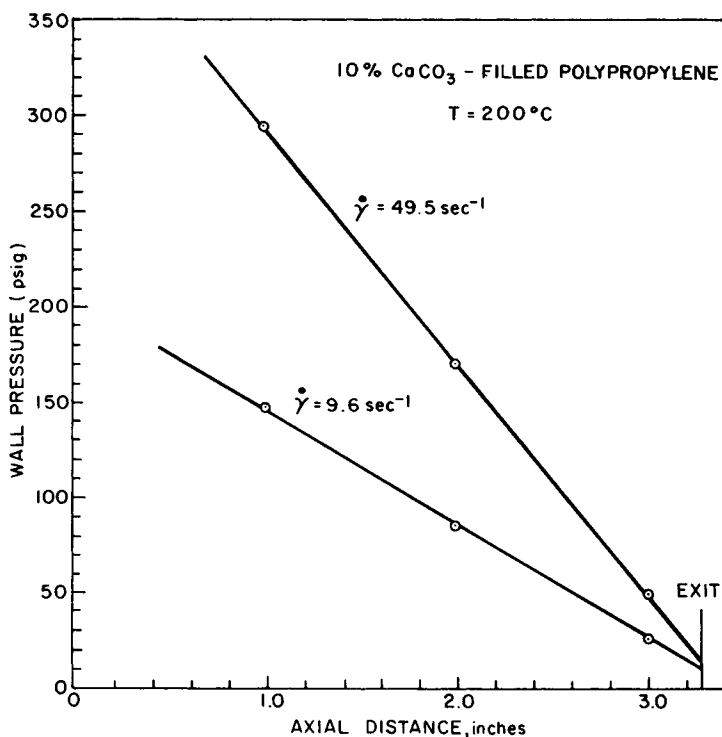


Fig. 1. Representative pressure profiles of 10%  $\text{CaCO}_3$ -filled polypropylene.

and that the extrapolation of the pressure profiles to the die exit gives exit pressures consistent with earlier studies for other polymeric materials.<sup>8,10,11</sup>

Once the constancy of the pressure gradient ( $-\partial p/\partial x$ ) is obtained in the flow channel, one can construct flow curves by calculating true wall shear stress from the expression

$$\tau_w = \left( \frac{-\partial p}{\partial x} \right) \frac{h}{2}. \quad (1)$$

Figure 2 shows flow curves for the filled polymers investigated at 200°C. Note that in constructing the flow curves, we used the true shear rate, obtained with the aid of the well-known Rabinowitch-Mooney correction:

$$\dot{\gamma} = \left( \frac{2n+1}{3n} \right) \frac{6Q}{wh^2} \quad (2)$$

where  $Q$  denotes the volumetric flow rate;  $w$ , the slit width;  $h$ , the thickness of the slit; and  $n$  is defined by

$$n = d \ln \tau_w / d \ln \left( \frac{6Q}{wh^2} \right). \quad (3)$$

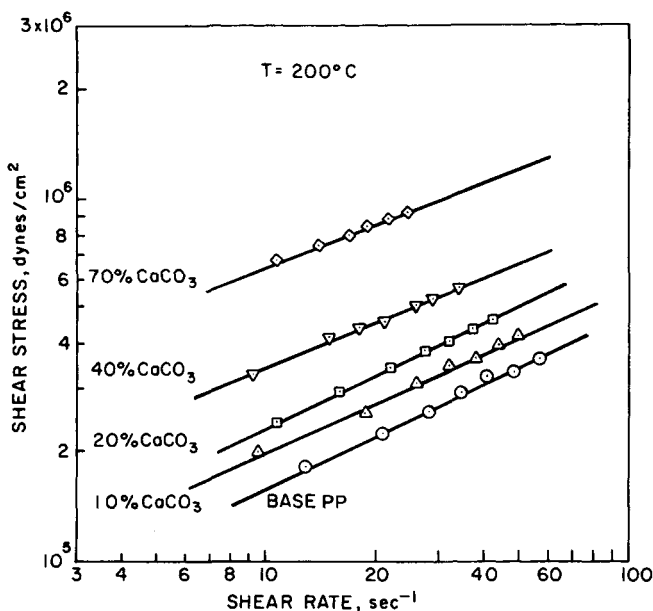


Fig. 2. Flow curves of  $\text{CaCO}_3$ -filled polypropylenes.

It is clearly seen from Figure 2 that the filled polymers investigated follow a power law,

$$\tau_w = K\dot{\gamma}^n \quad (4)$$

over the range of shear rates tested. Note that the shear rates tested in the present study were not low enough to exhibit yield stress of the filled polymers. Earlier studies<sup>4,6</sup> have shown that filled polymers exhibit yield stress in the flow curves when tested at very low shear rates. At present, a study is underway to investigate the effect of filler concentration on the yield stress of  $\text{CaCO}_3$ -filled polypropylene, using a Weissenberg rheogoniometer.

It is seen in Figure 2 that as the filler concentration is increased, the flow curve moves upward. In other words, at a fixed shear rate, a material having high filler concentration exhibits larger shear stress than a material with low filler concentration.

It is interesting to compare the flow curves presented in Figure 3 for the two base polypropylenes, one as received from the manufacturer and the other as extruded in a twin-screw compounding machine. It is seen that the material which had gone through the machine exhibits a shear stress considerably lower than the material as received from the manufacturer. This indicates that considerable shear degradation occurred when polypropylene passed through the screw bushings and kneading elements assembled in the compounding machine. Although the machine gives an intimate mixing of a base polymer with filler, it causes a breakdown of long-chain molecules, which can be detrimental to obtaining certain desirable

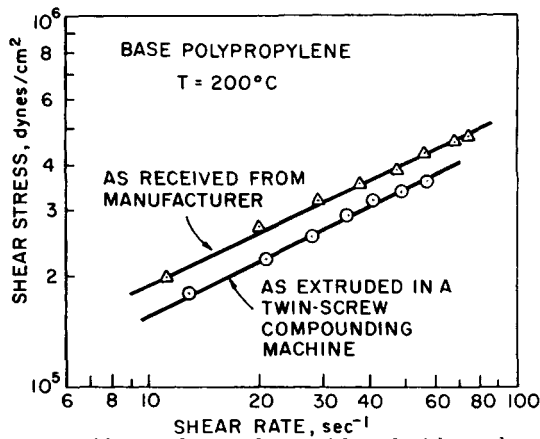


Fig. 3. Flow curves of base polypropylenes with and without shear degradation.

mechanical properties in the final product. It should be noted at this point that different amounts of shear degradation may have occurred with the different compositions of the sample tested.

**Effects of Filler Concentration and Temperature on Viscous Property**

Figure 4 gives plots of viscosity versus shear rate for the filled polymers investigated at 200°C. It is seen that, as expected, the viscosity increases with filler concentration. Similar plots are given in Figures 5 and 6 at 180°C and 220°C, respectively. It is seen also that melt viscosity decreases with temperature.

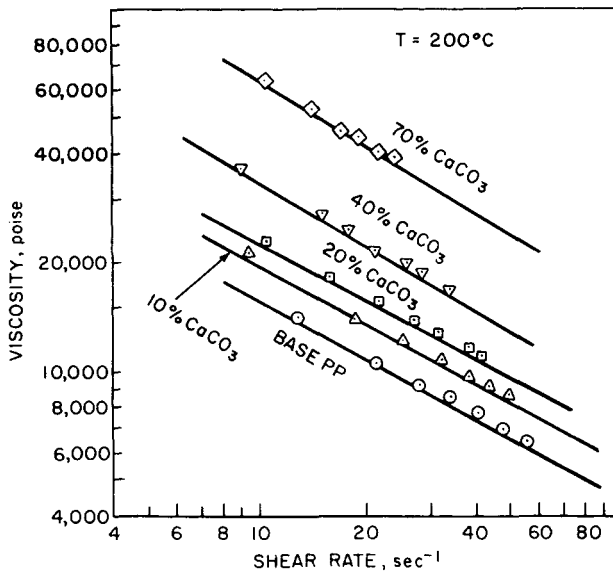


Fig. 4. Viscosity vs. shear rate for CaCO<sub>3</sub>-filled polypropylene melts at 200°C.

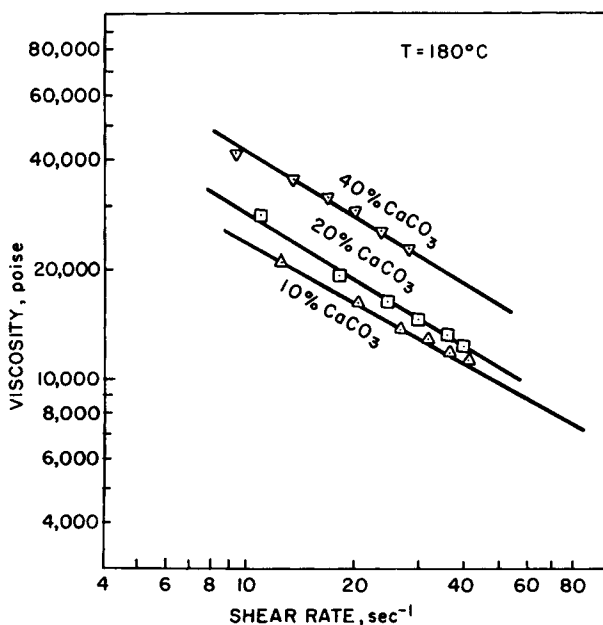


Fig. 5. Viscosity vs. shear rate for  $\text{CaCO}_3$ -filled polypropylene melts at 180°C.

In order to observe the temperature dependence of the viscosity, plots of  $\log \eta$  versus  $1/T$  are prepared, as given in Figure 7. It is seen that, over the range of shear rates (and hence shear stress) tested, the slopes of the plots are almost constant for samples of different filler concentrations,

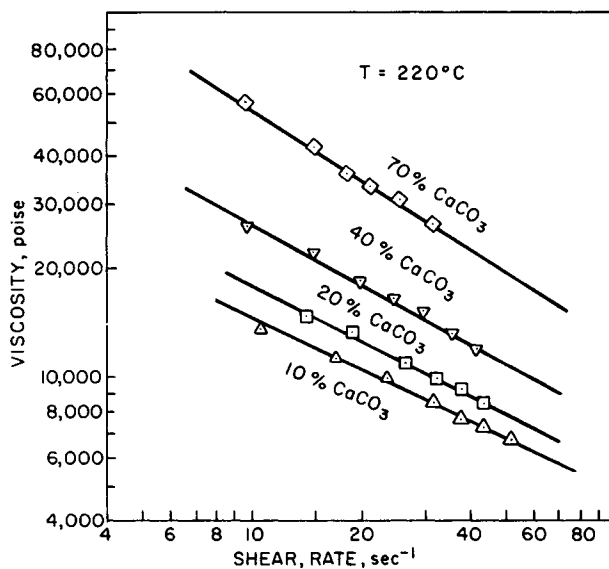


Fig. 6. Viscosity vs. shear rate for  $\text{CaCO}_3$ -filled polypropylene melts at 220°C.

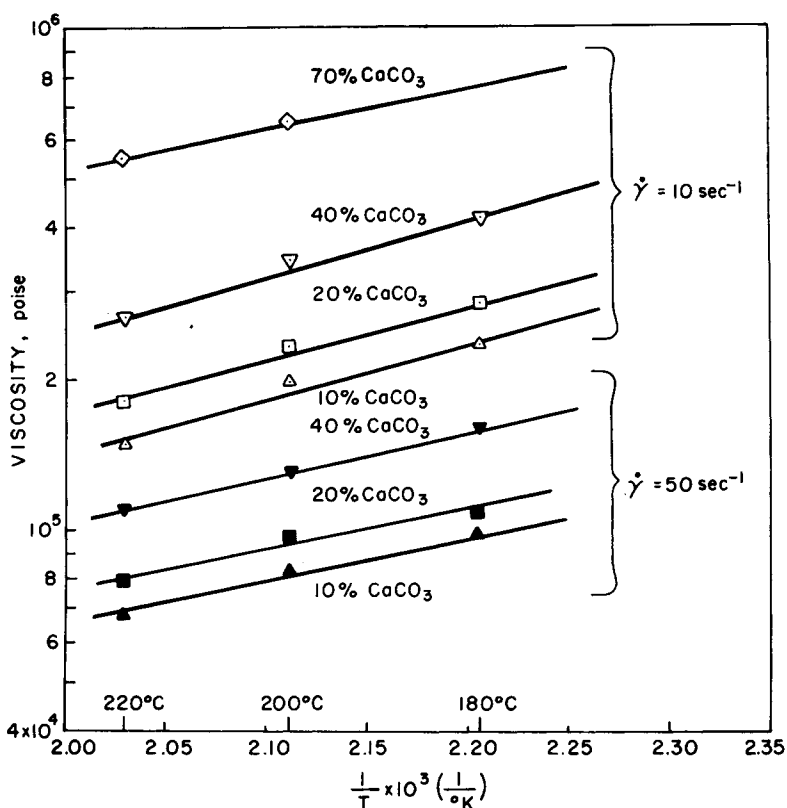


Fig. 7. Viscosity vs.  $1/T$  for  $\text{CaCO}_3$ -filled polypropylene melts.

indicating that the activation energy of the viscous flow of  $\text{CaCO}_3$ -filled polypropylene is almost independent of filler concentration. This result is in agreement with that of Vinogradov et al.<sup>5</sup>

### Effect of Filler Concentration on Elastic Property

Figure 8 shows plots of the exit pressure versus shear stress for  $\text{CaCO}_3$ -filled polypropylene melts at  $200^\circ\text{C}$ . According to Han,<sup>8,10,11</sup> the exit pressure manifests the existence of elasticity in a material. It is seen in Figure 8 that for a given material the exit pressure increases as the shear stress increases and that at a fixed shear stress the exist pressure decreases as the filler concentration increases.

According to the recent theory of Han,<sup>9</sup> exit pressures in polymer melt flow can be used to calculate the first normal stress difference  $\tau_{11} - \tau_{22}$  from the following expression:

$$\tau_{11} - \tau_{22} = P_{\text{exit}} + \tau_w \frac{dP_{\text{exit}}}{d\tau_w}. \quad (5)$$

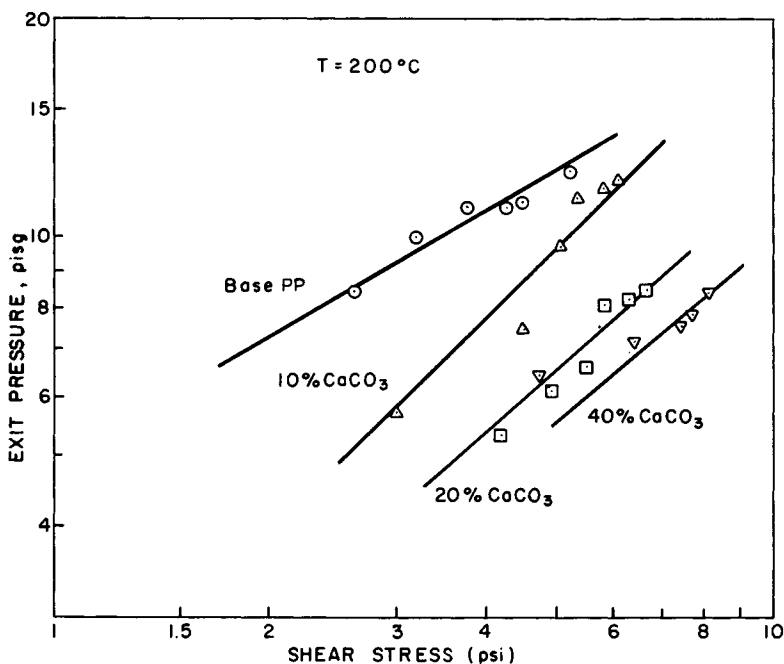


Fig. 8. Exit pressure vs. shear stress for  $\text{CaCO}_3$ -filled polypropylene melts.

Figure 9 shows plots of the normal stress difference versus shear rate for the filled polymers investigated. Again, it is seen that, as expected intuitively, the normal stress difference decreases as the filler concentration increases.

That polymers with high filler concentrations are less elastic than those with low concentrations can be explained by the fact that the filler itself increases the rigidity of the system. The increase in rigidity implies less

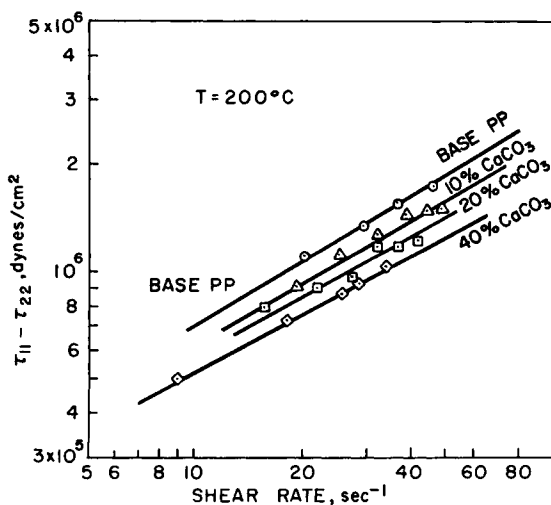


Fig. 9. Normal stress difference vs. shear rate for  $\text{CaCO}_3$ -filled polypropylene melts.



mobility of the macromolecular chains under the influence of the applied shear stress. It has been found that 70% CaCO<sub>3</sub>-filled polypropylene exhibits little elasticity. This result is in agreement with the recent study of Vinogradov et al.<sup>6</sup> These authors report that as the proportion of a filler (carbon black) to a polymer (polyisobutylene) was increased, the die swell ratio decreased and the critical shear stress (at which melt fracture starts to occur) increased. The increase in the critical shear stress of a filled system is accounted for by the decrease in elasticity. A most conspicuous example of this observation can be found in the rubber industry, which uses, among other things, a large amount of carbon black as filler. The addition of carbon black to natural rubber, which is otherwise not extrudable, makes extrusion possible. This is because the carbon black reduces the elasticity of the natural rubber.

### CONCLUSIONS

Both the viscous and elastic properties of calcium carbonate-filled polypropylene were determined using the Han slit rheometer. The experimental results indicate that the viscosity increases with filler concentration and that the elasticity decreases with filler concentration. This is in agreement with the results reported in the literature. The present study demonstrates once again the usefulness of the Han slit rheometer for the characterization of filled polymer systems in terms of viscous and elastic properties.

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