

## Effect of Microgels on the Viscoelastic Properties of Poly(dimethylvinylsiloxanes)

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### Synopsis

The course of dynamic viscosity  $\eta'$  and modulus of elasticity  $G'$  curves versus frequency of oscillations  $f$  was compared for poly(dimethylvinylsiloxanes) (PDMVS) samples of similar weight-average molecular weights containing 0.1-0.2% by weight of microgels and free of microgels. It was found that the presence of microgels considerably changes the viscoelastic properties of PDMVS, particularly in the low-frequency range. Only for samples with microgels a linear course of the above-mentioned curves is observed. The content of microgels was determined by the light scattering method, whereas the  $\eta'$  and  $G'$  versus  $f$  values were obtained with the use of the Weissenberg rheogoniometer.

### INTRODUCTION

The presence of microgels in polymer solutions influences many properties of these solutions, which makes a correct and unequivocal interpretation of the measured quantities difficult or even impossible.<sup>1</sup> The probable effects of microgels on the mechanical and processing properties of polymers have been pointed out, too.<sup>1-3</sup> The existence of a correlation between the viscoelasticity of polymers and their microgel content seems reasonable and justified in the light of the known considerable changes in these characteristics caused by differences in molecular weight averages or in the width of molecular weight distribution (MWD).<sup>4,5</sup>

Our results permitted a direct comparison between viscoelastic properties of PDMVS samples containing microgels and those of microgel-free samples. The microgel content was determined by the light scattering method.<sup>6,7</sup> The viscoelasticity of samples was characterized by the relations of dynamic viscosity  $\eta'$  and modulus of elasticity  $G'$  versus frequency of oscillations  $f$ .<sup>8</sup>

### EXPERIMENTAL

#### Light Scattering Measurements

Intensity of light scattering by toluene solutions of PDMVS samples was measured at 25°C with a Sofica 42000 photometer;  $dn/dc$  value was measured with a Brice-Phoenix BP 2000-V differential refractometer. All measurements were performed at  $\lambda = 5460 \text{ \AA}$  (green line of mercury lamp). Solvent and solutions were purified from mechanical impurities by centrifuging in a Phywe-

Pirouette laboratory centrifuge at 23,000 g for 60 min. Calculations were carried out with a Gier digital computer.

### Measurements of Viscoelastic Properties

These measurements were carried out with a Weissenberg rheogoniometer Model R-17 at 25°C by the method of forced oscillations in a wide frequency range with two cone-plate systems: 5 cm diameter, gap angle 2°2'42"; and 2.5 cm diameter, gap angle 2°1'43". Calculations were carried out with a digital computer Type ZAM 21 alpha.

TABLE I  
Characteristics of PDMVS Samples<sup>a</sup>

Sample no.	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_{2w} \times 10^{-3b}$	$\bar{M}_{2w}/\bar{M}_n$	$\gamma, \text{wt-}\%^b$
1	110	10,100	92	223	2.02	0.213
2	109	13,000	118	206	1.89	0.195
12	96	240	2.5			0
3	133	4,000	30	430	3.24	0.091
18	142	400	2.8			0
20	159	450	4.0			0

<sup>a</sup> Number-average molecular weights ( $\bar{M}_n$ ) were calculated from the curves of MWD based on polymer fractionations.<sup>5</sup> Fractions were characterized by viscosity measurements in toluene at 25°C. Viscosity-average molecular weights were calculated from the Haug and Meyerhoff<sup>9</sup> relation  $[\eta] = 8.28 \times 10^{-3} \bar{M}_v^{0.72}$  dl/g. Further details concerning fractionation and calculation of MWD are given in ref. 5. Weight-average molecular weights ( $\bar{M}_w$ ) of the whole samples were determined by the light scattering method with application of normal Zimm plots.

<sup>b</sup>  $\bar{M}_{2w}$  = Weight average molecular weights of the microgel-free polymers;  $\gamma$  = microgel content. The values of  $\bar{M}_{2w}$  and  $\gamma$  were determined by light scattering method without preparative separation of microgels from solutions, by the method of Lange<sup>7</sup> adapted for PDMVS polymer.<sup>8</sup> The presence of large microgel particles in solution has a very slight effect on results of intrinsic viscosity measurements.<sup>1,10</sup> Therefore, we could assume small effect of microgels on  $\bar{M}_n$  values obtained from integral MWD curves constructed based on viscometric measurements for fractions.

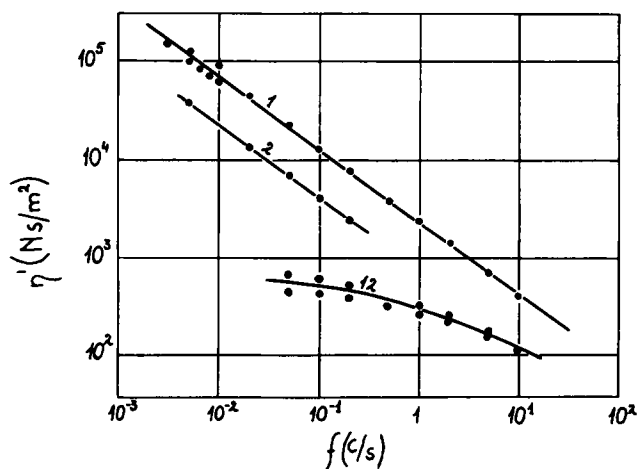


Fig. 1. Dependence of dynamic viscosity  $\eta'$  on frequency of oscillations  $f$  for samples 1, 2, and 12.

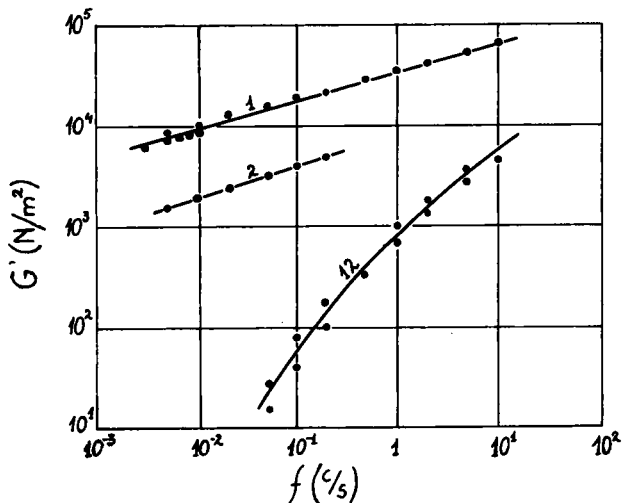


Fig. 2. Dependence of modulus of elasticity  $G'$  on frequency of oscillations  $f$  for samples 1, 2, and 12.

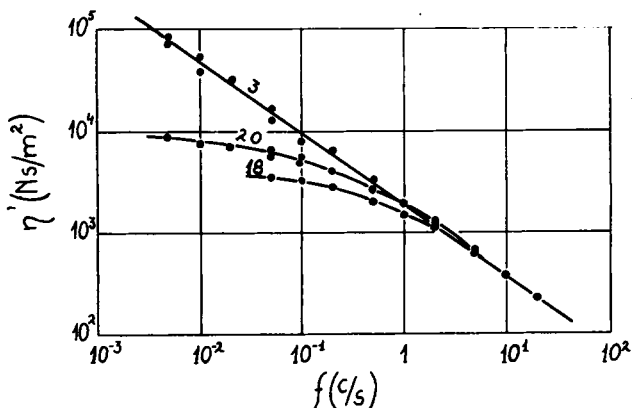


Fig. 3. Dependence of dynamic viscosity  $\eta'$  on frequency of oscillations  $f$  for samples 3, 18, and 20.

The PDMVS samples are characterized in Table I. Samples 1, 2, and 3 were synthesized without a molecular weight regulator, whereas samples 12, 18, and 20 were synthesized with a regulator.<sup>5</sup>

In Figures 1–4, curves of  $\eta'$  and  $G'$  versus  $f$  are compared for microgel-free and microgel-containing samples. Each figure gives curves for samples of similar weight-average molecular weights; in the case of microgel-containing samples, the  $\bar{M}_{2w}$  values were considered.

**RESULTS AND DISCUSSION**

The results presented in Figures 1–4 reveal a pronounced effect of the microgel presence in PDMVS samples on the course of curves describing their viscoelastic properties.

For many microgel-free samples of PDMVS, the slope of  $\eta'$  curves versus  $f$  and  $G'$  versus  $f$  changes with  $f$ , and these curves are distinctly curvilinear, whereas in

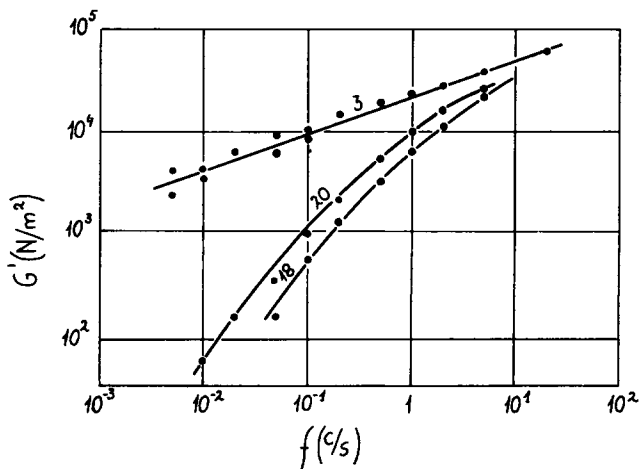


Fig. 4. Dependence of modulus of elasticity  $G'$  on frequency of oscillations  $f$  for samples 3, 18, and 20.

the case of samples with microgels (samples 1, 2, and 3 in Figs. 1–4), curves are linear. Such linearity was found only for three samples (those with microgels) from among 16 samples of PDMVS with different MWD's.<sup>11</sup>

The presence of microgels causes an increase in the measured values of  $\eta'$  and  $G'$  (to a higher degree at lower frequencies) and changes the slopes of curves. For samples with microgels, the average slope of dynamic viscosity-versus-frequency curves is higher, and that of modulus of elasticity-versus-frequency curves is lower than those for microgel-free samples of similar molecular weight. The relative changes in dynamic viscosity with frequency are larger than changes in modulus of elasticity.

Sample 3 has a much higher value of  $\bar{M}_{2w}$  than samples 2 and 1, but the position of  $\eta'$  and  $G'$  curves for sample 3 is not higher than the position of curves obtained for samples 2 and 1 (Figs. 3 and 4). This fact may be attributed to a lower content of microgels in sample 3. Differences between the values of  $\eta'$  and  $G'$  for microgel-containing polymers and microgel-free polymers are much smaller for the set of samples 3, 18, and 20 (Figs. 3 and 4) than for the set of samples 1, 2, and 12 (Figs. 1 and 2).

The considerable effect of small amounts of microgels on the course of  $\eta'$  and  $G'$  curves, observed mainly at low frequencies, is similar to the effect of high molecular weight fractions. For example, Zosel<sup>12</sup> has found that even a small amount of high molecular weight fraction (but not of microgel type) in polyisobutylene melt considerably increases the values of  $\eta'$  and  $G'$ , particularly in the low-frequency range. All  $\eta'$  and  $G'$ -versus- $f$  relations in that work were, however, curvilinear.

The occurrence of this effect of increasing  $G'$  and  $\eta'$  values mainly at low frequencies may be at least partly correlated to the fact that at lower frequencies larger fragments of molecules are displaced than at higher frequencies.<sup>13</sup>

These viscoelastic properties are very important for the processing operations of PDMVS rubbers. The high values of viscosity and of modulus of elasticity in the low-frequency range, as observed for microgel-containing polymers, are equivalent to poorer flowing properties and higher elasticity of such polymers.

Too high a dynamic viscosity and elasticity of these polymers impede their blending with fillers, make the mix brittle, contribute to falling off of the mix from the mixing mill during rolling operation, and prevent easy filling of the molds.

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