Flow Properties of a Linear-Gel Polymer System

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Synopsis

Flow curves (shear stress versus shear rate) were obtained for poly-(ethyl acrylate) containing up to 40% of gel particles over a range of shear rates from 3×10^{-3} to 7×10^{3} sec.⁻¹ with a specially designed biconical rheometer and a standard Instron capillary viscometer. Crosslink density of the gels was varied by emulsion-polymerizing ethyl acrylate with 3, 10, and 30% triethyleneglycol dimethacrylate. Particle sizes were varied by adjusting the concentration of emulsifying agent and by seeding techniques. Samples for study were prepared by blending and co-precipitating the linear and gel latices. The addition of gel always increases the shear stress at a given shear rate. However, this effect is greatest at the lowest shear rates. The flow properties of the gel-containing materials are related quantitatively to those of the linear material through a new parameter, the rate of viscous energy dissipation, and by two material constants. These are a yield stress and a pseudo zero-shear viscosity, both of these being functions of the amount, crosslink density, and particle size of the gel phase.

This investigation is concerned with the changes that the addition of gel to a substantially linear, amorphous polymer bring about in the fundamental rheological properties of the bulk material, and how these changes are related to the improved processing properties of the material. Probably the most important factor in understanding the behavior of these systems is the steady-state viscosity, i.e., the actual relation between shear stress and shear rate over as wide a range as possible.

It has been known that the processing properties of raw rubber could be markedly improved by operations which increased the amount of gel, or crosslinked material, in the polymer. The observed improvements in such properties as reduced swelling on emergence from an extruder die or calender nip, smoother surface finish, better shape retention, and higher extrusion rates are in many ways similar to those produced by the addition of carbon black or other fillers to the rubber. At first thought, this may seem completely contrary to what would be expected from the addition of an essentially nonviscous material to a viscous polymer melt.

^{*} Paper presented before the American Chemical Society Division of Rubber Chemistry, Detroit, April 20-May 1, 1964.

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During World War II and shortly thereafter, most of the work was aimed at improving the processing properties of styrene-butadiene rubber by gelling part of the polymer or by adding a divinylbenzene terpolymer latex to a linear rubber matrix.¹⁻⁵ A high-styrene rubber⁶ or thermoplastic, noncrosslinked polymer particles⁷ were shown to act similarly.

McCabe and Mueller⁸ investigating the flow properties of neoprenes filled with various nonrubber materials concluded that compounds with a lower flow index, that is, the more pseudoplastic ones, exhibited better extrusion properties. They obtained a good correlation between a reduction in die swell and the decreasing flow index.

Commercially, the acceptance of gelled rubbers for superior processing has increased rapidly in the past few years. The rate of production in 1961 was estimated at 3500 tons/yr.⁹ A British patent covers the production of "superior-processing" (SP) rubbers by blending a natural rubber latex containing cured particles, with excess curing agents removed by centrifugation, with an ordinary uncured latex and coagulating them together.¹⁰ Although stable, crosslinked natural rubber latices had been developed long before, ¹¹⁻¹³ they had not been used as processing aids, and the above patent is the basis for the commercially available natural SP rubbers.

Also presently available¹⁴ is a highly gelled natural rubber for mill blending in approximately a 1:3 ratio with both natural and synthetic rubbers to impart superior-processing properties to them. The success of this material in lowering die swell, permitting easier handling and greater resistance to post-extrusion deformation, and allowing a wider range of extrusion temperatures and screw speeds for smooth extrusion, all leading to increased productivity, has been well documented.¹⁴⁻¹⁷

Most producers of styrene-butadiene synthetics now offer a divinylbenzene terpolymer (SBR 1009). A highly gelled powdered nitrile rubber, has also been introduced, and one of its suggested applications is blending with other nitrile rubbers or different synthetics to improve processing properties.¹⁸

Most reports indicate that improvements in processing are obtained at least partially at the expense of certain physical properties of the finished product. However, Burke has claimed the use of a wide variety of vinylic fillers, i.e., crosslinked particles of colloidal size, as highly effective reinforcing fillers in an equally wide variety of rubbers and plastics. He also points out that this reinforcement occurs only when the gel and sol are latex-blended, i.e., when the gel is well dispersed, and cannot be achieved by mill blending.⁷

EXPERIMENTAL

An all-acrylic system was chosen with a linear masterbatch of pure poly (ethyl acrylate). It perhaps should be mentioned that commercial acrylic rubbers are polymerized with about 5% chloroethyl vinyl ether added to the ethyl acrylate^{19,20} to provide reactive sites for vulcanization, but since this investigation is not concerned with vulcanizate properties, this was not done.

The masterbatch polymer had an intrinsic viscosity of 1.27 in benzene at 30°C., indicating an average molecular weight of 310,000 according to the relation of Sumitomo and Hachihama.²¹

Variations in particle diameter for the gelled latices were obtained by varying the amount of surfactant in the emulsion polymerization or by using a seed latex for polymerization. Materials used are summarized in Table I. Triethyleneglycol dimethacrylate (TEGDM) was used in 3, 10, and 30% concentrations.

Poly(ethyl Acrylate) Latexes Used in Flow Experiments							
Sample	Designation	Crosslinking monomer (TEGDM), wt% ^a	Particle diameter, µ	Remarks			
1	Masterbatch	None	_	1% Dodecyl mercaptan			
2	Loose gel	3.0	0.056				
3	Intermediate gel	10.0	0.041				
4)	}		0.080				
5	$\operatorname{Tight} \operatorname{gel} \left. \right\}$	30.0	0.063	Double surfactant charge			
6			0.16	Sample 4 used as seed			
7)			0.30	Sample 6 used as seed			

TABLE I					
Poly(ethyl Acrylate) I	Latexes Used	in Flow	Experiments		

Crosslinking monomer was triethylene glycol dimethacrylate, TEGDM.

All the latices contained 30 + 2% total solids (close to 100% conver-The exact solids content was determined by drying in a vacuum sion). oven overnight at 100°C. In subsequent calculations, the small amount of nonrubber solids present was assumed to be the same in all latices.

Linear and gel latices (roughly 100 g. rubber) were blended in the desired proportions and 1 g. of antioxidant, sym. β -naphthyl-p-phenylenediamine dispersed with a pinch of sodium lauryl sulfate in 10 ml, of water and added to the stirred latex. The system was creamed (but not coagulated) by adding a solution of 200 ml. acetone and 300 ml. water, and finally coagulated immediately upon the addition of an aqueous solution of 12% MgSO₄.

The coagulate was exhaustively washed with water. As much water as possible was squeezed from the crumb, and it was dried in a vacuum oven at 100°C.

The biconical rheometer used in this work combines some advantages of two well-known rheological instruments, the Mooney plastometer and the cone-and-plate viscometer. In the biconical rheometer, the diskshaped rotor of the Mooney plastometer is replaced by a biconical rotor rotating in a disk-shaped cavity, giving essentially two cone-and-plate devices back-to-back, in which the material is molded around the rotor and maintained in the closed cavity between the rotor and the chamber walls.

The shaft of the rotor is driven with a constant torque by hanging weights from a pulley keyed to it, and its rotation is measured as a function of time.

The two platens are machined from solid brass blocks and cored with 1/4 in. holes equipped with pipe nipples and plugs for suitable passage of the temperature-controlling fluid.

Two rotors are used, with diameters of $2^3/_4$ and $1^1/_2$ in. The rotor heads are machined from $1/_4$ -in. stainless steel plate and keyed to shafts of $1/_4$ -in. precision-ground stainless-steel shafting.

For viscosity measurements, the angular deflection of the rotor was measured by a low-torque potentiometer.

Capillary data were obtained with a standard Instron capillary rheometer, in a floor model Instron testing machine. A stock Instron capillary, with L = 1.9995 in. D = 0.050 in. and an entrance angle of 90° was used.

Photomicrographs of the latex particles were taken with a Siemens Elmiskop I electron microscope at a beam strength of 80 kv.

Material was molded at 150°C. into disk-shaped samples for testing in a mold consisting of two 3-in. diameter holes cut in a 1/8-in. thick aluminum sheet by using a hydraulic press.

RESULTS AND DISCUSSION

Flow Curves

The flow curves (shear stress, τ , versus shear rate, $\dot{\gamma}$,) for the master batch and for compounds containing 10, 20, 30, and 40% of three different gels are shown in Figures 1, 2, and 3.

Each curve, covering nearly seven decades of shear rate, consists of three independently measured sections, obtained with the large and small biconical rotors and the Instron capillary rheometer. Both the biconical and Instron data were generally reproducible to within 5%.

The mechanical deficiencies inherent to this type of capillary device, such as pressure drop in the barrel and friction loss between the plunger



Fig. 1. Flow curves for mixtures of highly gelled latex particles of average diameter = 0.08μ with a linear master batch of poly(ethyl acrylate).

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Fig. 2. Flow curves for mixtures of gelled (intermediate crosslink density) latex particles with a linear master batch.



Fig. 3. Flow curves for mixtures of gelled (low crosslink density) latex particles with linear master batch.

and barrel wall have been elaborately discussed elsewhere, and the errors introduced by them shown to be small with careful experimental procedure.²² The interpretation of capillary-flow data has been the subject of many papers in itself. The Rabinowitsch correction²³ was applied to all the capillary data. Extensive previous work indicates that with the high $L/R^*(= 80)$ capillary used, end corrections are quite small.

The agreement shown, while not perfect, is surprisingly good considering the fundamentally different nature of the two types of experiments and the experimental and calculational difficulties involved.

Another factor to be considered in the interpretation of the capillary data is the phenomenon of melt fracture, or distortion of the extrudate emerging from the capillary. Such distortion was usually observed above shear rates of about 200 sec.⁻¹. As is obvious from inspection of the flow curves, however, it introduced no discernible discontinuities to the curves, so data in the region of melt fracture have been included with the understanding that flow in this region is subject to some as yet incompletely understood irregularities. The exact point at which extrudate distortion was noticed is indicated by an arrow on the figures.

The flow curve of the master batch is typical of those observed for polymer melts. At low shear rates it reaches a slope of 45° , with a zero-shear or lower Newtonian viscosity $\eta_0 = 5.3 \times 10^{\circ}$ poise. The slope of the curve decreases continuously with increasing shear rate, and no indications of an increase, or possible upper-Newtonian region, are observed at the highest shear rates.

Inspection of the flow curves immediately reveals some of the effects of adding gel to the master batch. The shear stress (and thus viscosity) at any shear rate is always increased by the addition of gel. Although this increase appears to be fairly constant at shear rates above 10 sec.⁻¹ the curves spread apart at lower shear rates. This effect is more pronounced in the cases of the "tight" (30% TEGDM) and intermediate (10% TEGDM) gels than it is for the "loose" (3% TEGDM) gel. It should be pointed out that these gels differ in particle size as well as crosslink density. These individual factors will be separately discussed later. Another interesting observation to be made is that, except at the lowest concentration of loose gel, the flow curves of none of the materials containing gel appear to approach a region of constant viscosity at the lowest shear rates attainable experimentally. In fact, the data for 30 and 40% intermediate and tight gel show a point of inflection and slight curvature away from the shear-rate axis at low rates.

Since it is generally accepted that polymer melts exhibit a lower-Newtonian region at sufficiently low shear rates, the preceding observation was carefully checked for experimental validity. Friction in the rheometer bearings, leakage around the shaft, crosslinking of the polymer during measurement all were investigated and eliminated as causes. This, together with the usual experimental reproducibility and the regularity of the phenomena with increasing gel content, lead to the conclusion that it is indeed a real property of these materials. Whether or not the curves would eventually reach a Newtonian region at shear rates much lower than those investigated here is not known.

One of the advantages of steady-state rotational viscometry is that such measurements minimize the effects of elasticity. Once steady-state flow has been reached in a rotational device (as it had for all shear stressshear rate measurements considered here), all the elastic response mechanisms should have reached their equilibrium strain, and further deformation should be purely viscous. This would indicate that the observed non-Newtonianism of these materials is not a result of uncorrected elastic effects on the measurements, but is strictly a viscous phenomenon.

Relation of Gel-Containing Materials to Master Batch

An a priori prediction of the flow behavior of gel containing linear polymers appears impossible because no procedures exist, at present, which will allow such predictions for the linear base material alone with any generality over a reasonable range of shear rates. The next line of attack, therefore, seems to be in finding some way of relating the flow properties of the gel-containing materials to those of the linear base material.

As a means for correlating viscosity, the rate of viscous energy dissipation $(\tau \dot{\gamma})$ appears to be a more fundamental parameter than either the shear stress or shear rate alone. This is illustrated by the fact that it is a mathematically even quantity; it is always positive, as is viscosity itself.

When the apparent viscosities (ratio of shear stress to shear rate) for the master batch and the tight gel systems were plotted as a function of $\tau \dot{\gamma}$ on logarithmic coordinates, it was easily seen that, for all data above shear rates of about 1 sec.⁻¹ the curves were parallel, displaced by a constant factor along the (log) viscosity axis. When divided by a zero-shear viscosity (the actual experimental value of 5.3×10^5 poise in the case of



Fig. 4. Flow relations for (1) Bingham plastic, (2) proposed model, (3) Newtonian, and (4) pseudoplastic flow: (---) idealized behavior; (--) actual behavior.

the master batch and an empirically chosen value for the gel-containing materials), the data in the above range were brought into coincidence, within the limits of experimental error. In terms of the flow curves, this procedure corresponds to shifting the curves along a line with a slope of -1.

The remaining fly in the ointment, then, is the "tailing off" of the flow curves at low shear rates. Looking at the curve for 40% tight gel, the impression is created that it might level off at some constant value, or yield stress, if continued to lower shear rates. Upon further consideration, the concept of a yield stress for these materials seems quite reasonable. Such behavior is often observed in the case of slurries of rigid particles in a Newtonian liquid, whose flow properties can be represented by the familiar Bingham plastic model.²⁴ A gel-filled polymer, particularly one in which the gel is fairly rigid, might be expected to show some similarities to these slurries. As with slurries, the yield stress would be expected to depend on the particle size, shape, and concentration, but in the case of gel-filled polymers, the rigidity of the filler should have some influence also, and a



Fig. 5. Master curve relating the viscous flow properties of gel-containing materials to those of the linear material.



Fig. 6. Yield stress τy as a function of gel fraction ϕ .

pseudoplastic rather than the linear shear-stress rate relation of the Bingham plastic should be observed when the yield stress is exceeded.

Based on the preceding considerations, a model has been developed to represent the viscous behavior of gel-filled amorphous polymers. It is proposed that the addition of gel influences flow in two independent ways: by introducing a yield stress, τ_y , which must be overcome before any viscous flow occurs, but once overcome, the net stress, $\tau' = \tau - \tau_y$, governs the flow, and by increasing the net viscosity, $\eta' = \tau'/\dot{\gamma}$, by a constant factor over that of the base material at any given value of the net viscous energy dissipation per unit volume, $\tau'\dot{\gamma}$. This implies that some sort of structure is formed by the gel below the yield stress, and that a certain amount of the applied energy is used to keep this structure broken up, and that the gel further hinders (by a constant amount) the ability of the remaining energy to produce the molecular slippage required for the viscous flow. The various flow relations discussed are qualitatively illustrated in Figure 4.



Fig. 7. Relative viscosity η_{rel} vs. gel fraction ϕ , where η_{rel} is the ratio of the pseudo zero-shear viscosity of the gel-containing material to the zero-shear viscosity of the linear master batch.

The success of the proposed model in representing the data for the tight gel materials over the entire experimental range is shown in Figure 5. From such a master curve, obtainable from the base material alone, the viscous behavior resulting from the addition of a given amount of gel to the base material can be predicted with the knowledge of two parameters for the gel-containing material, yield stress and the pseudo zero-shear viscosity, η_0 . The model fails at very low stresses when the actual behavior begins to deviate from the idealization as shown in Figure 4.

Figures 6 and 7 summarize the values of yield stress and pseudo zeroshear viscosity obtained for the three gel series. It is seen that adding gel increases both the yield stress and zero-shear viscosity. The pseudo zero-shear viscosity seems to rise up to 20% gel, level off slightly between 20 and 30%, and then rise rapidly above 30%. This behavior may tentatively be ascribed to the gel particles hindering the slippage of the matrix molecules at low concentrations, while at high concentrations, interactions between the gel particles themselves provide an increasingly serious hindrance to flow.

There has been much theoretical work done on the problem of the bulk viscosity of suspensions of various types of particles. As far back as 1920, Einstein presented a relation for the relative viscosity of dilute suspensions of rigid, spherical particles in a Newtonian liquid:

$$\eta_{\rm rel} = 1 + 2.5\phi \tag{1}$$

where ϕ is the volume fraction of particles.²⁵ There have since been many attempts to extend the relation to more concentrated suspensions, generally by adding terms of higher powers of ϕ .²⁶ It is significant that these relations all show the relative viscosity to depend only on ϕ and not in any way on the particle size.

(For the materials considered here, the densities did not vary significantly with the amount or kind of gel, so the weight and volume fractions may be considered equal.) Considering the fact that the diameters of the gel particles approach the order of magnitude of the extended chain length of the matrix molecules, and that the pseudo zero-shear viscosities are not actual, experimentally determined zero-shear viscosities, it is not too surprising that these equations do not represent the data very well. However, for the tight gel series, which should most closely approximate the rigid sphere model, the data appear to approach asymptotically the Einstein (and other) relations below $\phi = 0.1$.

The data for the less rigid particles fall below the Einstein relation at low ϕ . Attempts to derive similar equations for spherical particles with elasticity of shape involve the noninteraction of particles assumption,²⁷ giving relations linear in ϕ . This is not consistent with the data over the experimental range, but with proper choice of parameters, can predict values below those of the Einstein relation.

We must conclude that there does not now appear to be any way to predict quantitatively the pseudo zero-shear viscosities over a reasonable range of gel loading.

A similar situation prevails for the yield stress. The yield stress increases fairly regularly with gel content up to $\phi = 0.3$, after which it shoots up rapidly. This rapid rise corresponds to that noted for η_0' in the same concentration range, lending credence to the belief that an interaction of the gel particles is becoming the dominant factor in this region.

Photomicrographs revealed the two largest particle latices to have particles which did closely approach the "billiard-ball" ideal. The size distribution was quite narrow, in general only about a twofold variation being observed, so it was felt that a simple arithmetic average of the measured diameters of at least fifty particles would serve to represent the particle size adequately in view of the measurement difficulties.

Particle diameter, µ	Yield stress τ_y dynes/cm. ²	Pseudo-zero shear viscosity 70, poise	
0.063	6×10^3	8.3 × 10 ⁵	
0.080	$3.5 imes 10^3$	8.9×10^{5}	
0.16	0	9.1×10^{5}	
0.30	0	$1.28 imes10^{5}$	

TABLE II

Effect of Particle Size on Yield Stress And Pseudo-Zero Shear Viscosity (20% by Weight of Tight Gel in Linear Master batch)

The particles produced by primary polymerization were not nearly so uniformly spherical as were those from the seeded latices. In general, some were roughly eliptical, with ragged edges, the raggedness and nonuniformity increasing with decreasing particle size and crosslink density. Such particles might be expected to interact more strongly than those with smooth, hard surfaces. In the case of nonuniform particles, the major and minor diameters were averaged. The range of sizes was similar to that observed with the large particles.

As shown in Table II, the pseudo zero-shear viscosity increases slightly with increasing particle size. The increase is so slight, in fact, that it borders on the edge of experimental resolvability, but it is regular with particle size and so seems to be real. It will be remembered that relations for rigid spherical particles predicted no dependence on particle size.

The major effect of particle size, then, is on the yield stress, and it is seen that the yield stress increases with decreasing particle size. The previously mentioned study of aqueous slurries showed the yield stresses to decrease with the square of the particle size, and the two yield stresses large enough to be determined by the methods used here conform closely to such an inverse-square relation.

While two data points certainly do not confirm the relation adequately, the yield stresses for the three different gel crosslink densities are given in Table III, corrected to a common particle size of 0.1μ by the inversesquare relation for purposes of comparison. In any event, the results observed can be deduced qualitatively, and clearly show that the yield stress increases with the crosslink density (i.e., nondeformability) of the gel at constant loading and particle size. This might be expected, since the limit of no crosslinking represents an ordinary linear polymer, perhaps with a high molecular weight component, which should exhibit the usual type of flow curve with no yield stress. It is possible, however, that nongelled particles with a molecular weight high enough to maintain their identity under stress by a large number of interchain entanglements acting like crosslinks would behave like gel particles when in a matrix of lower molecular weight polymer.

	Yield stress, dynes/cm. ²			
	10 wt% gel	20 wt% gel	30 wt% gel	40 wt% gel
Tight gel	1.0×10^{3}	2.2×10^{3}	5.1×10^{3}	$7.7 imes 10^3$
Intermediate gel		$0.67 imes 10^3$	2.0×10^3	$7.6 imes10^3$
Loose gel	0	$0.31 imes 10^3$	0.66×10^{s}	$5.0 imes10^3$

TABLE III Yield Stresses Corrected to Common Diameter of 0.1 μ

In summary, it has been shown that both increases in particle size and crosslinking produce a slight increase in the pseudo zero-shear viscosity, the effect of crosslink density probably being a little greater. The yield stress, however, shows a strong inverse dependence on the particle size. Significant values were obtained only below a particle size of about 0.1 μ . The yield stress also increases substantially with particle crosslinking in the range of practical interest (up to 30% gel). Increasing the gel content appreciably increases both the yield stress and pseudo zero-shear viscosity, provided the particles are small and hard enough. It also appears that the

break point, where the flow curve begins to deviate from the proposed model and drop off toward the origin, depends on the tightness of the gel. The tighter the gel, the more closely the filled materials approach a true yield stress. Thus, the model fails at the highest shear rates for the intermediate gels, which by virtue of their small particle size have a high yield stress and a long way to drop off to reach the origin, causing the drop-off to begin at relatively high shear rates (see Fig. 4). This effect is masked by the inherently low yield stresses (arising from low crosslink density) at 10, 20, and 30% loose gel, but is again apparent where the high (40%) gel constant raises the yield stress.

The authors wish to thank Mr. Walter Lehmann for taking the electron photomicrographs used for particle size determination. Part of the support for this work came from the Ford Foundation.

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Résumé

Des courbes d'écoulement (tensions de cisaillement en fonction de la vitesse de cisaillement) sont obtenues pour le polyacrylate d'éthyle contenant plus de 40% de particules de gel dans un domaine de vitesses de cisaillement de 3×10^{-3} à 7×10^{3} sec⁻¹, au moyen d'un rhéomètre biconique et d'un viscosimètre capillaire 'Instron' standard. La densité du pontage des gels a été modifiée par une polymérisation en émulsion de l'acrylate d'éthyle avec 3, 10 et 30% de diméthacrylate de triethylèneglycol. Les dimensions des particules sont modifiées par ajustement de la concentration en agent émulsifiant et par des techniques d'ensemencement. Les échantillons à étudier sont préparés en mélangeant et coprécipitant les réseaux linéaires et les gels. L'addition de gel augmente toujours la tension de cisaillement pour une vitesse de cisaillement donnée. Cependant, cet effet est plus grand pour des vitesses de cisaillement plus faibles. Les propriétés d'écoulement des échantillons contenant du gel sont reliées quantitativement à celles des substances linéaires par un nouveau paramètre, la vitesse de dissipation de l'énergie visqueuse et par deux constantes du matériau. Celles-ci sont la tension à la limite d'élasticité et la viscosité à vitesse de cisaillement nulle; elles sont fonctions de la quantité de gel, de la densité du pontage et de la dimension des particules de gel.

Zusammenfassung

Flieusskurven (Scherspannung gegen Schergeschwindigkeit) wurden an Polyäthylacrylat mit bis zu 40% Gelteilchen in einem Schergeschwindigkeitsbereich von 3×10^{-3} bis 7×10^{3} sec⁻¹ mit einem speziell gebauten bikonischen Rheometer und einem Standard-Instronkapillarviskosimeter erhalten. Die Vernetzungsdichte der Gele wurde durch Emulsionspolymerisation von Äthylacrylat mit 3, 10, und 30% Triäthylenglycoldimethacrylat variiert. Die Teilchengrösse wurde durch Anpassung der Emulgatorkonzentration und durch ein Keimungsverfahren variiert. Die Proben für die Untersuchung wurden durch Mischung und gemeinsame Fällung der linearen und Gel-Latizes dargestellt. Zusatz von Gel führt immer zu einer Erhöhung der Scherspannung bei einer gegebenen Schergeschwindigkeit. Der grösste Einfluss besteht bei der niedrigsten Schergeschwindigkeit. Die Fliesseigenschaften der Gel enthaltenden Stoffe stehen zu denjenigen des linearen Stoffes durch einen neuen Parameter, die Geschwindigkeit der viskosen Energiedissipation, und durch zwei Stoffkonstanten in quantitativer Beziehung. Diese Konstanten sind eine Grenzspannung und eine auf Null reduzierte Scherviskosität, die beide Funktionen der Menge, der Vernetzungsdichte und der Teilchengrösse der Gelphase sind.

Received July 16, 1964