Suspending Potential of Gum Systems and Their General Flow Properties

By GREGORY CATACALOS and JOHN H. WOOD

Plotting of the logarithm of shear stress against logarithm of shear rate should be used to recognize whether the rheogram of a pseudoplastic gum system will become Newtonian or display a yield value at zero shear rate. Either Fitch or Casson plots give a reasonable measure of the yield value, although in general neither are found to hold rigidly. Rheograms may also be used to determine an index of pourability by considering the torque at some suitable higher shear rate. In this work a pourability index is defined as the logarithm of the torque at 50 seconds^{-1}. Since Chong has shown yield value to be a measure of suspending capability, suspendability is similarly defined as the logarithm of yield value. Increasing gum concentration generally leads from Newtonian to semipseudoplastic to pseudoplastic behavior. Yield value only occurs as a limiting case following this transition. The addition of a second agent such as Cab-O-Sil can develop the yield value at levels where neither it nor the other gum displays such behavior. A plot of yield value against concentration shows clearly that there is a critical concentration required to develop this parameter. A plot of yield value against pourability index permits a relative assessment of the suspendability obtainable for a given pourability. These plots, or tables derived from them, facilitate the choice of the most suitable gum system to give a desired degree of suspending capability.

THICKENED SYSTEMS suitable for the stable suspension of insoluble particles of pharmaceutical value have two rheological shear rate regions of practical importance. The moderate shear rate range, 20 to 100 seconds^{-1}, may be considered (1) the region of pouring. The other, the very low shear rate range, defines the existence of absence of a yield value term. Earlier, the importance of yield value for the permanent suspending of such diverse systems as golf balls, marbles, and sand was shown clearly (2) and the possible relation between yield value and sedimentation considered (3). More recently, Chong (4) demonstrated clearly the relationship between the suspending medium and the suspended particle in terms of minimum yield value required to prevent motion of particles of various radii and relative density gradients. He demonstrated the applicability of yield value as a criterion of suspendability (4, 5).

In the study of rheological curves as normally obtained, there is frequently a problem in extrapolation from low shear readings to a yield value. Several methods of yield value extrapolation have been presented in the literature. Normally these are stress (S) *versus* shear rate (D) curves (6), from S *versus* $D^{1/2}$ plots (7), and from $S^{1/2}$ *versus* $D^{1/2}$ plots (8). The latter two have been justified on theoretical grounds by their originators. Hereafter the latter two will be designated as Fitch and Casson plots, respectively. An alternate to graphical procedures has been the use of yield values calculated from equations of state (9). In general, this procedure is too laborous to be of practical value.

Suspending systems which display yield value character tend to be non-Newtonian, specifically pseudoplastic, with increasing shear. Accordingly, for each system a different shear dependency exists, so that materials of similar apparent viscosity at low shear rates can have notably different apparent viscosities at higher shear rates.

It, therefore, seemed desirable to set up from a direct plot of rheological curves parameters which permit the recognition and determination of yield values and pourability.

EXPERIMENTAL

All rheological studies were made at 25° on either the modified Brookfield LVT or the RVT as described elsewhere (10). Although ascending and descending rheograms were run, only the ascending rheograms are considered here since yield value suspension is a static force before flow, and pouring involves no shear in excess of that conveyed by that action. Of course, if pouring into another container for storage is involved and yield value recovery is not rapid, obviously this must be kept in mind in the rheological pattern of measurement. All data were plotted on logarithmic paper. Four basic types of rheograms are obtained and are shown in Fig. 1. First are those curves of type A; these are of slope unity and are therefore by definition, Newtonian, the intercept being the viscosity. The second, type B, is also linear through the range of operations and typifies the Power law behavior $T = k\ D^n$, where k is the intercept and n is the slope. As long as the Power law is obeyed, there is no yield value. In the type C is the well-known behavior of many pseudoplastic systems, the shifting to Newtonian at low shear rates. In general, any downward curvature from a type B toward a type C plot will yield a limiting slope of unity. The last, type D, displays

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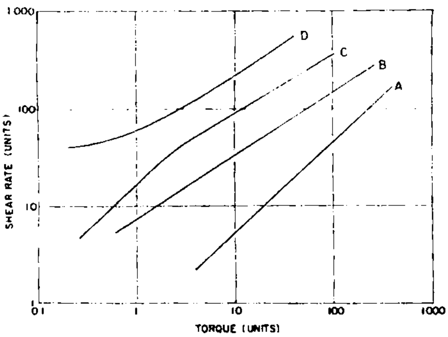

Fig. 1.—Basic classifications of rheograms. Key: A, Newtonian; B, typical Power law; C, Power law going Newtonian; and D, Power law with yield value.

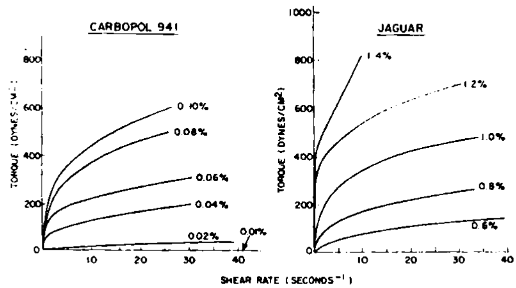

Fig. 2.—Rheograms of Carbopol 941 and Jaguar as a function of concentration.

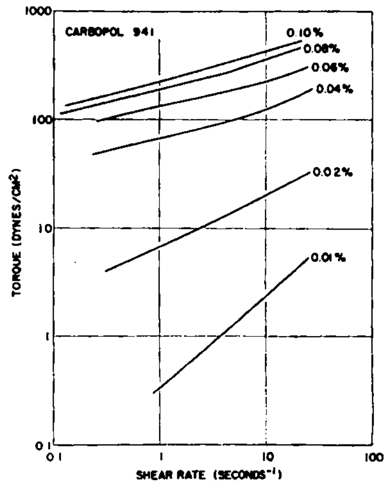

Fig. 3.—Logarithmic plot of Carbopol 941 rheograms.

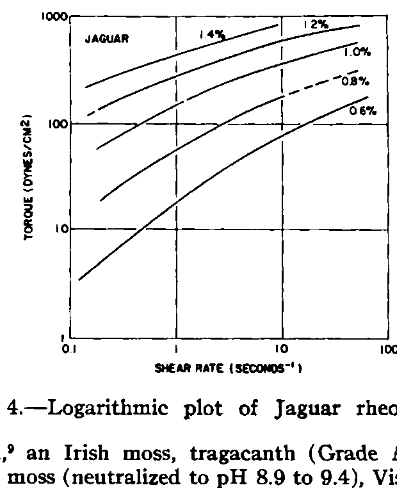

Fig. 4.—Logarithmic plot of Jaguar rheograms

curvature upwards from B and is a mathematical necessity for a definite yield value to exist, regardless of the extrapolation procedure to be used to determine that value.

A shear rate of 50 seconds^{-1} for pouring was taken as an arbitrarily suitable one from Henderson's estimates (1). Now both Scott-Blair (11) and Fryklof (12) have shown that the logarithm of the viscosity is directly related to the subjective evaluation of the consistency of a lotion or paste. Since apparent viscosity is directly proportional to shear stress for any shear rate, the logarithm to the base 10 of the shear stress at 50 seconds^{-1} was defined as the pourability index. Thus, an index of 2 has a viscosity of 2 poises, of 3, 20 poises, and of 3.5, 60 poises. This is the range of medium oils or of chilled 90 to 100% glycerol.

The composition of the gum systems examined rheologically and the essential elements of their preparation are given in the following paragraph. All solvent to gum ratios are on a w/w basis. Either Sorbo[1] (70% sorbitol)-water mixtures or glycerol-water mixtures were used, depending on the implication from the manufacturer's literature as to the preferred system with that gum. No attempt was made to use the same gum in both solvents.

All gum systems were hot hydrated with adequate stirring and then diluted to the desired concentrations. Where the pH was not in the neutral range when finished, the individuals were adjusted in pH as noted. Carbopol 941,[2] a cross-linked synthetic polymer, in water to Sorbo ratios of 40/60, 50/50, 60/40, 70/30, and 80/20 (pH adjusted to 7); the same in 50/50 with 0, 0.5, and 1.0% Cab-O-Sil,[3] a pyrogenic silica (pH adjusted to 7); carboxymethylcellulose (CMC 12 HP[4]) in 50/50 glycerol–water with 0, 0.25, 0.5, and 1.0% Cab-O-Sil; the following in 50/50 water–Sorbo: Guartec GF[5] and Jaguar[6] (neutralized to pH 8.9) both guar gums; the following in 50/50 water–glycerol: karaya,[7] a guar gum (neutralized to pH 8.9), Kelcosol,[8] a sodium alginate, Keltose,[8] an ammonium calcium alginate, Sea-Kem,[9] an Irish moss, tragacanth (Grade A),[7] an Irish moss (neutralized to pH 8.9 to 9.4), Viscarin,[9] a carrageenan, and TIC Colloid-600,[10] a sulfated Irish moss. The latter was hydrated at temperatures of 25, 40, and 60°, since cold hydration was implicitly possible.

RESULTS

Figure 2 shows typical rheograms for two gum systems, neutral Carbopol 941 and Jaguar as a func-

[1] Atlas Chemical Industries, Wilmington, Del.
[2] B. F. Goodrich Company, New York, N. Y.
[3] Godfrey L. Cabot, Inc., Boston, Mass.
[4] Hercules Powder Company, Wilmington, Del.
[5] General Mills, Inc., Minneapolis, Minn.
[6] Stein Hall & Company, Inc., New York, N. Y.
[7] S. B. Penick & Company, New York, N. Y.
[8] Kelco Company, New York, N. Y.
[9] Marine Colloids, Inc., New York, N. Y.
[10] Tragacanth Importing Company, New York, N. Y.

tion of gum concentration. Figures 3 and 4 show the corresponding logarithmic plots. These are of the type D for Carbopol 941 and type C for the Jaguar. In Figs. 5 and 6 these two gum systems are shown in both the Casson and Fitch plots. In Fig. 5 the yield value is clearly apparent, while in Fig. 6 the torques at shear rates below 4 seconds^{-1} suddenly drop off toward zero. The data from the various gum systems were treated similarly. Unless noted, the data reported are usually for 2 days after making of the mucilage. In the systems studied, in no case was a time of aging dependency noticed within the first 10 days.

Table I shows the effect on the yield value and pourability index for two of the Carbopol 941 concentrations of the variation in the ratio of water to Sorbo used.

In Table II the result of the addition of Cab-O-Sil on the rheological parameters is given. Its addition developed yield value and raised the pourability index.

The CMC systems become Newtonian at low shear rates, thus displaying type C properties. The addition of Cab-O-Sil raises the limiting zero shear rate viscosity until finally a yield value appears (see Table III). This is paralleled by a raising of the pourability index.

With karaya no yield value character was observed. With Tragacanth and Jaguar the curves extrapolated to yield values by both procedures, although the behavior was in curve C of Fig. 1. In all gum systems but CMC, increasing concentration resulted in a shift from Newtonian character toward pseudoplastic at low shears with the subsequent evolution at higher concentrations, except for karaya, of a yield value.

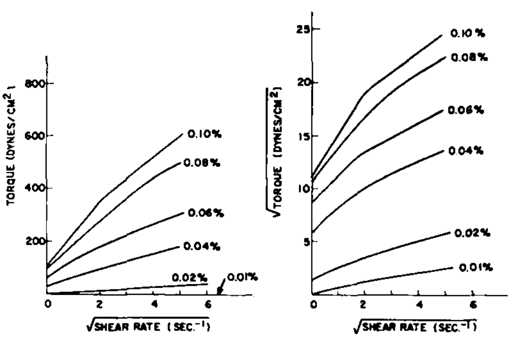

Fig. 5.—Fitch (left) and Casson (right) plots of Carbopol 941 rheograms.

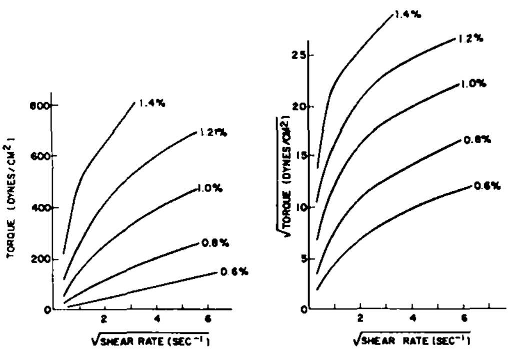

Fig. 6.—Fitch (left) and Casson (right) plots of Jaguar rheograms.

TABLE I.—EFFECT OF RATIO OF WATER TO SORBO ON YIELD VALUE AND POURABILITY INDEX OF TWO CONCENTRATIONS OF CARBOPOL 941 (NEUTRAL), MEASURED AT 4 HOURS AFTER MAKING

Ratio Water/ Sorbo	Yield Value (dynes/cm.²) 0.04%	0.08%	Pourability Index 0.04%	0.08%
40/60	11	80	2.14	2.79
50/50	32	97	2.38	2.81
60/40	18	69	2.11	2.59
70/30	21	80	2.15	2.60
80/20	28	78	2.18	2.58

TABLE II.—EFFECT OF CAB-O-SIL ON YIELD VALUE (dynes/cm.²) AND POURABILITY INDEX OF CARBOPOL 941 (NEUTRAL IN 50/50 SORBO/WATER), MEASURED AT 8 DAYS

	Cab-O-Sil Concn. 0.0%		0.5%		1.0%	
Carbopol 941 Concn.	Y.V.	P.I.	Y.V.	P.I.	Y.V.	P.I.
0.02%	...	0.97	...	1.39	3	1.74
0.04	...	1.51	16	2.16	9	2.18
0.06	4	1.90	21	2.39	26	2.47
0.08	14	2.19	34	2.60	40	2.65
0.10	34	2.44	43	2.70	72	2.74

Increased temperature of preparation for TIC Colloid-600 raised both the yield value and the pourability index.

Figure 7 shows the dependence of yield value upon the gum concentration for all systems. Included are the apparent values obtained from extrapolation of tragacanth and Jaguar, even though these are of the type C classification. It should be noted that in general the onset of finite yield value occurs for a critical concentration for each gum and that further concentration increases result in extremely high yield values. Only the 60° data are given for TIC Colloid-600. An average value is given for the Carbopol 941 and for the CMC systems.

Table IV gives values characterizing the critical parameters of each gum system. The suspendability is defined by analogy to the pourability as the logarithm of the yield value. Chong (4) found the logarithm of yield values to be related to the suspending requirements.

In Fig. 8 yield value is related to pourability. It is quite apparent that for a given gum the increase in yield value is paralleled by an increase in the pourability index. Only one line each was generated by the Carbopol and CMC systems, and by the different temperatures for the TIC Colloid-600 system. Since the lines are not all parallel, it also follows

TABLE III.—EFFECT OF CAB-O-SIL ON YIELD VALUE (dynes/cm.²) AND POURABILITY INDEX OF CMC-12 HP IN 50/50 GLYCEROL/WATER, MEASURED AT 8 DAYS

CMC-12 HP Concn.	Cab-O-Sil Concn. 0.0% P.I.[a]	0.25% P.I.[a]	0.50% P.I.[a]	1.0% Y.V.	1.0% P.I.
0.75%	2.03	2.06	2.08	4	2.34
1.00	2.29	2.32	2.38	10	2.59
1.25	2.52	2.60	2.60	12	2.79
1.50	2.69	2.77	2.87	15	2.96
1.75	2.90	2.99	3.04	19	3.06
2.00	3.04	3.18	3.13	21	3.19

[a] No yield value observed.

that the best suspending agent at lower values is not also the best, automatically, at high yield stresses, considering ease of pouring as the criterion of judgment.

DISCUSSION

When yield values were calculated by both the Casson and Fitch procedures, *i.e.*, by the $T^{1/2}$ *versus* $D^{1/2}$ and T *versus* $D^{1/2}$ methods, respectively, the Casson plot inevitably was slightly higher in resultant yield value than the Fitch plot. The agreement was always good. In some systems, one yielded a better straight line than the other; and in some neither was too satisfactory.

In general, when the Power law index is small, the Casson plot permits better straight lines. For the higher indexes, the Fitch plot is concave to the abscissa and the Casson convex. Thus the consideration of both plots leads to a more valid yield value.

The need for obtaining relatively low shear rates for yield value extrapolation is clearly evidenced by the logarithmic plot. Unless upward curvature has been established, the yield value obtained by mathematical or graphical extrapolations of low shear points is of no significance.

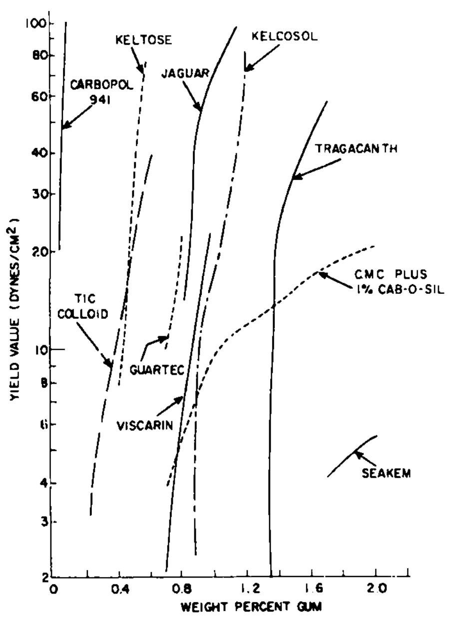

Fig. 7.—Dependency of yield value on gum concentration.

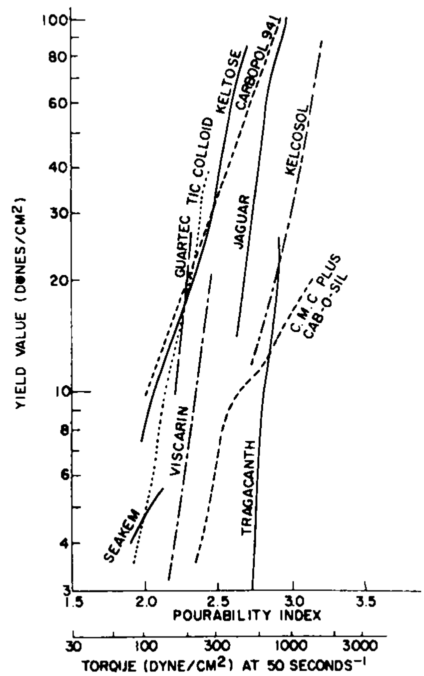

Fig. 8.—Dependency of yield value on pourability for various gum systems.

Thus in Figs. 5 and 6, if the lowest available shear rates had been for $D^{1/2}$ of 2, obviously quite different results would have been obtained. The Carbopol 941 yield values would have been much higher and the Jaguar ones finite and appreciable. Similar results were recently reported by Charm (13), who found yield values of different orders of magnitude for foods when measured on high and low shear rheometers.

The use of viscosity alone, without benefit of a yield value, cannot lead to a pourable stable suspension. Accordingly, the ability of an agent like Cab-O-Sil, which does not alone at low concentrations give a suitable system, to build yield value into such different systems as Carbopol 941 and CMC 12HP is of distinct value in the developing of practical suspending systems. It should be particularly noted that for low concentration of the primary gum, the Cab-O-Sil displayed no inherent yield value.

Recognizing that suspending power can be built into an otherwise desirable but inadequate suspending medium permits a latitude in formulation. Obviously, other systems than Cab-O-Sil may be considered, including the bentonite and montmorillonite clays, depending on the end use of the product. Thus for certain external applications Baymal[11] might well be considered.

The rheology of mixed systems is virtually an untouched area, although occasionally used in formulative practice on a "feel" basis.

The pourability index, as defined, is a suitable measure of personal judgment of pouring. Others might prefer to define it at any shear rate other than

Table IV.—Critical Parameters for the Gum Systems, Relating Pourability Index (P.I.), Suspendability (S), and Concentration

Gum	Concn. for $S = 1$, %	P.I. $S = 1$	P.I./S ($S > 1$)	S/P.I. ($S > 1$)
Carbopol 941	0.01	2.0	1.0	1.0
Keltose	0.4	2.1	0.7	1.5
Jaguar	0.8	2.6	0.3	3.5
Kelcosol	0.9	2.7	0.7	1.5
Tragacanth	1.3	2.8	0.3	3.5
TIC Colloid 600	0.4	2.2	0.4	2.5
Guartec GF	0.7	2.2	0.3	3.5
Viscarin	0.9	2.3	0.3	3.5
Seakem	(2.7)	...	...	...
CMC (+1% Cab-O-Sil)	1.0	2.6	1.8	0.5

[11] E. I. du Pont de Nemours & Company, Inc., Wilmington, Del.

our 50 seconds^{-1}, the choice in this work being a practical working range for extrapolation on the log stress-log shear rate plot for the rheometer used.

In the judgment of relative merits of different suspending systems, two ratios can prove valuable for comparison. These are the ratios of the suspendability to the pourability index and the reciprocal of this ratio. The first is a measure of suspendability of a given degree of flow, the other the ease of pouring for a definite degree of suspending ability. The first ratio defines the relative ordinate value in Fig. 8 for a given abscissa and the reciprocal the abscissa for a given value of the ordinate.

Both are useful terms to use to characterize in tabular form the data of Fig. 8 for given values of pourability or suspendability. The ratio, its parameters, along with the critical concentration to give a suspendability of unity, permit an excellent system characterization as is seen in Table IV.

SUMMARY

The use of log shear stress-log shear rate for low shear rate data is suggested as desirable for determining whether yield value character is, or is not, implicit in a given rheogram.

The practical difficulty of extrapolation to a yield value may, in practice, be estimated by either a Casson or Fitch plot.

Many gum systems, on increase in concentration of gum, show the development of yield value characteristics. These characteristics may be markedly enhanced by a second agent whose own yield value will be developed at low concentration.

Since yield value is a direct measure of suspendability and viscosity of pourability, a suspendability-pourability relationship has been developed for a series of gum systems. Tables and plots suitable for suspending gum characterization are given.

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Action and Interaction of Gibberellic Acid and B995 on *Datura innoxia*

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Thirty-three-day-old *Datura innoxia* seedlings were treated weekly for a period of 4 weeks with 50 mcg. of GA, 100 to 1000 p.p.m. solutions of B995, or combinations of both. The GA-treated plants indicated significantly increased height, increased stem dry weight, and generally decreased alkaloid concentration. Plants treated with the combination of the growth factors closely paralleled those treated with GA. Plants treated with B995 closely resembled controls, except for a decrease in alkaloid concentration in the roots at the last harvest. The results of a modified Dragendorff analysis are reported.

RESEARCH recently completed on several different compounds revealed that B995, known chemically as *N*-dimethylaminosuccinamic acid, produced growth retardation in plants (1). Numerous chemical compounds having the specific effect of retarding stem elongation have recently been described (2–9). These growth retardants cause a marked decrease in stem and petiole elongation and exert relatively little influence on root development or leaf expansion, unless administered in high doses. Lockhart (7) has indicated that several of the growth retardants interact competitively with gibberellin on stem growth, and that they act to retard stem elongation by partially blocking the system which provides active gibberellin to the growth mechanism. Others have indicated apparent interactions between gibberellin and certain retardants in *Ulothrix* growth (10), cell division of chrysanthemum (11), and in bean internode growth (12).

Most growth inhibitors are known to stimulate growth at dilute concentrations and inhibit at high concentrations (4, 10, 13). Low concentrations of Amo-1618 stimulated the growth of cucumber seedlings, whereas higher concentra-

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