

YIELD STRESS: A PREDICTIVE TOOL FOR DETERMINING SUSPENDING PROPERTIES?

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ABSTRACT:

There have been many publications on the measurement and use of yield stress as a means of determining the ability of a system to suspend. Although in theory it is a useful predictive tool, in reality, it will often be found to give erroneous results, particularly when attempting to draw comparisons between dissimilar systems. Alternative techniques can be used which, whilst not being perfect, will give results which are closer to the reality. Several of these methods are evaluated and compared.

ZUSAMMENFASSUNG:

In einer Reihe von Veröffentlichungen ist die Messung und Verwendung der Fließgrenze als Kriterium für die Fähigkeit eines Stoffsystems Partikel in Suspension zu halten, diskutiert worden. Obwohl ein nützlicher Ansatz, sind die Messergebnisse häufig durch enorme Schwankungen sowie einer ungenügenden Korrelation zwischen unterschiedlichen Stoffsystemen belastet. Alternative Methoden, auch nicht über jeden Zweifel erhaben, werden in diesem Beitrag vorgestellt und geprüft.

RÉSUMÉ:

Il existe beaucoup de publications sur la détermination du seuil d'écoulement et son application afin de préciser la capacité d'un système à suspendre. Bien qu'en théorie il est un outil de prédiction intéressant, en pratique, on obtient souvent des résultats erronés, surtout quand on essaie de comparer les systèmes dissimilaires. D'autres techniques peuvent être utilisées qui donnent des résultats plus proches de la réalité. Plusieurs de ces méthodes sont évalués et comparés.

KEY WORDS: yield-stress, suspension, prediction

1 INTRODUCTION

Barnes and Walters' publication, "The yield stress myth?" [1] induced significant debate as to whether a yield stress truly exists, both from proponents and adversaries of the suggestion. Irrespective of whether it exists or not, the concept is widely used in order to determine, amongst other parameters, the ability of a system to suspend components. Notwithstanding the widespread use of yield stress, and respecting the various precautions which need to be taken with its measurement [2], the values obtained can be misleading and may give rise to the drawing of

false conclusions. The concept of a yield stress, or yield value, is nevertheless of immense practical significance in many industries, including those of consumer products, oil-well drilling fluids, paints and mineral slurry dispersions, where frequently, stable suspensions are required. In this paper we look at some of the measuring techniques which can be employed. We also explain what we consider to be the most appropriate method to determine the capability of a system to suspend, by examining the rheological profiles of different polymers and relating them to the practical ability of the different systems to prevent material from separating from the matrix.

Polymer	% solids	pH	Brookfield LV results (at defined rpm)					
			0.6	3	6	12	30	60
HASE 1	0.7	7.4	113000	28000	14800	7950	3540	1960
HASE 2	0.55	7.1	78000	21800	12300	6900	3060	1720
x-ASE 1	1.5	7	82000	22200	12900	7750	3980	2500
x-ASE 2	1.5	7.1	56000	16400	9700	5800	2980	1830
x-HASE	1	7.4	119000	27200	14600	8050	2980	2180

Polymer	Height [mm]		
	0.5 h	2 h	8 h
HASE 1	14	55	-
HASE 2	8	16	39
x-ASE 1	0	0	2
x-ASE 2	1	13	32
x-HASE	0	5	11

Table 1 (left): Brookfield viscosities of the five polymers.

Table 2: Air bubble evolution in the polymer solutions (height evolution is measured towards the surface).

2 EXPERIMENTAL

The systems we investigated were simple aqueous polymer solutions, and in this way, we eliminated matrix effects which can also have a significant impact on rheology, and possibly complicate the interpretation of observations. Three basic classes of anionic acrylic polymers were chosen. These were the hydrophobically modified alkali soluble emulsion (HASE) polymers, the cross-linked alkali swellable polymers (x-ASE), and finally the cross-linked and hydrophobically modified alkali swellable emulsion polymers (x-HASE). The polymers were dispersed in water, neutralised with sodium hydroxide, and allowed to stand for 48 hours before determining their apparent viscosity. By apparent viscosity we refer to the flow of a polymer as perceived by the consumer, and we fixed this arbitrarily at 10 s^{-1} , or alternatively, as the value given by a Brookfield LV viscometer at 60 rpm. The Brookfield viscosities were determined at 22.5°C over a range of rotational speeds. The polymer concentrations were chosen such that each had a similar apparent viscosity.

Rheological measurements were all performed at 20°C using a TA Instruments AR-1000 controlled stress rheometer. Steady state flow curves were generated with a 4 cm, 4° acrylic cone with a gap of $109 \mu\text{m}$. Dynamic oscillation studies were run with an acrylic 4 cm parallel plate, and using a gap of $500 \mu\text{m}$. Steady state measurements were carried out after pre-shearing the samples at 10 s^{-1} for two minutes, and then allowing a 20 minute equilibrium period before applying increasing stress. Dynamic studies were run after 30 s of pre-shearing and a one hour equilibrium period. Practical suspending capability was determined by injecting into each sample 20 microlitres of air, and following the evolution of the resulting air bubble in the matrix. This is perhaps not the most common “ingredient” to suspend, but it does allow easy determination of this property, and for this parameter to be easily documented photographically. This size was chosen as it allows a rapid representation of the suspending ability to be obtained. Other air volumes were investigated, and although results obviously differ, overall trends remained the same. Small bubbles can be assumed to rise vertically without any horizontal deviation [3] and

the volume can be assumed to remain constant over the small depth changes involved. It is also assumed that the polymer solution is saturated, and so no air dissolves in the matrix.

3 RESULTS AND DISCUSSION

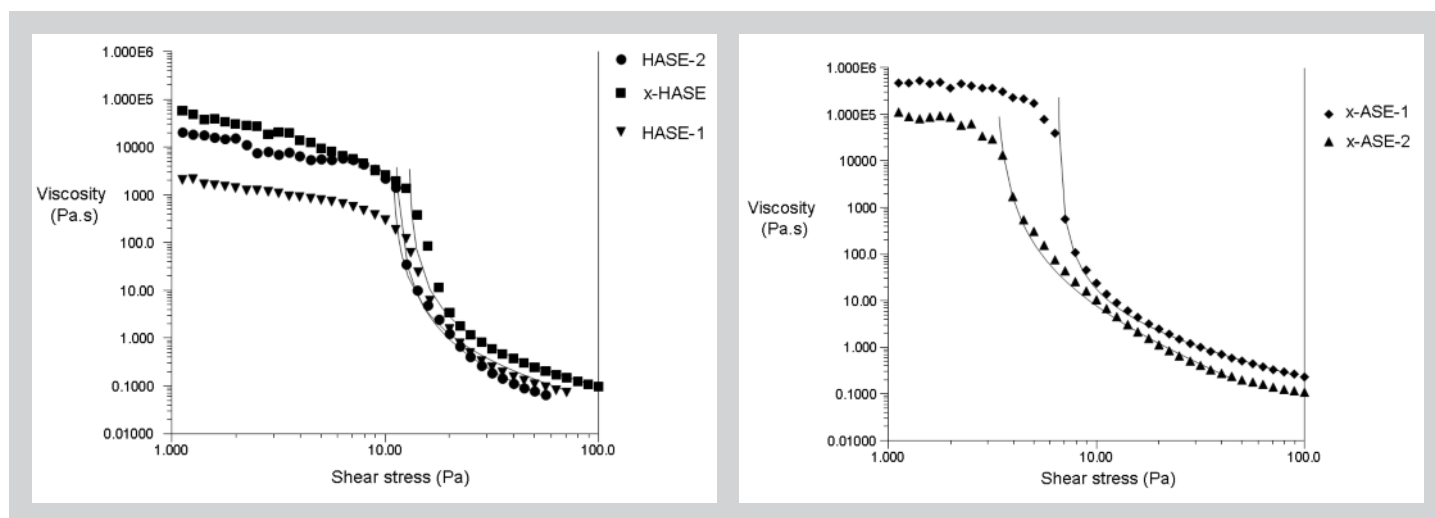
The viscosities of the polymer solutions measured by a Brookfield are given in Table 1. The 60 rpm viscosities, defined as the apparent viscosity, are similar, but as can be seen from the results at the other rotational speeds, the overall profiles of the polymers differ. The evolution of the $20 \mu\text{l}$ air bubbles injected into the bottom is shown in Table 2. From Table 2 it can be seen that x-ASE 1 shows the best suspending capability and HASE 1 the worst. Taking the values at 8 h, then the suspending capability is given by x-ASE 1 > x-HASE > x-ASE 2 > HASE 2 > HASE 1.

We can now compare these practical results with values obtained for the yield stress/value determined by different techniques. One of the simplest methods commonly employed is the measurement of the Brookfield Yield Value [4] given as:

$$YV[\text{Pa}] = \frac{\eta(0.5 \text{ rpm}) - \eta(1 \text{ rpm})}{1000} \quad (1)$$

Using this technique with a Brookfield RV viscometer, spindle 5 at 0.5 and at 1 rpm, the yield values in Pa obtained from the different polymer solutions were 40.4, 33.6, 34.0, 23.2, and 51.6 for HASE 1, HASE 2, x-ASE 1, x-ASE 2 and x-HASE, respectively. The first observation is that there are not particularly large differences between the values obtained, and secondly, the results do not correlate with the observed suspending capacity of the various polymers. The polymer HASE-1, which shows a high Brookfield yield value is the polymer with the least suspending ability.

Using a more sophisticated controlled stress rheometer, the steady state flow curves can be obtained, and using Herschel-Bulkley modelling [5], or by determining mathematically the break point of the curves (the onset-point), a value for the yield stress can be determined. Various authors have drawn attention to the fact that the yield stress can be considered and measured in different manners, and is dependent on the equilibrium times [6]. In this study, all samples were pre-sheared to the same degree, and were sub-



jected to the same equilibrium time before the flow curves were generated. The Herschel-Bulkley model is described by the equation

$$\tau = \tau_o + \eta \dot{\gamma}^p \quad (2)$$

where τ is the applied stress, τ_o the yield stress, η the viscosity, $\dot{\gamma}$ the shear rate, and p is the power law exponent or pseudoplasticity index. Figures 1 and 2 show the flow curves for the polymer solutions (hydrophobically modified polymers and x-ASE, respectively). A simple observation of the two graphs shows that the x-ASE polymers exhibit a point of inflexion of the flow curves at an applied stress significantly below that of the HASE polymers. By applying Herschel-Bulkley modelling, a value for the yield stress can be obtained. The results of the modeling are shown in the line traces on each graph. Although not a perfect fit to the experimental data, the modeling gives results which are sufficiently close to enable conclusions to be drawn. These results are summarized in Table 3 and are compared with the Brookfield Yield Values.

Using either technique, the x-HASE polymer shows the greatest value, and from the practical experiments, was second only to the x-ASE 1 in terms of its ability to suspend. HASE-2 was better than HASE-1, which is the order obtained from the Herschel-Bulkley yield stress determinations, but not from the Brookfield yield values. There is a major problems with the data obtained from the two x-ASE polymers, x-ASE 1 being the best polymer for suspension, and x-ASE 2 being better than either HASE-1 and 2. Using either of the above methods, relatively low values are found for both the x-ASE polymers. Although within a given class of polymers a degree of coherence can be seen, when different types of polymers are compared, poor correlation is observed.

We also ran viscoelastic measurements, looking at the $G' - G''$ point of intersection in a stress sweep experiment at constant frequency,

followed by the determination of the values of the elastic modulus within the linear viscoelastic region. This former analysis has the advantage that it can be determined with a relatively good degree of precision. At this point, the material passes from the predominantly elastic to the predominantly viscous regime. As such, it would be expected to follow the same trends as those obtained from the Herschel-Bulkley yield stress determined from the flow curves. The actual values determined are higher, but the overall trend is similar, with the HASE polymers being closely grouped, and the two x-ASE matrices being significantly lower (Table 4). This lack of correlation between the two values has been reported elsewhere [7].

However, if we look at the values obtained for the elastic modulus from an oscillatory frequency sweep within the linear viscoelastic regime (plateau value of G') then a very different picture emerges. The polymer with virtually no suspending ability, HASE 1, shows the lowest value for the elastic modulus, and the highest value is given by polymer x-ASE 1, which has the best suspending properties. The remaining polymers are also correctly ranked, and this would appear to be a better predictive tool for determining suspensibility than the classic yield stress determinations. Going back to Figures 1 and 2, but expressing the data in terms of viscosity against shear rate, rather than shear stress, and comparing the viscosities obtained under conditions of low applied stress i.e. when the system is in a "creep" regime rather than flowing [7] it also

Figure 1 (left):
HASE polymers: Viscosity as a function of shear stress.

Figure 2:
ASE polymers: Viscosity as a function of shear stress.

Table 3 (left below):
Comparison Herschel-Bulkley and Brookfield analysis.

Table 4 (right below):
Comparison $G' = G''$ and plateau value of G' , i.e. G_o .

Polymer	Herschel-Bulkley	Brookfield	Polymer	$G' = G''$ [Pa]	G_o [Pa]
HASE 1	9.2	44.4	HASE 1	31.7	11.2
HASE 2	10.7	33.6	HASE 2	32.3	18.7
x-ASE 1	12.6	51.6	x-ASE 1	28.5	57.2
x-ASE 2	5.4	34	x-ASE 2	9	91.5
x-HASE	3.1	23.2	x-HASE	7.7	41.7

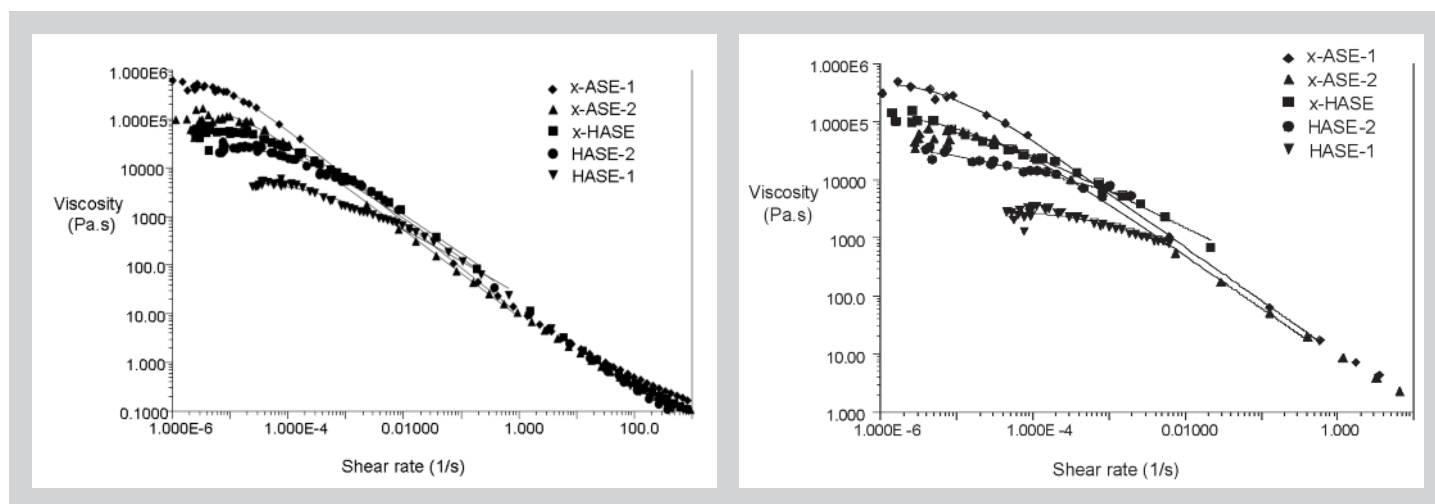


Figure 3 (left): Viscosity as a function of shear rate after 3 minutes equilibrium time.

Figure 4: Viscosity as a function of shear rate after 15 minutes equilibrium time.

Table 5 (below): Zero shear viscosity η_o determined by different techniques (H.-B. is the Herschel-Bulkley yield stress, Brookfield is the value obtained for the Brookfield yield value, and G' is the plateau value for the elastic modulus obtained in stress sweep experiments).

appears that results more coherent with the visual observations can be obtained.

If the low shear viscosities are modelled using the Williamson model, then a value for the viscosity extrapolated to zero shear can be obtained. The Williamson model was chosen as it gave a good fit to the experimental data, as can be seen by the model results (solid lines) which have been fitted to the experimental data (points). The Williamson model is a sub-model of the Cross model, and applies to the low shear region of the flow curve. The model is defined by the equation:

$$\eta = \eta_o - K \left(\frac{d\gamma}{dt} \right)^{n-1} \quad (3)$$

where η_o is the zero shear viscosity and K the consistency coefficient. The modeling was performed over the shear rate range from 1 to 10^{-5} s^{-1} except for the x-ASE 1 which was modelled over the range 1 to $5 \cdot 10^{-5} \text{ s}^{-1}$. These ranges were chosen in order to limit the impact of some of the “noisier” data points at the very low shear rates.

When determining flow curves, particularly at very low applied stresses, it is important to realise that data can be obtained under different experimental conditions. For each given applied shear stress data point measurement, the equilibrium time can be defined, and generally, in order to obtain the data within an acceptable timeframe, a short time span is employed. However at very low shear stresses, the sample is not flowing, but is in a creep regime, and as such, the

values obtained can vary significantly as the equilibrium time is varied. For Figures 3 and 4, each data point was given a maximum equilibration time of 3 and 15 minutes respectively. Under these conditions, the zero shear viscosity values (η_o [Pa.s]) calculated by the Williamson model are given in Table 5. For comparison, we have also included in Table 5 values obtained by some of the alternative techniques. The polymers are listed in decreasing order of their suspending capability as defined by the ability to suspend the 20 μl air bubble.

Looking at these results, it is clear that modelling the zero shear viscosity based on data obtained with a prolonged equilibrium time of 15 minutes is giving results which concord well with the practical data of bubble suspending ability. Even if a compromise is made, and short equilibrium times of 3 minutes are used in order to reduce overall analysis times, then suspendability predictions are better than those obtained using the yield stress values. Turning to the use of the Herschel-Bulkley yield stress as a predictive tool, it would also appear that within a given class of polymers, this value gives a good indication of the suspending ability, as is illustrated by the results obtained for the x-ASE 1 versus the x-ASE 2, and for the HASE-2 versus the HASE-1. However, when comparing the results obtained from different classes of polymers, erroneous conclusions can be drawn. The Brookfield yield value would appear to be less precise, as it gives an incorrect prediction for HASE-1 versus HASE-2.

CONCLUSIONS

Within a specific family of polymers, Yield Stress determinations using Herschel-Bulkley modelling provide a simple manner for defining the ability of a system to suspend. However, comparisons between polymers of differing structures can lead to misleading results. For dissimilar systems, it is probably advantageous to use the zero shear viscosity as a means for establish-

Polymer	η_o (3')	η_o (15')	G'	H.-B.	Brookfield
HASE 1	736900	770200	91.5	5.4	34
x-HASE	76820	235600	57.2	12.6	51.6
x-ASE 2	109100	96690	41.7	3.1	23.2
HASE-2	26360	40080	18.7	10.7	33.6
HASE 1	4775	5010	11.2	9.2	44.4

ing suspendability. Under ideal conditions using long equilibrium times, this can be a very effective predictive tool. However, due to time constraints, more rapid analysis times are generally employed, leading to less precision in the values obtained. It is nevertheless a better technique than yield stress determination for unlike systems.

For rheometers equipped with oscillatory capabilities, determination of the elastic modulus is also an option, and if the plateau modulus is determined from a frequency sweep within the linear viscoelastic regime, this would appear to provide data which conforms closely to visually observed stability. Although the above data is presented for air bubble suspension, we have also used these tools to compare behaviour of numerous systems in which particle suspension has been a requirement. Overall, we have noted that similar conclusions can be drawn.

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