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 Veröffentlichung 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 erroné, surtout quand on essai 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.

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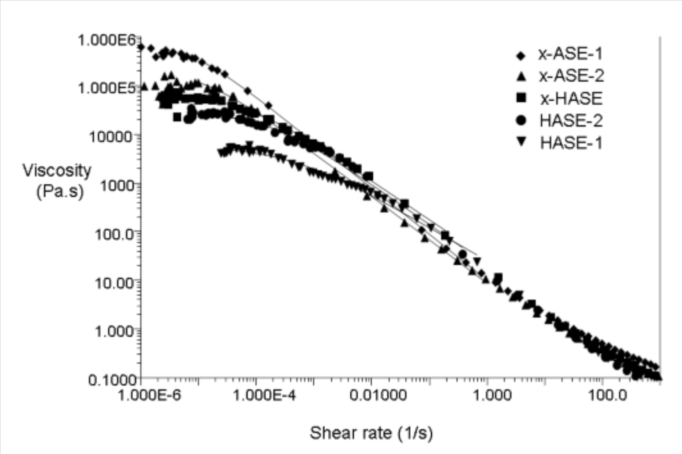

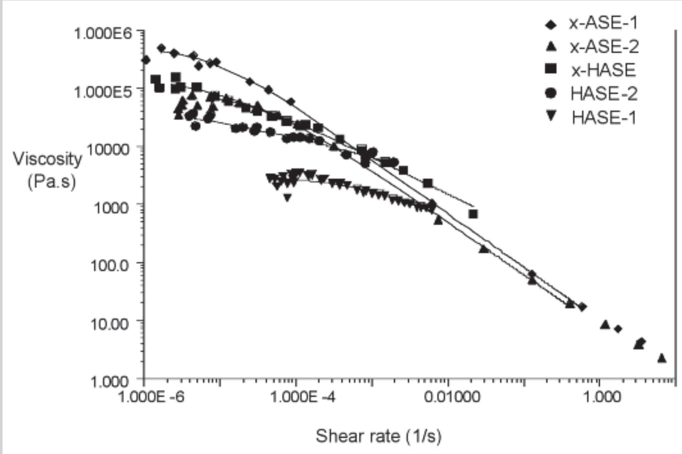

Figure 3 (left): Viscosity as a function of shear rate after 3 minutes equilibrium time.

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:

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

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 $5 \cdot 10^{-5}$ 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.

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

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-

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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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