

Stircasting of transparent organic alloys: thixotropy and rosette formation

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The fluid flow of a stircast slurry is very complex due to its thixotropic behaviour, i.e. at a fixed fraction of solid the viscosity is shear-rate and time dependent. The fraction of solid in its turn depends on the temperature gradient and the cooling rate in the stir caster. In order to understand the effects of the variables upon final alloy composition, particle size distribution and fluid flow, it is necessary to simultaneously perform viscosimetric measurements and microscopic observations. Metals do not allow this, but transparent organic compounds do. Therefore we used 98% pure succinodinitrile as a model alloy to study nucleation and solidification during stirring. Our microscopic observations of solidifying succinodinitrile in a stirred cell showed that it formed the same spherical or rosette-shaped particles as aluminium alloys. Our viscosimetric studies showed that partially solidified succinodinitrile behaves thixotropically.

1. Introduction

The application of vigorously stirred partially solidified alloys in casting, known as stircasting or rheocasting, was in recent years the topic of interest in a number of studies [1-6]. The thixotropic behaviour of the partially solidified slurries, as studied in detail by Joly and Mehrabian [3] is very complex due to the fact that the viscosity is shear-rate and time dependent at a fixed fraction of solid. Not much work however has been done on the fundamental understanding of the particle formation (nucleation, growth and clustering) and the origin of the thixotropic properties, though Vogel *et al.* [4] and Lee *et al.* [5] developed a model for the formation and melting of grain boundaries between spherical particles.

In order to get more information about the influence of the shear rate, the temperature gradient and the cooling rate on the final microstructure, and on the thixotropic behaviour at a fixed fraction solid one has to do simultaneously both viscosimetric measurements and microscopic

observations. This is clearly not possible for metals. It is however well-known that some organic materials act in a similar way as metal alloys during solidification [7-11]. So an investigation using 98% pure succinodinitrile as a model alloy for stir casting, with the aim to find out if succinodinitrile exhibits the same microstructure and thixotropic behaviour as metal alloys do when they solidify during stirring, was undertaken.

2. Experimental procedure and results

The microstructures were observed in an aluminium cell with two individually thermostated optical windows and with a flat glass plate in between to stir the melt. The cell was filled with 98% pure succinodinitrile. The 2% impurity content causes a freezing range of several degrees in which the fraction of solid can be varied. The bottom window was kept 1 K below the temperature of the upper window in such a way that a solidification front was visible between the windows. Solidification was observed through a

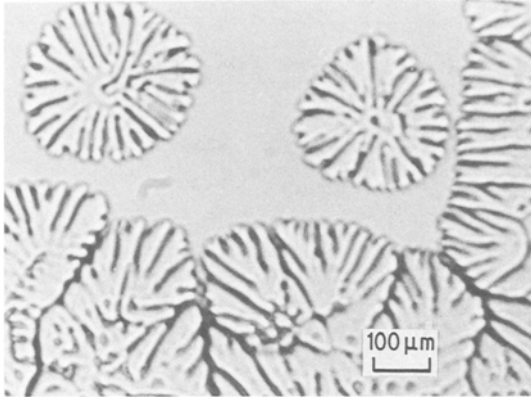


Figure 1 Spherical or rosette-shaped structure of succinodinitrile due to stirring during solidification.

microscope with an attached time-lapse camera.

In the unstirred condition the alloy grew with a dendritic structure as expected. When the melt was stirred, however, the particles solidified in a spherical or a rosette-like microstructure, as shown in Fig. 1. If the stirring action is stopped, the dendritic growth reappeared, as shown in Fig. 2. From this we can conclude that the microstructure of stirred solidifying succinodinitrile is analogous to the structure of stirred metal alloys.

The viscosity measurements were performed with a Searle type viscosimeter, which means that the cup is fixed and the rotor stirs the sample and measures the torque. The instrument was a Haake RV2 with a PG142 programmer. The slit between cup and rotor is 1 mm. Fig. 3 shows the experimental procedure. The temperature of the melt is lowered by 2 K min^{-1} down to a fixed temperature between solidus, T_S , and liquidus, T_L , (Fig. 3a) at a constant rotational speed,

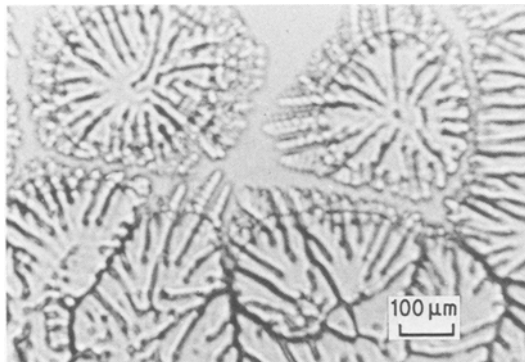


Figure 2 Dendritic growth reappears on a rosette-shaped particle as stirring stops.

$\omega = 256 \text{ rpm}$ (Fig. 3b). During nucleation, the growing nuclei gave a sudden increase of the shear stress, τ . After the shear stress had reached a steady value we did some experiments by varying the rotation speed and the time variables t_r , t_u , t_d , t'_d which are defined in Fig. 3b. (Fig. 6 shows an experiment in which the shear rate is varied step-wise). In the experiments of Figs 4 and 5 the rotation speed is decreased linearly during the down-times t'_d and t_d and subsequently increased linearly during the up-time t_u , while during the rest-time t_r the melt is not stirred at all. In our experiments t_u and t_d were equal.

If the shear rate, $\dot{\gamma}$, (which is a function of the rotational speed, ω , is plotted against the shear stress, τ , during a loop time ($t_u + t_d$), a hysteresis loop is found, as shown in Fig. 4. The area of the loop is a measure of the thixotropy. At one fixed temperature several loops were recorded with different times t_r , t_u , t_d and t'_d (t'_d is the down-time in a previous loop). These time schedules influence the area of the loop. Other variables that influence the hysteresis loop are e.g. the fraction of solid, the cooling rate and the temperature gradient, but they will not be discussed here except for the remark that the area of the loop increases with an increasing fraction of solid.

The experiments in which one of the time variables t_r , $t_u = t_d$ and t'_d were varied and the others kept at a constant value, showed the following variations in the area of the hysteresis loop. With increasing times t_r and t'_d the area of the loop increased, but with increasing $t_u = t_d$ the area of the loop decreased. When t'_d is decreased down to zero (i.e. $t'_d < 0.1 \text{ sec}$) the hysteresis loop almost disappears, as shown in Fig. 5. For the experiment in Fig. 4 the calculated apparent viscosities for points A to H are respectively 151, 183, 188, 97, 53, 64, 87 and 120 mPa (or cP), i.e. the apparent viscosity first increases a little bit and then suddenly decreases by a factor of 2 (between C and D) with an increasing shear rate. The apparent viscosity of succinodinitrile however is from one to two orders of magnitude lower than in the case of Sn–15 wt% Pb [1].

The step-wise variation of the shear rate of Fig. 6 clearly shows a time dependent shear stress, which is a thixotropic feature. The time for re-establishment of the steady state is about 1 min, which is of the same order of magnitude as in the case of Sn–15 wt% Pb as reported by Spencer *et al.* [1]. The course of the shear stress shows a

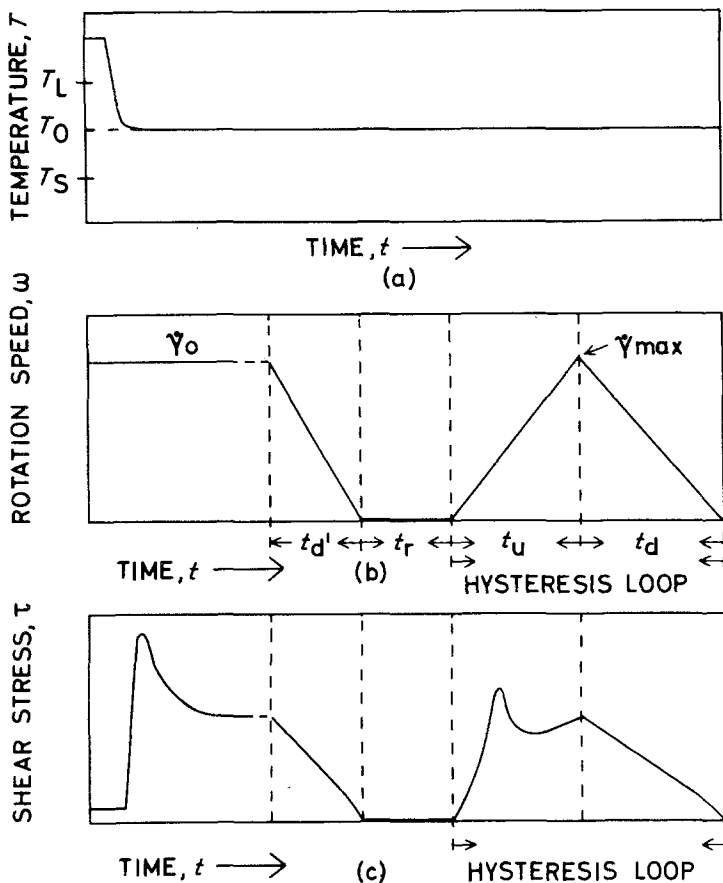


Figure 3 Procedure for viscosimetric measurement of succinodinitrile showing (a) temperature, (b) rotation speed and (c) torque against time plots; (b) and (c) also give the procedure for hysteresis loops.

big, rapid change and then a small, slower change, which does not fit with an exponent.

3. Discussion

The time and shear-rate dependence of the viscosity may be explained by a clustering mechanism [3].

During the period t_d in which the shear rate is decreased to zero, clusters can be formed by a re-arrangement in the slurry.

This re-arrangement might induce an increased volume-fraction of entrapped liquid, which causes an increase in the apparent viscosity. If the shear

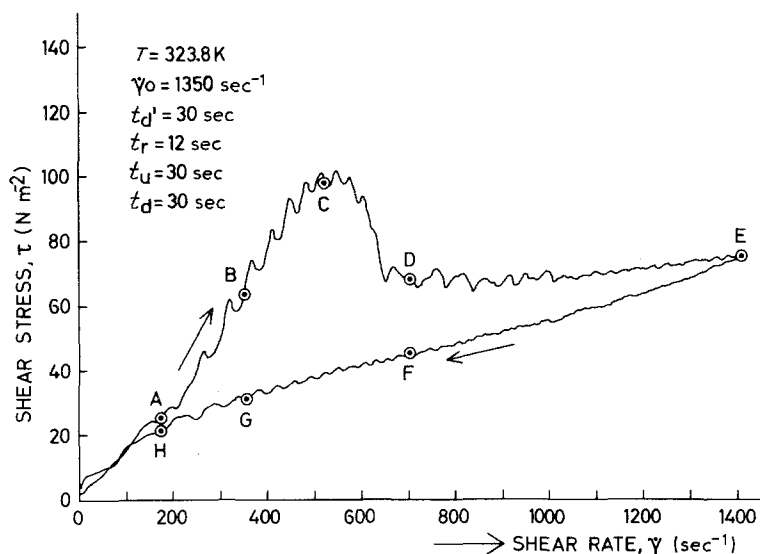


Figure 4 A hysteresis loop of partially solidified succinodinitrile, according to the procedure illustrated in Fig. 3 after t_r . The temperature, T , is constant.

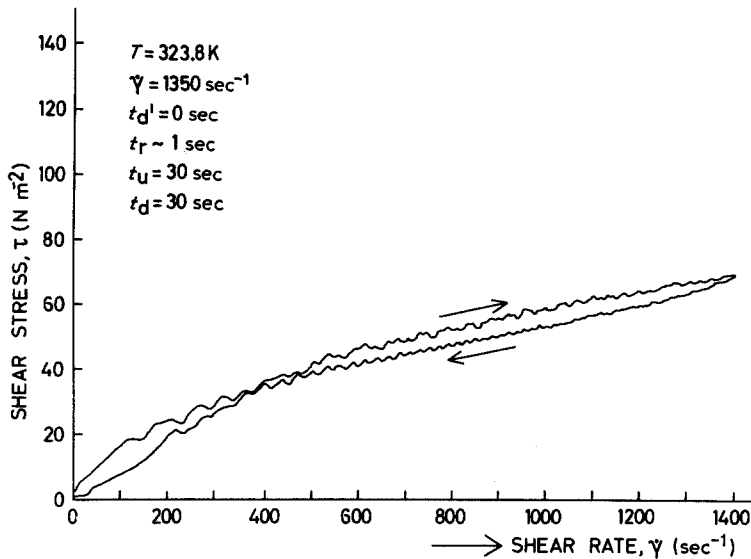


Figure 5 Hysteresis almost disappears when the down-time t_d' of the previous experiment is almost zero. Temperature, T , is constant.

rate is increased during the period t_u the clusters dissociate in smaller particles. When the previous down-time t_d' and rest-time t_r are very small, as in Fig. 5, there is almost no hysteresis since the clusters will not have sufficient time to form. The times for clustering on lowering the shear rate, and fragmentation on raising the shear rate, are of the order of 10 to 30 sec (Fig. 6). This result is

compatible with the fall of viscosity η in Fig. 4 when the up-time is 30 sec. The mechanism of clustering may be the formation of low-energy grain boundaries at special orientations, as previously proposed [4, 5] but apart from the reaction requiring time there is so far nothing in these results to support or dispute that model. The clustering reaction will require time since the

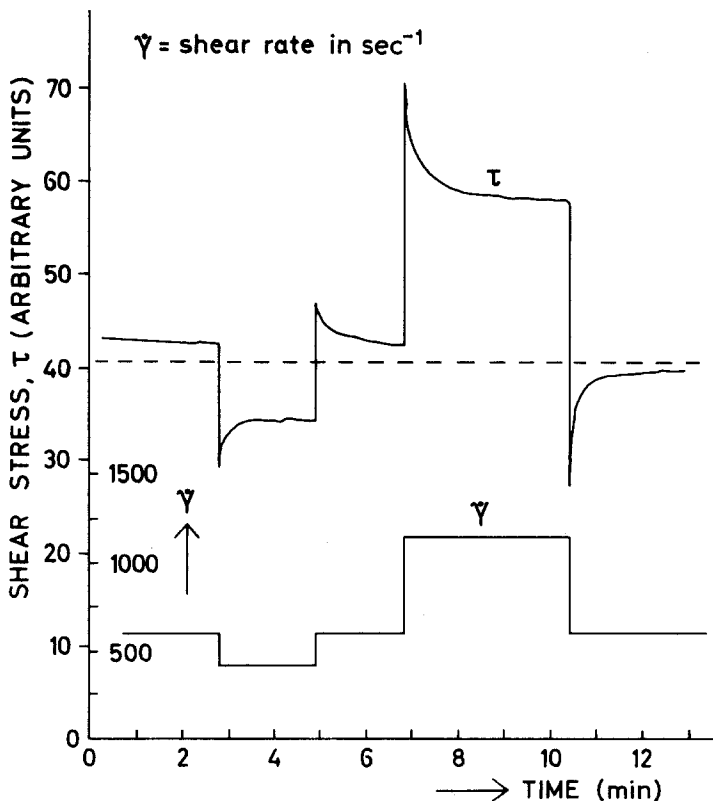


Figure 6 Step-wise shear rate, $\dot{\gamma}$, changes (at the bottom) show the third dependence of the shear stress, τ , (at the top). Temperature is constant.

impurity-rich liquid between the particles must be removed by diffusion or flow. Moreover, due to the fact that the change in shear stress is not exponential, one may expect at least two clustering mechanisms.

A full investigation of the mechanism of clustering and fragmentation should be possible by direct observation of the process in this transparent system. Results of the observations will be published when they are made and analysed.

4. Conclusions

As a conclusion we can say that succinodinitrile, when it is partially solidified during stirring, shows the same microstructure as stircast alloys and also behaves thixotropically, so succinodinitrile is a good model substance for the study of stircasting of metal alloys.

Acknowledgements

The authors would like to thank Dr R. D. Doherty for his stimulating ideas and discussions, Dr H. Nieswaag for his valuable discussions and Professor Dr L. L. van Reijen for the critical reading of the manuscript.

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Received 20 May

and accepted 18 August 1981