The Production of Rubber-Modified Polystyrene. Some Criteria Influencing the Selection and Design of the Agitator System

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Synopsis

The importance of selecting the most suitable form of agitation for the prepolymerization step in the production of rubber-modified polystyrene by a bulk polymerization procedure is related to the non-Newtonian behavior of the polymerizing system and to the existence of a minimum shear rate requirement. The procedure for the design and calibration of a small-scale reactor system is described which is shown to produce an adequate phase inversion of the prepolymer and from which data can be evaluated for any change in scale of the operation. Structural patterns in the final polymer are linked with average shear levels in the reactor.

INTRODUCTION

In previous papers,[1,2] the conditions for agitation of the prepolymer during the production of rubber-modified polystyrene to give a smooth phase inversion of the system have been discussed with respect to its non-Newtonian nature and also related to the fact that there exists a minimum shear rate below which, in practice, phase inversion does not occur. In order to make polymer on any reasonable scale of operation, these findings must be examined in more detail so that they may be correctly applied to a design procedure for a reactor system. By providing complete experimental information for the small-scale reactor system described, the procedure can be related to any change in scale of operation (or enable a comparison to be made with these results) by the established design procedure summarized.

The problem has been approached in two stages, the first being a selection of the most suitable form of agitator, by an assessment of the performance of those considered appropriate, followed in the second stage by a performance analysis with scale-up in mind.

The selection of the agitator for the present system should satisfy separate criteria, namely the minimum shear requirement,[2] and must also ensure the smooth formation of the second phase, so that the flow pattern

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should possess (a) complete overall circulation with no stagnant or slow moving regions, (b) some regions of sufficient shear stress to disperse any gel or aggregates of dispersed phase particles. The pseudoplastic character of the system, together with its moderately high apparent viscosity, could necessitate the use of an impellar which shears a large fraction of the fluid, so that almost all stagnant zones of low shear rate, and hence high viscosity, may be avoided.

In the second stage, data to be used for scale-up purposes is evaluated to meet criteria specifically evolved for pseudoplastic fluids. Magnusson[3] first proposed the use of conventional plots of power number N_p, versus Reynolds number N_{Re}, based on a calculated apparent viscosity in the Reynolds number. Metzner and Otto,[4] however, suggested calculating an apparent viscosity μ_a by this technique and proposed a useful procedure for predicting power consumption using fundamental viscometric data. They assumed that fluid motion in the vicinity of the impeller could be characterized by relating average shear rate to impeller speed as

$$\dot{\gamma}_{av} = (du/dr)_{av} = kN. \tag{1}$$

Thus, the data required are those necessary to evaluate the constant k, and in general this approach is found to be valid as confirmed by the work of Calderbank and Moo-Young[5] and others, who list values of the constant k for different agitators. It follows that by adopting this approach, the reactor system can be calibrated over a wide range of shear rates prior to a determination of structural variation in the final polymer as a function of the prepolymer shear history.

STAGE 1

Procedure and Discussion

The reactor vessel was of 700-ml capacity, all glass type QQFR700F, fitted with an all metal top to accommodate a low-friction stirring shaft which could be accurately aligned. The vessel was maintained at the reaction temperature (70°C) by means of external infrared heaters operated through a control system. All polymerizations were catalyzed by benzoyl peroxide to give a rate of polymerization of 3%/hr.

The temperature of the reacting mass was measured by an iron–Constantan thermocouple which, depending on the agitator type, was either located in a hydrodynamically designed pocket or in the stirrer shaft. Precautions were taken to ensure that the temperature was uniform, although this was not found to be a problem at this scale of operation. The reactor was fitted with a nitrogen gas purge to ensure that the polymerization was carried out in an inert atmosphere. Four different agitators, viz., propeller, anchor, gate, and helical ribbon, were tested by carrying out polymerizations beyond the phase inversion point to about 20% conversion. Initial estimates were made for the speed of the agitators to ensure that they operated at an average rate of shear above the minimum
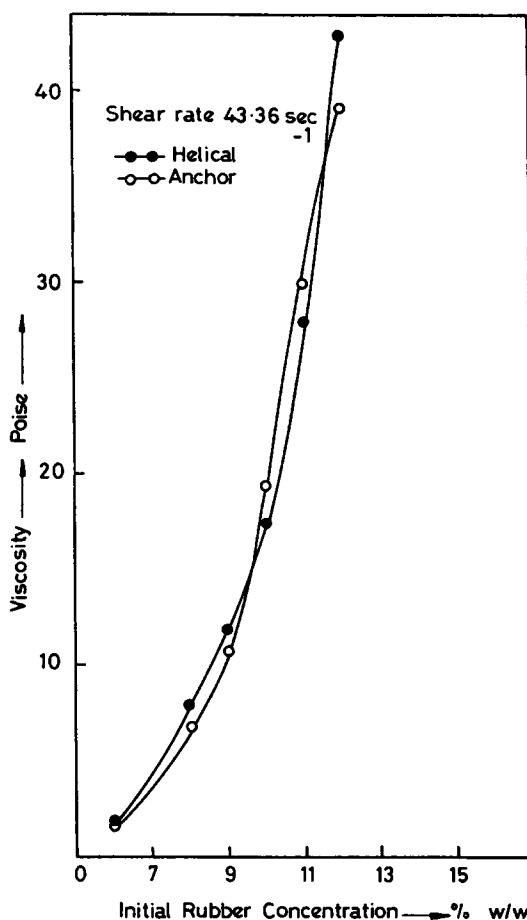
Fig. 1. Comparison of helical ribbon and anchor agitators. Plot of initial rubber concentration vs. apparent viscosity at phase inversion.

value previously determined.[2] Then, by operating each stirrer in a transparent liquid of viscosity similar to that of the polymerizing solution and recording the movement of colored plastic spheres by the use of a cine camera, it was established that under these conditions there were no dead spaces in the reactor.

Some test of agitator suitability had to be devised, and the best compromise for this was as follows: (a) The rheological behavior of the dispersed systems was compared at the same rate of shear, using the different agitators. (b) The time delay for phase inversion was assessed. (c) The structure of the final polymer from each type of agitator was compared.

It will be appreciated that there is a high element of subjectivity in these tests which, it must be stressed, are only designed to evaluate the agitator in giving a smooth phase inversion of the prepolymer. It is claimed[6] that after phase inversion the rubber particle size can be reduced

to a desired degree by high shear and that in this way the impact property
of the final polymer is improved. It would therefore appear that by con-
trolling the phase inversion and therefore the initial form of the rubber
particles, subsequent size control could be facilitated. However, the same
patent also claims that the avoidance of shearing prior to phase inversion
is critical because of the deleterious effect of prephase inversion shearing
on the impact strength of the product, but nevertheless quotes shear
rates in this step comparable with those of our previous recommendations.[2]
Faced with the possibility of an anomaly, it was considered inadvisable to
link any test of agitator suitability with the impact strength of the final
product at this stage.

The investigation revealed that the anchor and helical ribbon agitators
both facilitated phase inversion, the latter being somewhat the better;
also the particle size from anchor agitation was observed to be significantly
larger than that for the helical ribbon system. The propeller operated
very poorly and did not give an inverted final product, the gate-type
stirrer tended only to rotate the mass without any appreciable mixing and
hence also resulted in a poor structure. Very little difference between the
helical ribbon and anchor is observed in Figure 1 which shows the graph
of initial rubber concentration versus apparent viscosity at phase inversion
(obtained at a constant shear rate of 43.36 sec^{-1}).

It was felt that there was a sufficient overall indication that the helical
ribbon gave a more desirable product, and this agitator was made the
basis for further study.

STAGE 2

As discussed earlier, the objective is to characterize the polymerization
system in terms of the power number N_p-versus-Reynold number N_{Re}
relationship. In order to obtain the relationship, it is necessary to measure
the power input to the agitator as a function of its speed, which may
conveniently be obtained from noting the electric power to the motor
using a watt meter. The shaft of the stirrer was driven by means of a
chain-and-sprocket transmission from the motor; frictional loss was re-
duced to a small calculable quantity by using a thrust bearing for the
sprocket wheel on the agitator shaft. Details of the system together with
dimensions for the ribbon agitator are shown in Figure 2.

The procedure adopted is based on the method proposed by Metzner
and Otto,[4] and since this involves the use of the Reynolds number and
hence a viscosity term in addition to the shear stress–shear rate data on the
polymerizing mass,[1] a further calibration of the reactor with both New-
tonian and non-Newtonian fluid is required. In order to stress the impor-
tance of a knowledge of the non-Newtonian nature of the system, and the
need for ensuring that $\dot{\gamma}_{av} \geq \dot{\gamma}_{min}$ in the reactor system,[2] the complete
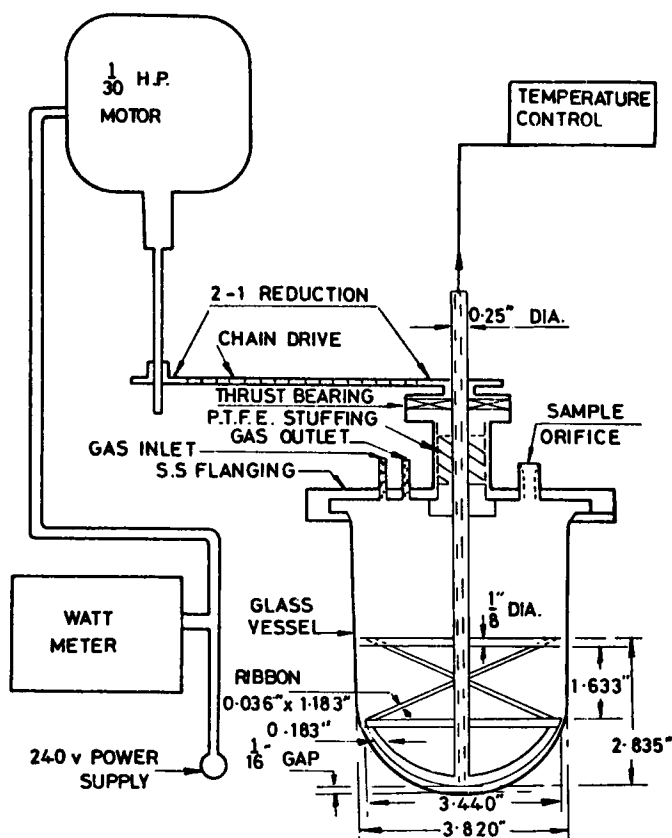stepwise procedure adopted for the calibration is given.

Fig. 2. Reaction vessel, helical ribbon agitator, and drive mechanism.

Procedure

1. The power number-versus-Reynolds number curve, Figure 3, was experimentally determined for the reactor system using a Newtonian fluid, glycerol.

2. Power data at various agitator speeds were then measured using a non-Newtonian liquid, viz., a 1.25% solution of sodium carboxy methyl cellulose (SCMC). These data were then used to calculate the power number N_p at each agitator speed.

3. For selected values of the calculated N_p, the corresponding Reynolds number N_{Re} was read from Figure 3. Thus now knowing the liquid density ρ, the agitator diameter d, and the Reynolds number N_{Re} for each agitator speed N, the apparent viscosity μ_a corresponding to each value of N and each N_{Re} was calculated. From this, a plot of apparent viscosity μ_a versus agitator speed N was prepared (Fig. 4).

4. For the non-Newtonian liquid SCMC, the apparent viscosity μ_a was determined at various shear rates $\dot{\gamma}$ in the plate-and-cone viscometer
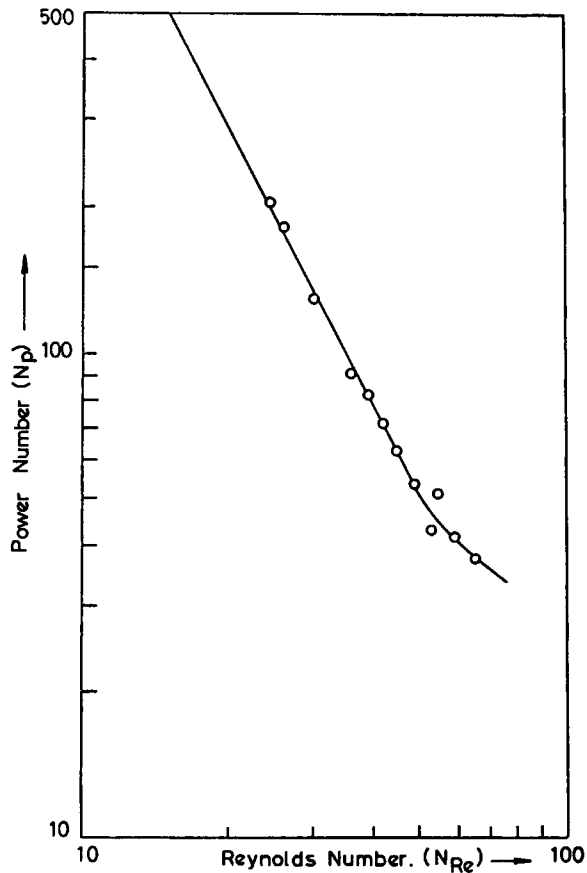
Fig. 3. Power number-vs.-Reynolds number calibration plot for the reactor system using glycerol.

at 25°C, and the apparent viscosity was plotted against shear rate, as in Figure 5.

5. From the plots of μ_a versus N and μ_a versus $\dot{\gamma}$, the corresponding values of $\dot{\gamma}$ and N were read off for the same apparent viscosity μ_a. These values of $\dot{\gamma}$ were then plotted against the corresponding values of agitator speed N, as shown in Figure 6. Measurement of slope of this plot gave the proportionality factor k in eq. (1) as 96.6.

This can be checked theoretically by the application of the concentric cylinder model as proposed by Bourne and Butler,[7] and which was used as the basis for the original estimate in stage 1. Thus, for high d/D ratio,

$$\dot{\gamma} = \frac{\text{tangential speed of inner cylinder}}{\text{gap width}}. \tag{2}$$

Substituting the dimensions as shown in Figure 2 into eq. (2), and since $d/D = 0.964$,
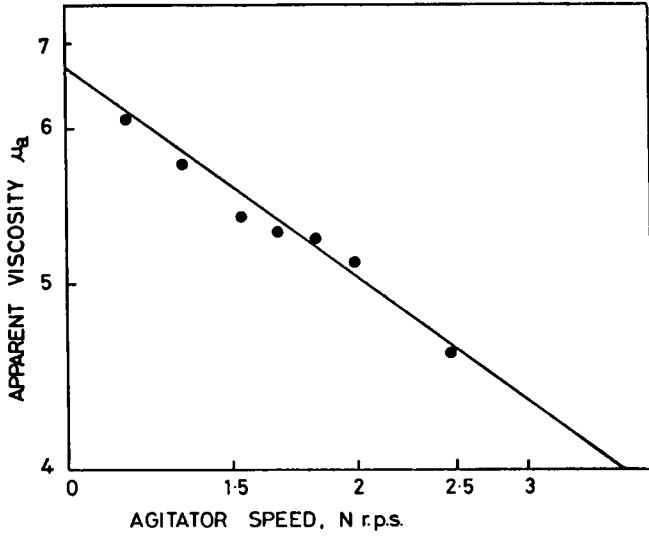
$$\dot{\gamma} = 173N.$$

Fig. 4. Apparent viscosity-vs.-agitator speed calibration plot for the reactor system using SCMC.
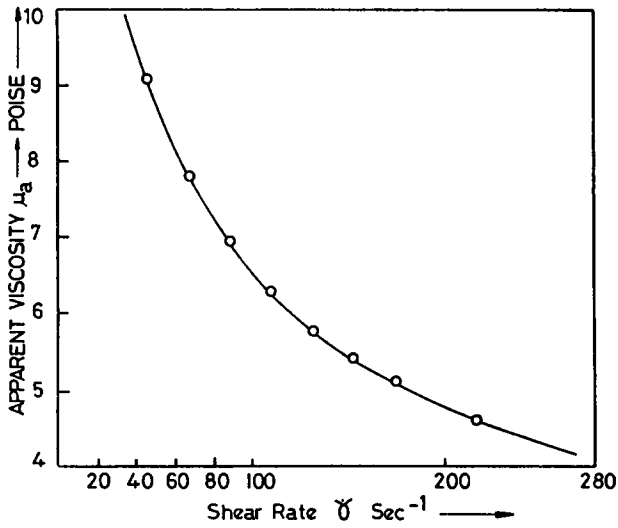

Fig. 5.   Apparent viscosity vs. shear rate for SCMC at 25°C.

Comparing with eq. (1), the theoretical k for the solid concentric cylinder is given as 173.   The practical value of k is a function of the ratio of pitch to diameter and also of d/D.   In the present case, the former ratio is 0.5. Hence, from the data of Bourne and Butler[7] (see their Fig. 12),

$$\frac{\text{practical power}}{\text{theoretical power}} = \frac{\text{practical } k}{\text{theoretical } k} \simeq 0.5$$
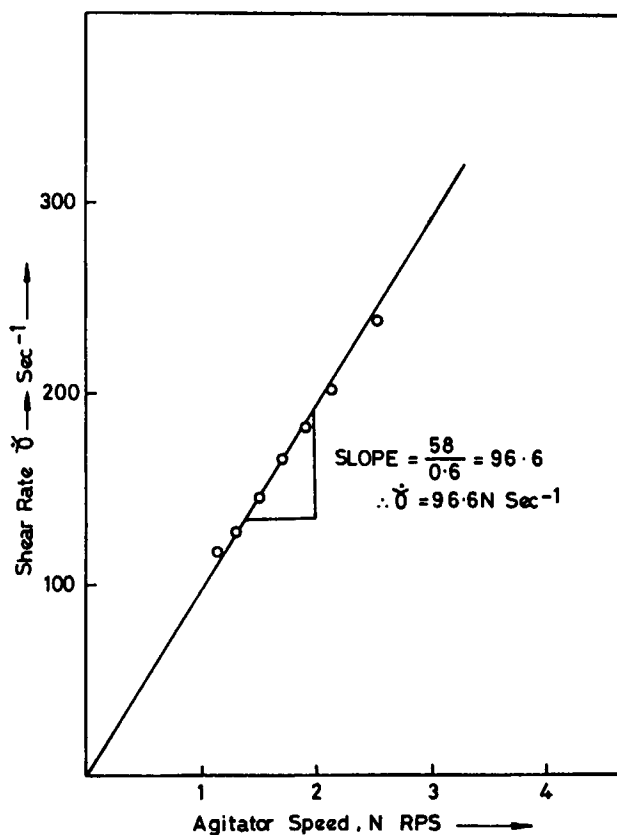
Fig. 6. Shear rate vs. agitator speed for the reactor system. The proportionality factor $k = 96.6$ from the slope of this plot.

Hence, practical $k = 173 \times 0.5 = 86$, which is in reasonable agreement with the experimental value obtained by the Metzner and Otto method.

Proceeding now to the rubber-modified polystyrene system, an 8% rubber-in-styrene solution was polymerized in the reactor at a selected constant speed of agitation. The viscosity, density, and power input were noted at appropriate time intervals and the degree of polymerization determined by a solids content method, all determinations being made at the temperature of polymerization. Using the relationship between power P and conversion c, shown plotted graphically in Figure 7, together with the previously determined relationship between viscosity and conversion,[1] the relationship between power number and Reynolds number is then best obtained by digital computation, since the effect of change in agitator diameter d is more easily explored by means of the following stepwise procedure.

6. The power number N_p corresponding to a particular conversion c_1 is calculated as $P_1/\rho_1 N^3 d^5$, using the appropriate values of density ρ_1, noting that we are working at the constant speed N.
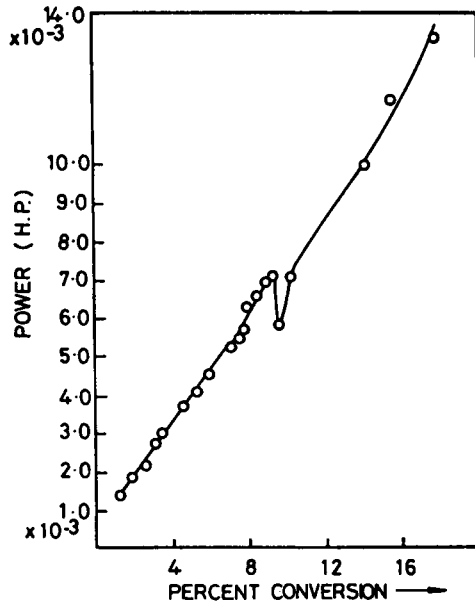
Fig. 7. Power vs. per cent conversion for the 8% rubber-in-styrene polymerizing system
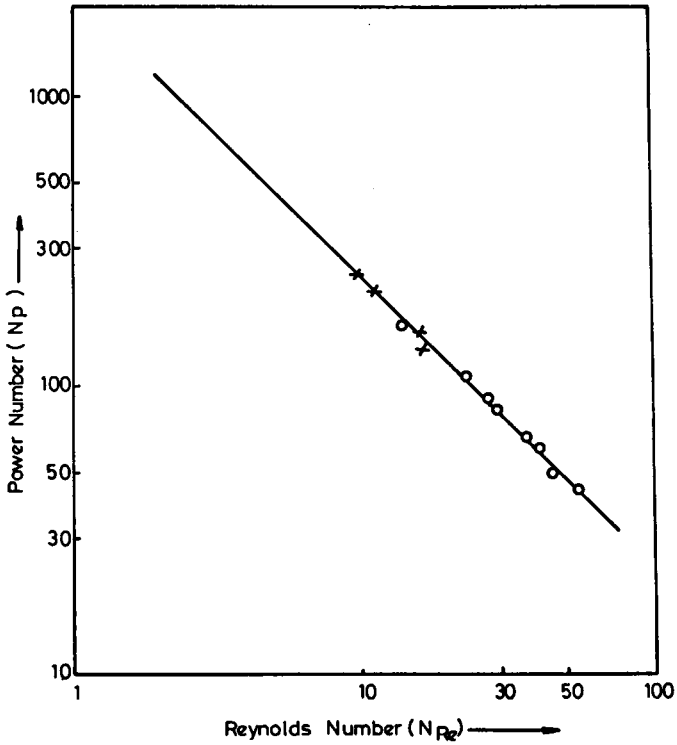
Fig. 8. Power number vs. Reynolds number relationship for the two-phase system.

7. Using the previously determined relationship between shear ratio and N, and the value of $(\dot{\gamma}_{av})_1$ at N together with the apparent viscosity μ_a (obtained from the data at conversion c_1 and shear rate as given), the value of N_{Re} is calculated as $N d^2 \rho_1/\mu_a$.

8. Thus, the relationship between N_p and N_{Re} is obtained by calculating pairs at different conversion levels. Finally, the steps are repeated for other values of N rps. The result is shown graphically in Figure 8.

DISCUSSION

For the 8% rubber system in the apparatus as described, since the minimum shear rate below which phase inversion does not occur is approximately 130 sec^{-1}, using the value of $k = 96.6$, the speed of the helical ribbon agitator has to be equal to or above 80 rpm to achieve a satisfactory phase inversion, a prerequisite for impact properties in the final polymer. Operating the stirrer at speeds lower than 75 rpm may result in a noninverted final product with the characteristic network structure. However, it is to be remembered that in the reactor system it is the average shear rate that is calculated, whereas in the cone-and-plate system[2] the shear rate is uniform. Samples taken from the reactor system at 80 rpm, apparently in their equilibrium inverted structure and sheared for a short time in the cone-and-plate viscometer at 130 sec^{-1}, show a marked change
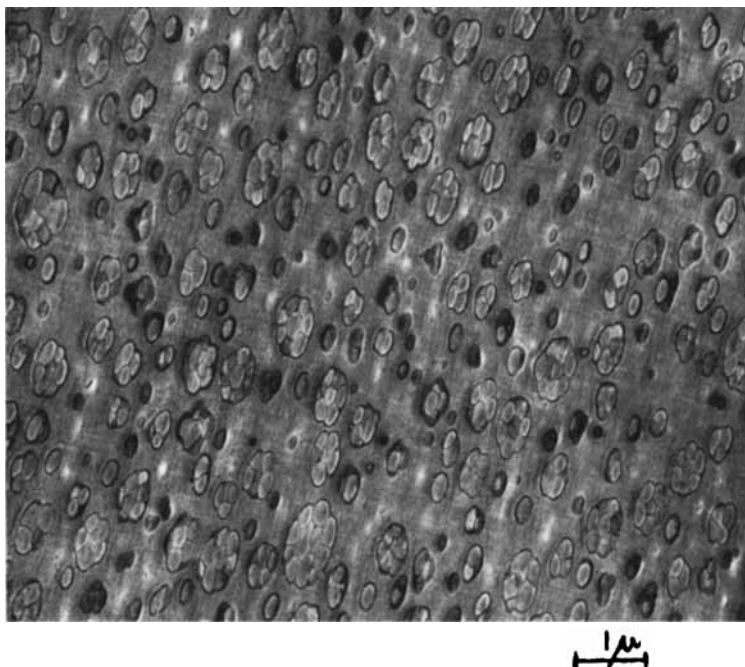

Fig. 9. Electron photomicrograph of final polymer showing the structure resulting from aggregation of few subparticles.

in structure resulting in an increase in dispersed droplet size. This apparent anomaly can be explained by the fact that at this stage in the process, the dispersed phase does not consist of simple droplets but clusters or aggregates. It is postulated that, provided the minimum shear requirement is met, a dispersed phase is produced which consists of independent droplets of roughly equal size. These droplets quickly form composite larger particles the structure of which is dependent on both shear level and mixing time. Thus in general, when $\dot{\gamma}_{av} > \dot{\gamma}_{min}$, clusters of few subparticles are formed, as illustrated in Figure 9; whereas when $\dot{\gamma}_{av} \simeq \dot{\gamma}_{min}$, large composite particles are formed containing many subparticles, as in Figure 10. This can be considered to be a consequence of the better
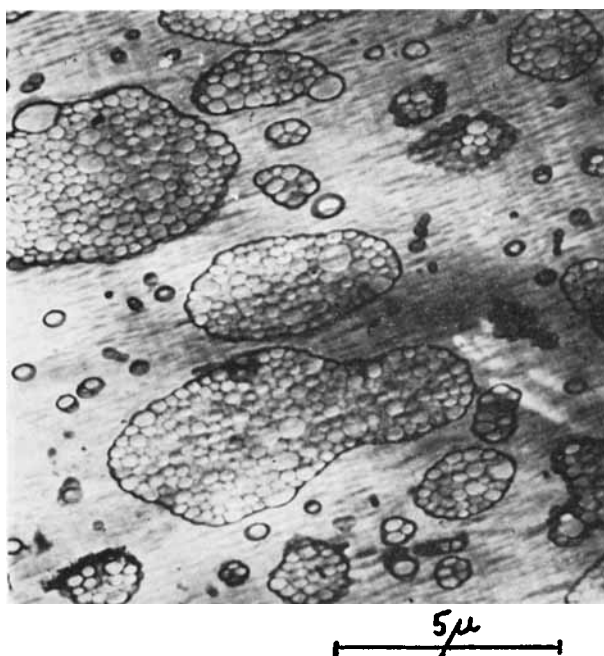

Fig. 10. Electron photomicrograph of final polymer showing structure resulting from aggregation of many subparticles.

dispersive mixing at the higher shear level, resulting in the easier separation of the stable constituent subparticles. Examination of electron micrographs of various finished polymers also leads to the conclusion that coalescence of the subparticles within the droplets is quite rare, but an example is shown in Figure 11. This should more easily occur in the higher shear field of the cone-and-plate viscometer, as mentioned earlier (but where there is no mixing); however, in the reactor system, the higher shear is obtained with improved mixing, and therefore the cluster size is reduced resulting in a smaller surface area of the particle and consequently a reduced force for coalescence.

This explanation can be linked to the suggestion that variation in impact strength frequently observed between polymers of the same rubber content may also be due to variation in the composition of the rubber particles. It is thought by Bucknall[8] that subinclusions of the glassy polystyrene within the rubber particles increases the volume of matrix that
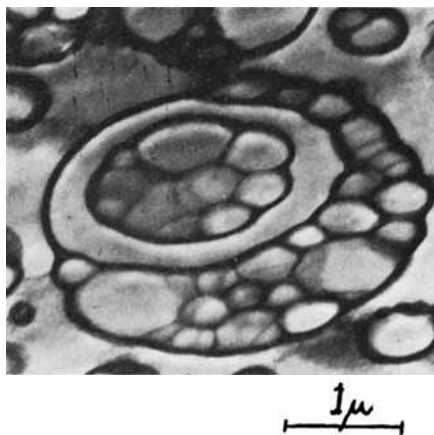

Fig. 11. Electron photomicrograph of composite particle within final polymer illustrating coalescence within a droplet.
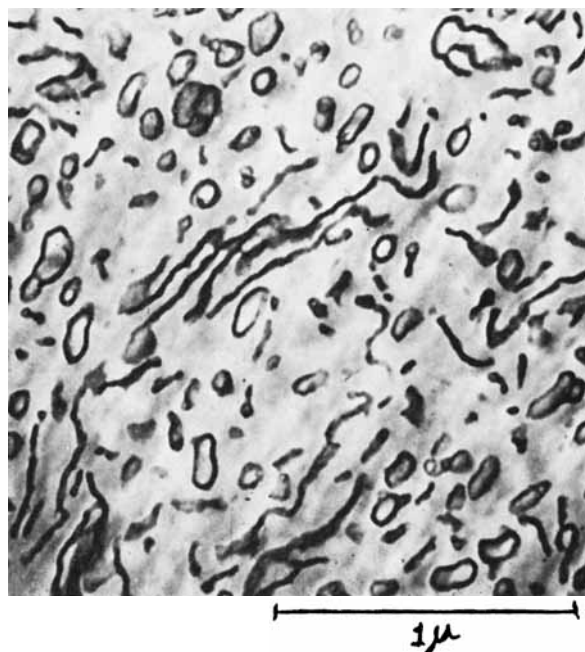

Fig. 12. Electron photomicrograph of final polymer showing the threadline structure resulting from the prevention of aggregation of subparticles.

is subject to the stress-concentrating effects of the particles leading to an increased rate of craze initiation and hence higher impact strengths.

Mass transfer of styrene monomer from the composite particles in the postphase-inversion stage will be facilitated in the case of composite particles made up of a few subparticles; whereas in the case of the more complex structure, transfer to the continuous phase will be less easy, and such structures could be expected to contain higher proportions of glassy polymer within the rubber phase in the finished product. Mechanical tests on polymers made under otherwise identical conditions except for this structural variation support this argument. Indeed, if aggregation of droplets is prevented at the phase inversion point so that the final product consists of finely dispersed discreet rubber particles originating mainly from separated subparticles, as shown in Figure 12, then the material becomes quite brittle.

CONCLUSIONS

The role of agitation in the production of HIPS during the bulk polymerization of a styrene solution of a butadiene rubber is identified with the following requirements:

1. Prior to phase inversion—the maintenance of phase equilibrium by the continual formation of new droplets.

2. Near phase inversion—the restriction of close packing of droplets by dispersive mixing.

3. At phase inversion—first the maintenances of the minimum shear requirement for inversion to occur; second, control of droplet structure via subparticle aggregation.

4. Postphase inversion—control of mass transfer of styrene from droplets to the continuous phase.

Because of the critical nature of step 3 in the process and its dependence on the average shear rate in the reactor, calibration for the power number-versus-Reynolds number relationship has been investigated (see Figure 8) and shown to be comparable for a heterogeneous system with phase reversal, with the usual N_p–N_{Re} relationships available for homogeneous Newtonian and non-Newtonian liquids.

Symbols Used

c	per cent styrene polymerized
D	inside diameter of reaction vessel
k	constant
d	outside diameter of ribbon agitator
N	rotational speed of agitator
N_p	dimensionless power number, $P/\rho N^3 d^5$

N_{Re} dimensionless Reynolds number, $Nd^2\rho/\mu$

P power consumption

t mixing time

$\dot{\gamma}$ shear rate

ρ fluid density

μ fluid viscosity

Where subscripts are used, these are clearly defined in the text.

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