

## The Production of Rubber-Modified Polystyrene. II. The Significance of Shear in the Phase Inversion

G. F. FREEGUARD and M. KARMARKAR

*Department of Chemical Engineering, University of Nottingham, England*

### Synopsis

Phase inversion of the two-phase system consisting of a polystyrene-in-styrene phase distributed in a rubber-in-styrene phase is shown only to occur above a minimum shear rate, which is experimentally determined for a range of rubber concentrations. The conditions for agitation of the system to give a smooth and nondelayed inversion point are separated into meeting two requirements, one of which is related to mass transfer to the discontinuous phase and the other, to meeting the shear requirement; these are discussed in terms of the known rheological behavior of the system.

### INTRODUCTION

In the preceding paper,<sup>1</sup> the rheological characteristics of the two-phase system rubber/styrene-polystyrene/styrene were evaluated as a precursor to the analysis, during *in situ* polymerization, of those factors which lead to product optimization. It has been established that during polymerization the system becomes progressively more non-Newtonian to the phase inversion point and that the equation

$$\log \frac{\mu}{\mu_c} = 2.5 \left( \frac{\mu_d + a\mu_c}{\mu_d + \mu_c} \right) (\phi + \phi^{5/3} + \phi^{11/3}), \quad (1)$$

where  $\mu$  = solution viscosity,  $\mu_c$  and  $\mu_d$  = viscosity of continuous and dispersed phase,  $\phi$  = volume fraction of rubber phase, and  $a = -0.505$ , predicts the apparent viscosity with reasonable accuracy. The importance of shear forces in mixing to promote mass transfer between phases at the inversion point is now discussed in connection with the apparent fluid viscosity, since this paper is concerned with a study of the phase inversion in a constant shear environment and relates this to the problem of mixing within the polymerizing system.

Thermodynamically, phase inversion is an instantaneous process since the phase equilibrium is defined by the thermodynamic properties of the system. However, in practice, this may not be the case and there may be a considerable delay in reaching the new equilibrium condition, during which time the inverting phases are in metastable equilibrium. The principle reason for this delay can be attributed to the necessity for significant mass,

transfer between phases. This is a function of the "thickness" of the fluid and, in general, mass transfer is easier when viscosity is lower. The homogenization of a fluid mass can be accomplished by effective agitation and mixing of the system; mixing and agitation are, however, two terms which are frequently used synonymously; and in view of the importance of these concepts in this series, it is important to clarify this point. In fact, it is possible to agitate a system without any resulting mixing action, and it is also possible to mix without agitation, through the action of molecular diffusion. Thus, in the latter case it is conceivable that phase inversion could proceed through the action of molecular diffusion of styrene between phases, or alternatively in the former case for there to be insufficient agitation of the system for inversion to occur.

Mixing involves two fundamental processes: circulation of the fluid and dispersion through shear forces. Circulation patterns depend on the geometry of the reactor design, whereas shear forces are fundamental to the rheological behavior of the system.

### EXPERIMENTAL

A constant shear environment cannot be produced by using conventional stirrers; however, the cone-and-plate viscometer used in the preceding paper is designed for this purpose, since the shear rate is constant throughout the sample and is preset by selecting a particular speed for the appropriate cone. Thus, the novel approach adopted was to use the Ferranti-Shirley viscometer as a miniature reactor, although there are certain limitations that must be borne in mind. The principal of these is that there is little or no mixing action within the fluid so that the reactor could only be used over narrow ranges of conversion.

The plate of the viscometer was maintained at 70°C (maximum permissible operating temperature 75°C) by circulating oil from a constant-temperature bath, a digital temperature readout being available. The disadvantage of using only a very small sample was somewhat compensated for by the constant temperature of the samples due to good heat transfer. Secondary flow effects arise if the cone angle is larger than 1°; and to avoid this, cones of angles smaller than this were used. This places a restriction on the range of the viscosity of the samples investigated; however, the original range of rubber loadings of 6%–12% could be easily accommodated. Initially, the loss of styrene monomer was reduced by the use of a guard ring around the cone, but since contact with air was not excluded, the polymer at the edges showed slight signs of discoloration during the time taken for an experiment. Thus, to avoid contact with air which may result in a change of polymerization rate, the apparatus was further modified and an aluminum ring was fixed onto the plate by means of four screws. This effectively formed a trough which when filled with polymer completely immersed the cone. In order not to introduce wall effects, the distances from the inside edge of the trough to the edge of the cone was kept greater than 1

cm (30% of the radius of the cone). Nitrogen gas saturated with styrene vapor was passed over the sample by introducing it through the annular rings.

Before use with the polymerizing system, the apparatus was extensively tested using 50-poise silicone fluid to ensure that wall effects were not present and that reproducible and accurate viscosities were measured.

It will be appreciated by reference to the data presented previously that near the phase inversion point, the torque readings on the cone would be expected to decrease rapidly before increasing relatively slowly, initially making visual recording difficult. Hence the dc voltage signal from the measuring unit of the viscometer was split into two, one output was connected as usual to the galvanometer in the indicating unit and the other was connected to a data logger which digitized at the rate of 1 digitization/sec. The digital output could be either punched on paper tape in a format suitable to

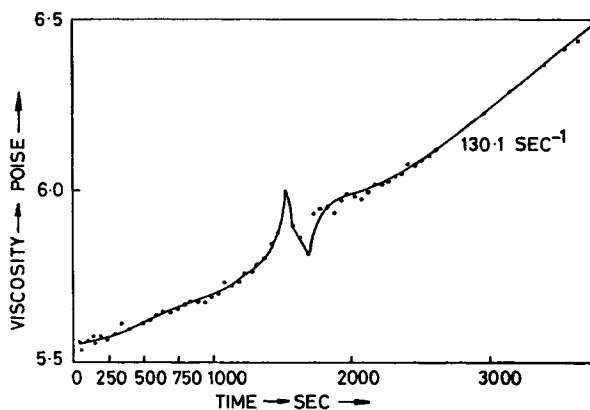


Fig. 1. Viscosity as a function of time for sample sheared at  $130 \text{ sec}^{-1}$  through phase inversion in cone-and-plate viscometer.  $T = 70^\circ\text{C}$ .

be handled on a KDF-9 computer or handled on-line by a PDP8 computer working through a suitable interface on a time-shared basis. Full details of the computer systems form part of an associated investigation and are to be published separately.

The polymerization was initially conducted in the reactor as previously described; however, close to the phase inversion point, as judged from the viscosity and phase contrast microscopy, a sample was transferred to the trough on the plate of the viscometer. The cone speed was set and the gap closed; in about 10 sec a steady reading was obtained on the indicating unit when the data logger could be switched on. Usually, measurements were made until the phase inversion had occurred in the 1-liter reactor system, to ensure that adequate data had been collected. The cone and plate were then disengaged so that samples taken from the inside edge of the cone, center of the cone, and center of the plate could be examined with the phase contrast microscope. This experimental pattern was followed for each

rubber concentration using a range of shear rates from  $21.7 \text{ sec}^{-1}$  to  $217 \text{ sec}^{-1}$  over eight increments. After processing, the data is conveniently presented as a graph of apparent viscosity versus time, as shown in Figure 1.

## RESULTS AND DISCUSSION

For each rubber concentration it was established that there was a minimum shear rate below which phase inversion does not occur. This result is summarized in Figure 2, which shows a plot of the minimum shear rate versus the initial rubber concentration. Furthermore, in all experiments conducted at shear rates above this minimum value, phase inversion was rapid and the curve exhibited the expected sigmoidal shape. Using the data previously presented to calculate the corresponding shear stresses, it is seen that these vary from  $330 \text{ dynes/cm}^2$  at 6% rubber concentration to  $2300 \text{ dynes/cm}^2$  at 12%. However, it has been previously pointed out that there could be a danger in representing the data in terms of stress since no distinction has been made in terms of the normal and tangential forces, and there is some indication that these could become comparable in the inverting system.

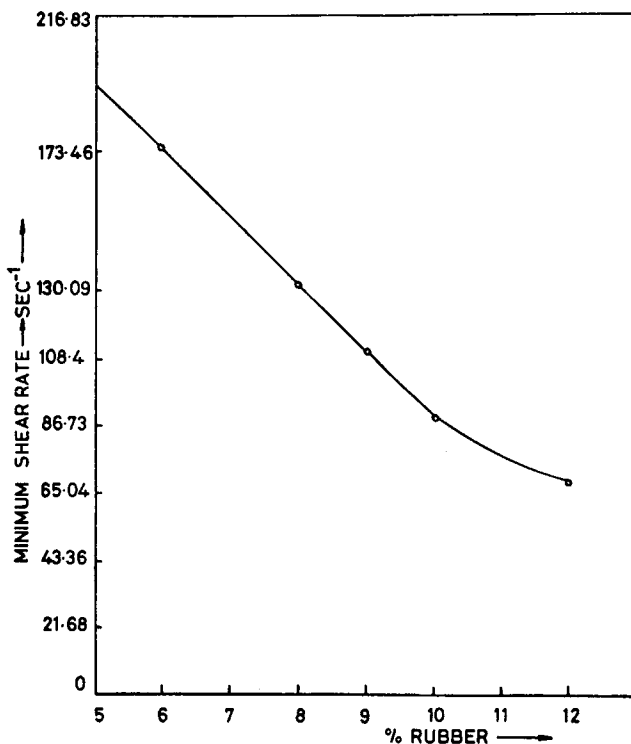


Fig. 2. Minimum shear rate ( $\text{sec}^{-1}$ ) for phase inversion of the two-phase systems as a function of rubber concentration.

The results of these experiments clearly indicate that in a reaction vessel with a conventional agitator, phase inversion can only occur when there is a balance between the shearing and mixing actions. Without shear and with no mixing, no inversion of the phases will take place; good mixing and less than the minimum shear also results in the noninverted product.

As a reactor, the plate and cone is an idealized case where the shear rate is uniform throughout the fluid. In any conventionally agitated vessel there is maximum shear in the vicinity of the agitator blades, and this decreases very rapidly as distance from the blade increases giving rise to a considerable variation in shear rate. Therefore, it is necessary to relate the minimum rate of shear  $\dot{\gamma}_{\min}$  found by use of the plate-and-cone viscometer to the average rate of shear  $\dot{\gamma}_{\text{av}}$  in the reactor, where to a first approximation it will be appreciated that a properly inverted product will only be obtained when  $\dot{\gamma}_{\text{av}} \geq \dot{\gamma}_{\min}$  and that the speed of inversion will be some function of  $(\dot{\gamma}_{\text{av}} - \dot{\gamma}_{\min})$ , so that within limits the higher the average shear, the shorter will be the time for total inversion. Under idealized conditions of constant shear, inversion is seen to occur almost instantly at shear rates above the minimum value.

The situation may now be examined in the light of mass transfer requirements between phases, as set by the equilibrium conditions. Phase equilibrium measurements similar to those described by Molau,<sup>2</sup> shown graphically in Figure 3, indicate that in the initial stages of the polymerization, a relatively small change in the polystyrene concentration promotes a large change in the relative volume,  $\Psi$ , of the two phases. This is best illustrated in Figure 4, where the tangent to the curve  $d\Psi/dc$  is plotted as a function of concentration, from which it is apparent that if equilibrium between phases is to be approached, mass transfer of styrene from the rubber phase to the polystyrene phase must be greater during the early stages of polymerization. In fact, the initial stage of the process through the phase

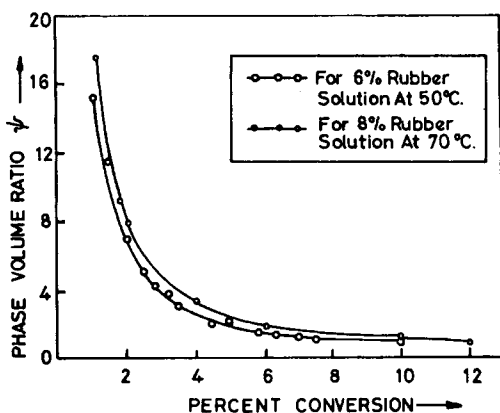


Fig. 3. Phase volume ratio as a function of degree of conversion for the polymerization of 6% and 8% solutions of polybutadiene rubber in styrene.

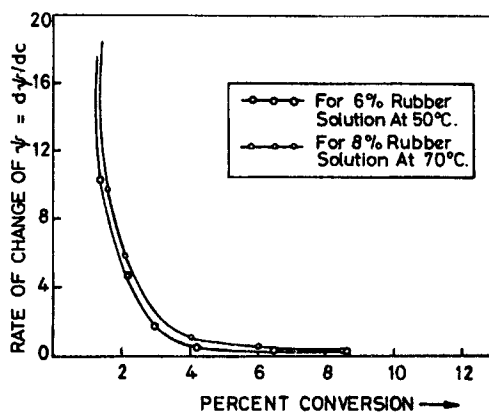


Fig. 4. Rate of change of phase volume for the polymerizing system as a function of conversion.

inversion point may be conveniently examined in detail as controlled by this requirement.

At about 2% polystyrene concentration, the form of the discontinuous phase is established as solution droplets; there is also a rapid growth of this phase volume. However, it does not follow that there is subsequent transfer of styrene from the continuous phase to these droplets. The styrene concentration of the polystyrene phase calculated from Figure 3 shows little change between 2% and 9% conversion, indicating the absence of a strong driving force for styrene diffusion into the original droplets. Thus, droplets formed initially will tend to continue almost unchanged in concentration and hence volume and size, and therefore the discontinuous phase formation is more likely to be through the formation of new droplets.

The role of agitation in the initial stages is seen as promoting the formation of droplets and hence new surface area rather than the assistance of droplet growth by promoting mass transfer through the droplet surface. This can be achieved with the simplest form of agitation and can accommodate the relatively high rates of surface area generation consistent with high initial rates of polymerization.

If droplets of comparable size are continuously formed phase inversion could be delayed until a volume ratio of approximately  $1/3$  is reached, since under conditions of close packing the discontinuous phase could occupy 74% of the total volume of the system. Under such circumstances, the viscosity of the system will continue to rise as indicated by eq. (1), thus making it progressively more difficult to attain the minimum shear necessary to invert. It can be expected that the graft copolymer will additionally stabilize these droplets and therefore coalescence will not readily occur.

Thus, near phase inversion, the role of agitation is seen as restricting the approach to close packing by dispersive mixing through shear. For-

tunately, since the system is pseudoplastic, there exists a route for lowering the viscosity barrier; hence the existence of a minimum shear rate.

### CONCLUSIONS

The requirement for agitation is seen as meeting two distinct functions during in situ polymerization. The first is indicated as being closely associated with the form of the phase equilibrium diagram for the two-phase system and related to it by the polymerization rate. The second is highly dependent on the non-Newtonian nature of the system and occurs under conditions of low phase growth rate. Generally, these two conditions are not mutually exclusive, and the conditions which satisfy the second requirement usually satisfy the first, an obvious exception to this being the cone-and-plate system itself. In the uniform shear field produced in this instrument, providing that the shear rate is greater than the limiting value, phase inversion is observed to occur almost instantaneously, as demonstrated by Figure 1.

Finally, it should also be noted that the existence of the minimum shear rate influences the measurement and representation of the viscosity data near the inversion point. If the sample is sheared at a higher rate than  $\dot{\gamma}_{\min}$ , it is possible to complete phase inversion in a sample taken from a reactor where phase inversion was incomplete, with a corresponding change in its rheological character. It is therefore recommended that, where possible, measurements be made below  $\dot{\gamma}_{\min}$  for evaluating the rheological behavior of the reactor fluid, and this is particularly important if the data are to be used for analysis of the trends in power law index and consistency index, as previously described.<sup>1</sup>

We wish to thank the International Synthetic Rubber Company for providing the rubber used in this investigation, and Dr. C. I. Pulford for his assistance with the design of the data processing system.

### References

1. G. F. Freeguard and M. Karmarkar, *J. Appl. Polym. Sci.*, **15**, 1649 (1971).
2. G. E. Molau and H. Keskkula, *J. Polym. Sci. A*, **4**, 1595 (1966).

Received October 21, 1970