

The Production of Rubber-Modified Polystyrene.

I. Rheological Behavior of the Polymerizing System

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Synopsis

The rheological behavior of the two-phase systems consisting of a polystyrene-in-styrene phase distributed in a rubber-in-styrene phase is shown to exhibit increasing non-Newtonian behavior up to the phase inversion point, as a consequence of its two phase nature. The equation

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

is recommended for the prediction of the viscosity of the polymerizing mass up to phase inversion during the production of HIPS by the in situ bulk polymerization of styrene in the presence of dissolved rubber.

INTRODUCTION

Of the three methods used for the production of rubber-modified polystyrene (High Impact Polystyrene, HIPS), viz., mechanical blending, latex blending, and in situ polymerization of styrene in the presence of dissolved rubber, it is the latter process that is generally considered to be the more advantageous, industrially. The process involves the polymerization of a solution of an elastomer in the monomer styrene, and it is claimed that agitation of the polymerizing system is of crucial importance for the production of "high impact" material.¹ Shortly after the beginning of the polymerization, a phase separation occurs to give rubber-styrene and polystyrene-styrene phases in the form of an oil in oil emulsion,² POO. A phase inversion of this emulsion takes place in the first stage of the polymerization which leads to the formation of rubber solution droplets. The final polymer consists of a continuous polystyrene phase and a discontinuous rubber phase, which is particulate in nature. The exact mechanism whereby the rubber particles impart good impact properties to the system is still under discussion, but it is certainly without dispute that if agitation is omitted from the above procedure, an interwoven network structure can be produced with very poor impact properties. By understanding first how the rubber particles are formed and then by producing controlled structure, more progress toward elucidating the toughening mechanism is to be expected.

The current literature available on the rheological behavior of the polymerizing mass is that by Bender³ and Molau⁴ and is of a semiquantitative nature. It is first reported³ that the viscosity of the prepolymer increases with increasing styrene conversion and passes through a maximum and then a minimum followed by regular increase along a line of lower slope on a semilogarithmic plot of viscosity versus conversion (see also Fig. 1). It was noted that just prior to phase inversion, the prepolymer was rough and stringy with a tendency to climb the stirrer shaft, indicating high normal shear stress. After inversion, the prepolymer was smooth and fluid; inversion occurred between the curve maximum and minimum.

Molau et al.⁴ have successfully reproduced the sigmoidal curve by blending the appropriate concentrations of rubber and polystyrene solutions in the presence of 0.6 wt-% 73:30 styrene-butadiene A-B-type block copolymer as emulsifier. They observed that the viscosities of solutions of rubber in styrene are considerably higher than those of polystyrene solutions and argue that since initially it is the rubber solution that is the continuous phase, the viscosity of POO emulsions is representative of the rubber phase, while at phase inversion it becomes representative of the polystyrene phase. Thus, on phase inversion there is a drop in viscosity followed by a gradual increase as more polystyrene is formed and its concentration in the viscosity-determining phase increases. There are thus apparent limitations in the data available; it is not likely that the system behaves as a Newtonian fluid, and thus the shear rate at which the viscosities are measured is of importance. It is interesting to note that Bender does not report his rate of shear and that Molau has worked at a constant value of 88.0 sec⁻¹. Furthermore, both workers have made measurements at 25°C, which is not practical as far as a polymerizing system is concerned.

The purpose of this paper is to classify the rheological behavior of the prepolymer prior to phase inversion when the rubber solution is the continuous phase. The exact nature of the agitation necessary to promote phase inversion is discussed in a subsequent paper, while a further paper will show how these findings are related to a design procedure for the reactor with a view to optimizing product structure and properties.

EXPERIMENTAL

Polymerizations were carried out in a reaction vessel of 1-liter capacity maintained at 70.0°C by means of external infrared heaters through a control system. The rubber employed was I.S.R. polybutadiene in the concentration range 6%–12%, and the reaction was catalyzed by 0.2% benzoyl peroxide to give a polymerization rate of approximately 3%/hr at the reaction temperature. During the course of the reaction, samples were regularly withdrawn from the reactor, and for each, the shear rate–shear stress relationship was determined at 70°C by the use of a Ferranti-Shirley cone-and-plate viscometer. The level of conversion was also determined for each sample by a total solids determination (and also residual monomer by GLC),

and the progress of the reaction was followed optically by observations on a phase contrast microscope.

Computer programs were developed to calculate first apparent viscosities and then by means of the least-squares procedure to fit this data to the power law equation in the form

$$\log \tau = n \log \dot{\gamma} + k$$

where τ denotes shear stress, $\dot{\gamma}$ is shear rate, and n and k are the power law index and consistency index, respectively.

RESULTS AND DISCUSSION

The pseudoplasticity of the system is typically illustrated in Figure 1, which shows apparent viscosity of the polymerizing mass over the important range of styrene conversion at a variety of shear rates for the 8% rubber system. By reference to Figures 2 and 3, it is to be further noticed that the power law index n passes through a minimum, while the consistency index k

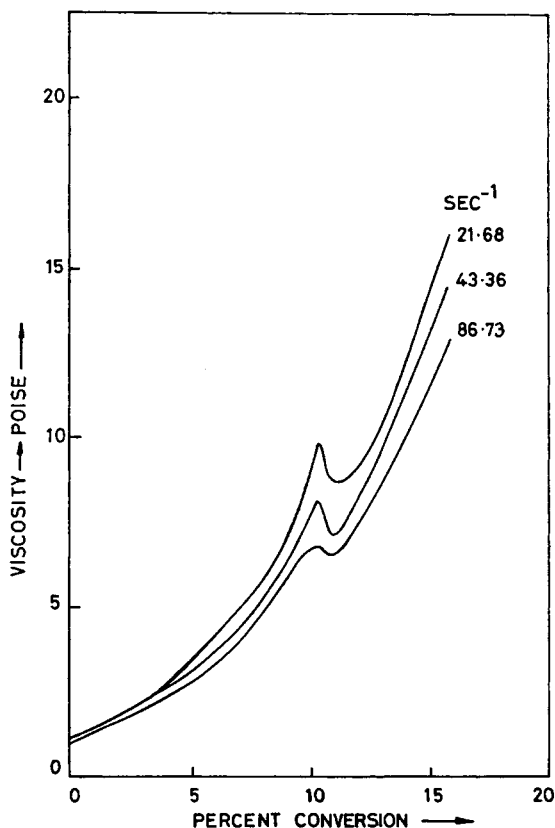


Fig. 1. Apparent viscosity (poise) as a function of shear rate for the polymerization of a solution of polybutadiene rubber in styrene. $T = 70^{\circ}\text{C}$.

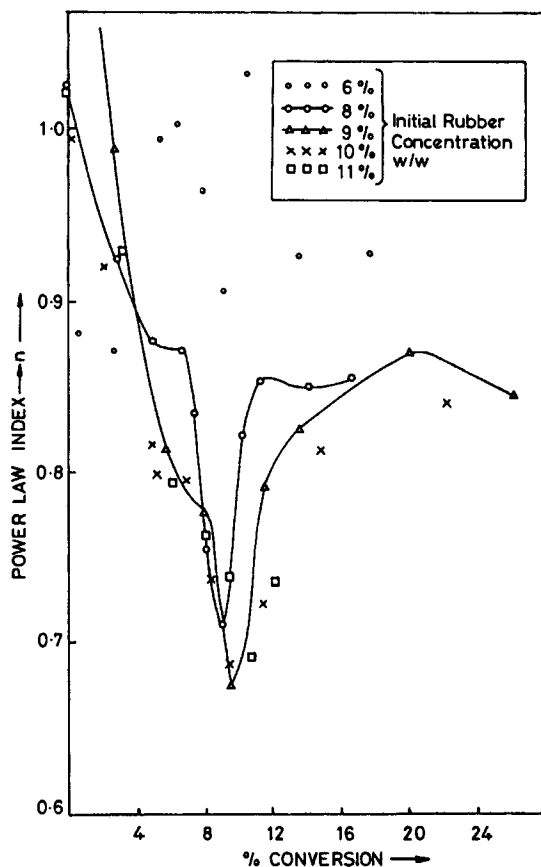


Fig. 2. Power law index n as a function of degree of conversion for the polymerization of a solution of polybutadiene rubber in styrene.

passes through a maximum at the inversion point. The decrease in n that occurs in the polymerizing system indicates a progressive departure from Newtonian behavior, whereas the increase in k accounts for the observed increase in apparent viscosity as shown in Figure 1.

Before considering exactly how representative the system's apparent viscosity is of the continuous phase viscosity, it is necessary to give some thought to the part played by the gradual increase of polystyrene in the system as a whole. In terms of the phase volume diagram, for two incompatible polymers, as the per cent conversion increases, the rubber phase volume decreases since there is a volume increase of the polystyrene phase. Therefore, there must be a concentration effect in the rubber phase; but the situation in the polystyrene phase can only be evaluated by recourse to the phase diagram. This will be fully considered in a subsequent paper. However, at present it is sufficient to appreciate that the earliest that phase inversion can occur is when the phase volume of the polystyrene phase only just ex-

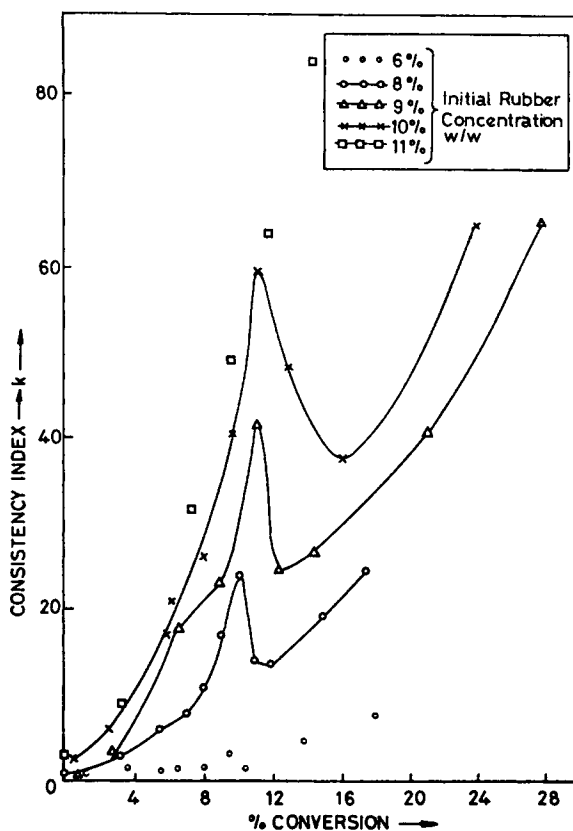


Fig. 3. Consistency index k as a function of degree of conversion for the polymerization of a solution of polybutadiene rubber in styrene.

ceeds that of the rubber phase. At this time, the concentration in each of the phases of the inverting systems should be, to a first approximation, double their concentration in the system as a whole.

Considering now, for example, the case of an 8% rubber solution; it will be seen from Figure 2 that the value of the power law index at phase inversion is approximately 0.7, in contrast to the measured value of 0.98 (indicating near-Newtonian behavior) for the 16% rubber in styrene solution alone. From an analysis of all the systems studied, it is concluded that the rheological behavior of the polymerizing system is mainly determined by the two-phase volume characteristics rather than specific properties of the continuous phase.

In a simplified treatment, Molau⁴ has shown that the viscosity curve can be reproduced by adding solutions of the two individual components in the presence of graft copolymer. Derived and empirical correlations for water-in-oil-type emulsions are available,⁵ and the following have been fitted to the data with the aid of the "Multifit" computer program⁶ to test their suit-

ability as an aid for predicting the apparent viscosity as a function of conversion to the inversion point:

$$\mu = \mu_c(1 + 2.5\phi + a\phi^2 + b\phi^3 + \dots), a = 4 \text{ to } 14 \quad (1)$$

$$\ln \frac{\mu}{\mu_c} = \frac{K_E \phi}{1 - S\phi}, K_E = 2.5, S = 1.35 \quad (2)$$

$$\mu = \mu_c \exp(K\phi) \quad (3)$$

$$\mu = \mu_c \frac{1}{1 - \phi^{1/3}} \quad (4)$$

$$\mu = \mu_c \left[1 + 2.5\phi \left(\frac{\mu_d + a\mu_c}{\mu_d + \mu_c} \right) \right] \quad (5)$$

$$\log \frac{\mu}{\mu_c} = 2.5 \left(\frac{\mu_d + a\mu_c}{\mu_d + \mu_c} \right) (\phi + \phi^{5/3} + \phi^{11/3}) \quad (6)$$

where μ = viscosity of the system; μ_c and μ_d = viscosity of continuous and dispersed phase; and ϕ = volume fraction of rubber phase.

It is to be noted that eqs. (5) and (6) assume some contribution from the discontinuous phase viscosity since the situation is not completely analogous to the water-in-oil emulsions where, because the viscosity of the dispersed phase is very much lower than that of the continuous phase, its contribution may perhaps be neglected. Equation (5) with $a = 0.4$ is derived from theoretical hydrodynamics by Taylor⁷ and becomes identical with the Einstein equation governing the viscosity when the second phase consists of solid spheres when μ_d is infinite. Equation (6) is a modification of eq. (5) by Leighton and Leviton⁸ by the introduction of a power series in which the term $\phi^{5/3}$ agrees with a proposal by Smoluchowski,⁹ but $\phi^{11/3}$ is only of empirical significance.

Good fits were only obtained with those formulas which included some contributions from the discontinuous phase viscosity. The best agreement is obtained using eq. (6), and the recommended value for the constant a is -0.505 when the fit is within 7%.

A further refinement would be to take account of the part played by the graft copolymer. In the case of W/O emulsions it has been observed that the viscosity of the system is higher the higher the emulsifier concentration. The case of POO emulsions produced by in situ polymerization is more complex, since the graft is formed by a reaction involving the rubber already present in the system. Effectively the rubber concentration is lowered at a rate which is dependent on the grafting rate with a consequent lowering of the continuous phase viscosity together with a secondary viscosity effect due to graft emulsifier. When comparing systems where the only difference is a higher graft concentration, the net effect is that the viscosities are generally lower at the same conversion level.

CONCLUSIONS

It is established that the polymerizing system is pseudoplastic due to its two-phase nature and that the maximum deviations from Newtonian behavior occur at the phase inversion point. In practice, using eq. (6), the apparent viscosity of the system can be predicted as a function of the polymerization rate by establishing the percentage conversion and from a knowledge of the phase equilibrium diagram.

The minimum value of the power law index may well be of significance with respect to mass transfer between phases at the inversion point. Brodnyan et al.⁶ have observed that as the flow behavior index drops to about 0.7 in the case of polyisobutylene solutions, normal stresses increase to about the same level as the shearing stresses. In this work, the rubber used was selected because it does not markedly exhibit the Weissenberg effect at the phase inversion point. However, some rubbers present a problem at phase inversion in that the solution climbs the stirrer shaft to such an extent that fluid contact with the vessel wall is lost and no mixing occurs. A suggestion is that in such cases the flow behavior index has become less than the critical value resulting in high normal stresses; such a correlation would be useful as a screening procedure for the selection of the rubber.

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