

Dispersion of Microgel in Impact Polystyrene

B. W. BENDER, *Texas-U. S. Chemical Company, TEXUS Research Center, Parsippany, New Jersey*

Synopsis

During the bulk agitated polymerization of styrene containing dissolved SBR, a phase inversion was found to occur at fairly low styrene conversion levels. Below this inversion point, the continuous phase was rubber-in-styrene, while above it the rubber-in-styrene became dispersed in a continuous phase of polystyrene-in-styrene. At the point of phase inversion, there was a marked reduction in bulk viscosity, large changes in polymer intrinsic viscosity, and in the light transmission of 5% polymer solutions in toluene. At partial styrene polymerizations, the dried prepolymer films were insoluble in 2-butanone before phase inversion had occurred and soluble thereafter.

After partial polymerization of the styrene in the bulk agitated stage, polymerization was completed in aqueous suspension. To get the ultimate dispersion of the rubber particles, which became crosslinked to form microgel, it was necessary to carry the bulk agitated polymerization well beyond the phase-inversion point. The size of the final microgel particles was related to the initial viscosity of the SBR with the more viscous rubbers forming larger microgel particles. The desirable microgel particle size was indicated to be in the 1-10 μ range. When suspension polymerization was carried out before phase inversion was completed in the bulk agitated stage, the fully converted polymer contained very large networks of crosslinked grafted rubber gel and was insoluble in toluene.

Introduction

Impact polystyrene, when made by polymerizing styrene in the presence of dissolved rubber, consists of a matrix of styrene homopolymer containing a dispersed microgel of grafted, crosslinked, rubber particles. The properties of impact polystyrene are highly dependent on the number, size, and character of the dispersed particles. The present work was intended to determine how dispersion of the rubber particles occurs and how the size of the microgel particles may be controlled.

Experimental

Solutions of rubber in styrene were partially polymerized under nitrogen in a slowly stirred 1-gal. reactor at 85-95°C. to form a prepolymer. A typical recipe is: styrene, 920 g.; SBR, 80 g.; *tert*-dodecyl mercaptan, 2.0 g.; Ionol CP, 2.0 g.; benzoyl peroxide, 0.5 g.; dicumyl peroxide, 0.5 g. The SBR generally used was SYNPOL 1061C (Texas-U. S. Chemical Co.), which is a hot emulsion copolymer containing 77% butadiene and 23% sty-

rene and having a Mooney viscosity of 40 ML-4 at 212°F. It is emulsified with fatty acid soap and stabilized with a phosphite-type antioxidant.

When the prepolymer was intended for further study as such, the reaction was shortstopped at a given conversion level with one gram hydroquinone dissolved in 2-butanone. Conversion in the prepolymer stage was in the range of 2–40% during the study.

When complete conversion of the styrene was desired, an aqueous suspension of the prepolymer was formed by adding to the reactor 2000 g. water containing 0.07% poly(vinyl alcohol), 0.02% alkyl aryl sulfonate, and 0.08% sodium chloride.

Polymerization was completed in 16–20 hr. at 130–140°C. with sufficient agitation to keep the particles suspended. The impact polystyrene was recovered in the form of beads which were washed and dried. Finally, the beads were passed through a 1-in. laboratory extruder at 350°F. followed by granulation.

Prepolymer Behavior

The bulk viscosity of the prepolymer increased with increasing styrene conversion, passed through a maximum then through a minimum followed by a regular increase along a line of lower slope on semilog plot of viscosity versus conversion. Phase inversion, as judged by subsequent tests, occurred between the maximum and minimum, designated as points *A* and *B* respectively, in Figure 1. Stirring behavior in the reactor indicated that the prepolymer became not only less viscous but also less viscoelastic in its rheological behavior. Just prior to phase inversion, the prepolymer was rough and stringy and tended to climb the stirrer shaft, indicating high normal shear stress. After inversion, the prepolymer was smooth and fluid

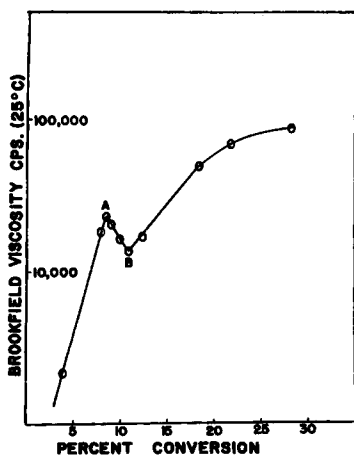


Fig. 1. Brookfield viscosity at 25°C. of bulk rubber-styrene prepolymers at various styrene conversion levels.

and would not climb the stirrer shaft even at high conversion and higher viscosities.

Prior to the attainment of the minimum viscosity, a dried film of the prepolymer prepared by evaporating the unreacted styrene would not

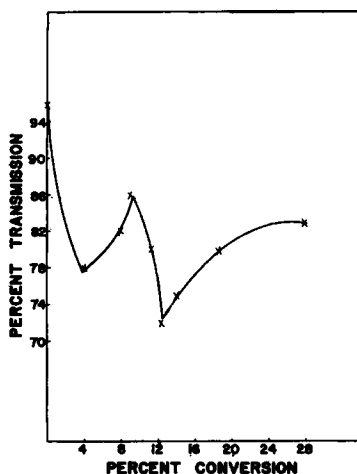


Fig. 2. Light transmission of 5% solutions of dried prepolymer in toluene at various styrene conversion levels.

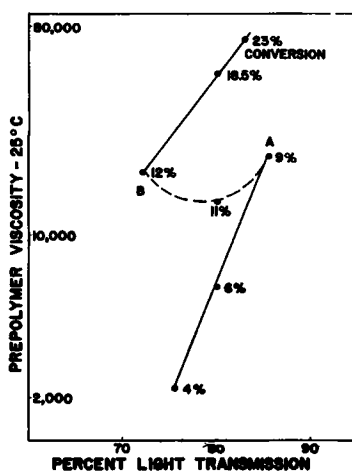


Fig. 3. Relation between bulk viscosity of prepolymer and light transmission of 5% solutions of dried prepolymer in toluene.

disintegrate in 2-butanone, since the continuous phase (rubber) is not soluble. After the minimum viscosity point, the prepolymer film, prepared and treated in like fashion, disintegrated quickly, as the polystyrene continuous phase dissolved to form a turbid solution containing suspended rubber particles.

Dried prepolymer films, at various styrene conversion levels, were made into 5% solutions in toluene for light transmission tests with a Fisher photometer using a blue filter. The turbidity here was caused by the presence of a dispersed phase which dissolved at higher dilutions. Irregularities in the curve of light transmission versus conversion (Fig. 2) occurred at the same conversion levels where the decrease in viscosity was noted. The inversion of phases is made more apparent by plotting prepolymer bulk viscosity against light transmission of 5% solutions (Fig. 3); inversion occurred between points designated *A* and *B* at 9 and 12% conversion, respectively.

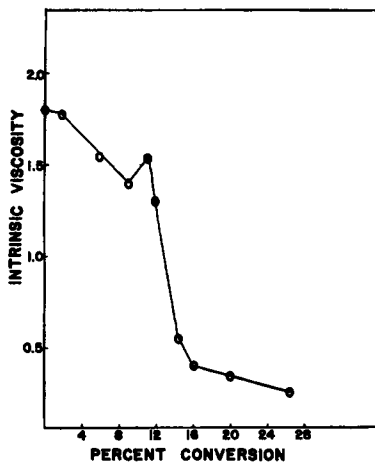


Fig. 4. Intrinsic viscosity of dried prepolymer at various styrene conversion levels.

Intrinsic viscosities of the dried prepolymer film decreased rapidly as styrene conversion proceeded and showed some irregularities in the area of phase inversion (Fig. 4). Up to 9% conversion, the values obtained were typical of the rubber used, while beyond 14% conversion the values were more typical of the styrene homopolymer.

Grafting

It was considered that the irregularities in the curves of light transmission and intrinsic viscosity during phase inversion might be related to the grafting of polystyrene to rubber. Turbidimetric titrations were carried out on 0.02% solutions of dried prepolymer film in toluene, methanol being used as the nonsolvent (Fig. 5).

The presence of soluble graft is indicated by the intermediate peaks in the differential plots at 9.0 and 11.2% conversion.¹ The prepolymer at 11.2% conversion was fractionated by partial precipitation with methanol from a toluene solution at the ratios of nonsolvent to solvent indicated by the turbidimetric titration for each of the three respective fractions. Each separated fraction showed a single peak in the differential plot of its tur-

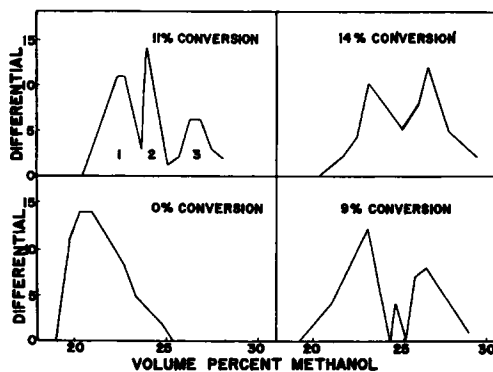


Fig. 5. Differential plots for turbidimetric titrations of rubber-styrene prepolymers at various styrene conversion levels.

bidimetric titration. Styrene determinations indicated the compositions listed in Table I.

TABLE I

| Fraction | Wt.-% of total | Styrene content, % | Calculated | |
|----------|-------------------|-----------------------|----------------------|---------------------------|
| | | | Rubber content, % | Polystyrene content, % |
| 1 | 26.3 | 31 | 90 | 10 |
| 2 | 47.5 | 70 | 39 | 61 |
| 3 | 26.2 | 100 | nil | 100 |

The total dried sample at 11.2% styrene conversion contained 42% rubber and 58% converted styrene polymer. At this conversion level, where phase inversion was just completed as judged by the viscosity curve, slightly over half of the converted styrene appeared have been grafted to the rubber.

Under the experimental conditions of this work, the entire polymer remained soluble in toluene until styrene conversion exceeded 80%, at which point insoluble microgel began to appear as crosslinking occurred at high styrene conversions. The total insoluble microgel at 100% styrene conversion usually ranged about double the weight of initially dissolved rubber, representing a degree of grafting of polystyrene to rubber of 100%, or a grafting efficiency of 8% in systems containing 8% rubber initially.

Microgel Particle Size

Under the experimental conditions of this work, it was found necessary to carry the agitated bulk-stage conversion of styrene well beyond the phase-inversion point before making the aqueous suspension to get the ultimate dispersion of microgel particles in the finished impact polystyrene.^{2,3} At 25-30% conversion in the prepolymer stage, the final microgel particles

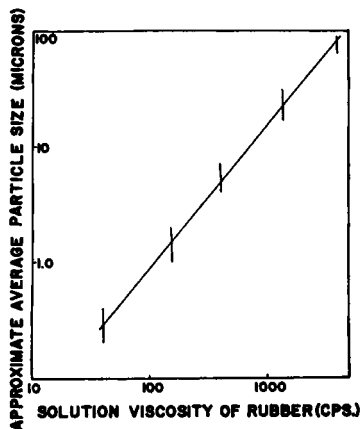


Fig. 6. Relation of microgel particle size in impact polystyrene to the viscosity of the initial 8% rubber solution in styrene.

were mostly in the range of 4–7 μ with the particular rubber used (SYNPOL 1061C). Particle size was judged both by phase-contrast microscopy and by microfiltration with good agreement. Carrying the agitated bulk-stage reaction beyond 25–30% conversion did not further reduce the microgel particle size.

When the agitated bulk-stage reaction was discontinued short of the phase-inversion point and conversion completed in suspension, the final impact polystyrene was insoluble in toluene. It swelled but did not disintegrate, indicating the presence of large continuous networks of cross-linked graft. When the agitated bulk reaction was discontinued at 11–14% conversion, immediately after the minimum viscosity point, the finished product contained a mixture of small and large microgel particles (4–70 μ). When phase inversion was not completed in the bulk agitated stage, before completion of polymerization in suspension, the resulting impact polystyrene was shear-sensitive. Physical properties were dependent on the number of passes through the extruder or on time of milling.

A series of impact polystyrenes was prepared containing 8% of several different experimental SBR copolymers whose viscosities ranged from very low to very high, about 3–130 Mooney. The bulk agitated stage was carried to 30% styrene conversion before polymerization was completed in suspension. Microgel particle size was determined by phase-contrast microscopy and by microfiltration. Microgel particle size was found to be related to the initial viscosity of the rubber solution, with the higher viscosity rubbers producing larger microgel particles (Fig. 6).

Discussion

Viscosity-conversion curves had the same general shape for all of many rubbers tested at various rubber content levels with differing intensities of agitation and over a range of temperatures in the bulk polymerization

stage. The exact conversion level at which phase inversion occurred and ultimate rubber dispersion was obtained depended on many factors, including the intensity of agitation, kind and quantity of dissolved rubber, temperature, and molecular weight of the styrene homopolymer formed. Hence, the results shown here cannot be quantitatively generalized.

It is reasonably well established, however, that the dispersion of microgel in impact polystyrene begins with a phase inversion in the bulk agitated stage. Substantial grafting of polystyrene to rubber occurs prior to phase inversion. The graft may facilitate phase inversion by acting as a compatibilizing agent for the rubber and polystyrene solutions.

After phase inversion occurs, the dispersed droplets of rubber or graft in styrene become smaller and more viscous as they are broken up by shearing and deprived of solvent by continued styrene polymerization. At some point, these dispersed, swollen, particles become so viscous that they are not further reduced in size by continued bulk agitation. At this point, the minimum size of the ultimate microgel particles has probably been established for the particular rubber used.

It is perhaps fortuitous that the microgel particles observed in this study correspond quite well in size with the rheological units described by Mooney⁴ in dry rubber shearing. The reported size of the rheological unit increased with rubber viscosity and was in the range of 3–26 μ for natural rubber in the viscosity range 20–76 Mooney.

In the present experimental series, the impact polystyrene containing the smallest microgel particles, 0.2–0.4 μ , had low notched Izod impact strength, averaging 0.4 ft.-lb./in. of notch. It is not known whether this low value resulted from the small particle size or the weak, semiliquid character of the rubber. Impact polystyrene with microgel in the 1–15 μ range showed impact strength of 1.5–2.5 ft.-lb./in. which is normal at the 8% rubber content used. At about 15 μ or larger, the microgel particles become visible in thin extruded sheet. Thus, the desirable microgel particle size appeared to be in the 1–10 μ range.

References

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2. Amos, McCurdy, and McIntire (to Dow Chemical Company), U. S. Pat. 2,694,692.
3. Stein and Walter, (to Monsanto Chemical Company), U. S. Pat. 2,886,553.
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Résumé

Au cours de la polymérisation, en bloc et sous agitation, de styrène dans lequel se trouve dissous du SBR, une inversion de phase se produit pour un assez faible degré de conversion du monomère. En dessous de ce point d'inversion la phase continue est constituée de "caoutchouc dans du styrène." Tandis qu'au delà de "caoutchouc dans le styrène" se disperse en une phase continue de "polystyrène dans le styrène." Au point d'inversion de phase, il se produit une réduction importante de la viscosité globale ainsi que des variations importantes dans la viscosité intrinsèque du polymère et dans la transmission lumineuse d'une solution de 5% de polymère dans le toluène. Au stade de polymérisation partielle du styrène, les films de prépolymère séché sont insolubles dans

la 2-butanone avant l'inversion de phase et y sont solubles après ce point. Après avoir polymérisé, en partie le styrène en absence de solvant et sous agitation, on achève la polymérisation en suspension dans l'eau. Afin d'obtenir une dispersion poussée des particules de caoutchouc qui se pontent et forment des gels, il est nécessaire de pousser la polymérisation en bloc sous agitation bien au delà du point d'inversion de phase. La taille des particules finales de microgel est liée à la viscosité initiale du SBR, les caoutchoucs les plus visqueux formant les particules de microgel les plus grandes. La taille souhaitée pour les particules de microgel est de l'ordre de 1 à 10 microns. Si on commence la polymérisation en suspension avant que l'inversion de phase ne se soit réalisée lors de la polymérisation en bloc sous agitation, le polymère obtenu après conversion totale contient de très grands réseaux de gel de caoutchouc ponté et n'est pas soluble dans le toluène.

Zusammenfassung

Bei der Polymerisation von Styrol mit einem Gehalt an gelöstem SBR in Substanz unter Rührung trat bei ziemlich niedrigem Styrolumsatz eine Phasenumkehrung auf. Unterhalb dieses Inversionspunkts war die kontinuierliche Phase Kautschuk-in-Styrol, während oberhalb desselben Kautschuk-in-Styrol in einer kontinuierlichen Polystyrol-in-Styrolphase dispergiert war. Beim Phaseninversionspunkt traten eine merkliche Reduktion in der Viskosität des Systems, gross Änderungen der Viskositätszahl des Polymeren und der Lichtdurchlässigkeit 5%iger Polymerlösungen in Toluol auf. Bei teilweiser Styrolpolymerisation waren die getrockneten Polymerfilme vor der Phaseninversion in Butanon unlöslich und danach löslich. Nach teilweiser Polymerisation des Styrols unter Rührung wurde die Polymerisation in wässriger Suspension zu Ende geführt. Um im Endzustand eine Dispersion der Kautschukteilchen, die unter Bildung eines Mikrogels vernetzt wurden, zu erhalten, war es notwendig, die Polymerisation in Substanz unter Rührung weit über den Phaseninversionspunkt durchzuführen. Die Grösse der im Endzustand erhaltenen Mikrogelteilchen stand zur Ausgangsviskosität des SBR in Beziehung, wobei die stärker viskosen Kautschuk grössere Mikrogelteilchen bildeten. Die erwünschte Grösse der Mikrogelteilchen lag im Bereich von 1–10 μ . Bei Durchführung der Suspensionspolymerisation vor vollständiger Phaseninversion der Polymerisation in Substanz unter Rührung enthielt das Polymere bei vollständigem Umsatz sehr grosse Netzwerke aus vernetztem aufgepfropften Kautschukgel und war in Toluol unlöslich.

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