

Evaporation of Solvent in Mixed Polymer Systems of Limited Miscibility

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Synopsis

The evaporation of the solvent 1,2,3,4-tetrahydronaphthalene from the ternary system polystyrene/polybutadiene/tetrahydronaphthalene was studied. Ternary solutions of precisely known weight concentrations were prepared and then dried under vacuum and elevated temperatures. When the solution was assumed completely dried to a solid, the solvent content was calculated by difference. The deviation between the two solvent contents, namely, that known by exact weighing of components and that calculated after drying, was found to be significant, the reason for this discrepancy resting in the fact that solvent is assumed entrapped in the polystyrene fraction of the polymer residue. The possibility of the formation of interpenetrating networks causing this solvent entrapment is discussed as is a possible means of achieving more efficient solvent evaporation.

INTRODUCTION

Evaporation of solvent from various polymers is frequently encountered in industrial applications of paints, lacquers, and adhesives; loss of plasticizer is of concern in vinyl plastics materials. In our investigations into the behavior of ternary systems of two polymers and a solvent showing limited miscibility,^{1,2} it was important to know the rate and efficiency of evaporation of the solvent from the system under vacuum and heating. Since little information was available on such a process, a more lengthy study has been carried out. These results should be relevant to many of the applications mentioned above and to laboratory procedures using this technique.

EXPERIMENTAL

Choice of System

The system chosen for this particular study is polystyrene (PS) and polybutadiene (PBD) in the solvent 1,2,3,4-tetrahydronaphthalene (tetralin). Kampf et al.³ have shown that upon evaporation from solution, butadiene-styrene block copolymers show relatively complete phase separation by aggregation of like blocks, depending on experimental conditions. Experimental parameters, such as the volume ratio of the components, influence the equilibrium shapes of the aggregates. The relationship between the incompatibility of polystyrene and polybutadiene and its effects on the properties

TABLE I
Characteristics of Polystyrene Samples

Sample	Suppliers' data ^a			Experimental data		
	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
PS1	20.8 ± .8	20.2 ± .8	<1.06	—	—	—
PS2	36.0	33.0	<1.06	36.6	33.7	1.09
PS3	51.0	49.0	<1.06	—	—	—
PS4	111.0	111.0	<1.06	123.6	107.8	1.15
PS5	200.0	193.0	<1.06	—	—	—
PS6	—	—	—	84.6	38.5	2.20
PS7	—	—	—	299.8	100.6	2.98
PS8	200.0	—	—	179.7	84.8	2.12

^a Data for PS1 through PS5 supplied by Pressure Chemical Co.; data for PS8 supplied by Monomer-Polymer Laboratories.

TABLE II
Characteristics of Polybutadiene Samples

Sample	Suppliers' data ^a			Experimental data		
	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
PBD1 ^b	17.0 ± 1.7	16.0 ± 1.6	1.06	—	—	—
PBD2 ^c	170.0 ± 17	135.0 ± 13	1.26	161.3	119.5	1.35
PBD3 ^d	—	—	—	92.8	46.1	2.04
PBD4	—	—	—	332.6	136.3	2.44

^a Data for PBD1 and PBD2 supplied by Phillips Petroleum; data for PBD3 supplied by Polysar Ltd.; PBD4 supplied without data by Monomer-Polymer Laboratories.

^b 43.5% cis, 49.1% trans, 7.4% vinyl, 0.4% antioxidant 2,6-ditertiarybutyl-4-methylphenol.

^c 47.1% cis, 44.5% trans, 8.4% vinyl, 0.4% antioxidant 2,6-ditertiarybutyl-4-methylphenol.

^d 40.0% cis, 56.0% trans, 4.0% vinyl, 1.0% antioxidant 2,6-ditertiarybutyl-4-methylphenol.

of high-impact polystyrene has been previously studied,⁴⁻⁸ while phase separation of the PS/PBD system in various solvents has been studied in both our laboratories and those of others.^{1,2,9-12}

A further reason for studying the PS/PBD system is the fact that these are the only two polymers available commercially in suitable quantities with reasonably narrow molecular weight distributions so that distributional effects may be isolated and minimized.

The characteristics of the polystyrene and polybutadiene samples are given in Tables I and II, respectively. Included are both data provided by the suppliers and determined in our laboratories using gel permeation chromatography (Waters 301).

The choice of the solvent 1,2,3,4-tetrahydronaphthalene (tetralin) is in keeping with other related studies being conducted in our laboratories.

Preparation of Mixtures

Initially a weighed amount of polystyrene was dissolved in a weighed amount of the solvent tetralin. The amounts were sufficient to make be-

tween 15 to 20 g of solution at the desired polymer concentration. These concentrations range from 5% to 20% polymer by weight in this study. The weight per cent polymer was chosen such that it was slightly greater (~1%) than the estimated cloud point concentration for the corresponding three-component system of interest at 29°C. This temperature was also chosen in keeping with earlier published work on phase separation in this system. The solution was then placed in a sealed container and agitated by shaking until a completely homogeneous solution resulted. An identical procedure was followed for polybutadiene so that PBD in solution had a similar weight concentration.

The two solutions were then used to create a variety of mix points ranging from 0% PS:100% PBD to 100% PS:0% PBD, where the percentages represent (weight of polymer *i*/weight of total polymer) × 100%. The desired amount of PS/tetralin solution was weighed into a preweighed one-dram vial. The desired amount of PBD/tetralin solution was added and the vial weighed again. The total weight of such a ternary mixture would be approximately 3 g. The mixture was then agitated by shaking until a uniformly turbid mixture resulted.

Drying of the Samples

The uniformly turbid mixture prepared above was immediately added to a preweighed one-dram vial and the total weight determined. This vial was then placed in a vacuum oven (Precision Thelco #19) and dried at 80°C under 29 inches Hg vacuum. Weighing of the vials was done every 4 to 6 hr until the loss in weight was determined to be less than 0.0002 g/hr. At this point, the mixture was assumed "completely dry" and the mix point composition was determined. The drying of some of the samples was discontinued at this time, but for the majority of the samples drying was continued to determine how much of a change would occur with further drying.

RESULTS AND DISCUSSION

The mix point compositions determined by both methods discussed above, namely, the actual makeup composition determined by weighing of components and the composition determined by the drying technique, are shown in Figures 1 and 2. These results illustrate the efficiency with which tetralin can be removed from a polystyrene/polybutadiene/tetralin mixture by the drying technique above. The majority of the mix points dried to "complete dryness" is situated below the true mix point, indicating that the tetralin was not completely removed. A few mix points, when dried, fall above the true value, indicating to some extent the inaccuracies of such a method for determining compositions.

When all of the points shown in Figures 1 and 2 are considered, it is seen that the range of the deviation in tetralin content is +0.897% to -1.725%, giving a mean systematic difference of -0.475% tetralin with a standard deviation of 0.654% tetralin. These statistics describing the difference between the actual value known by direct weighing and the value calculated after drying to "complete dryness" show the extent to which the polymer mixture entraps the solvent.

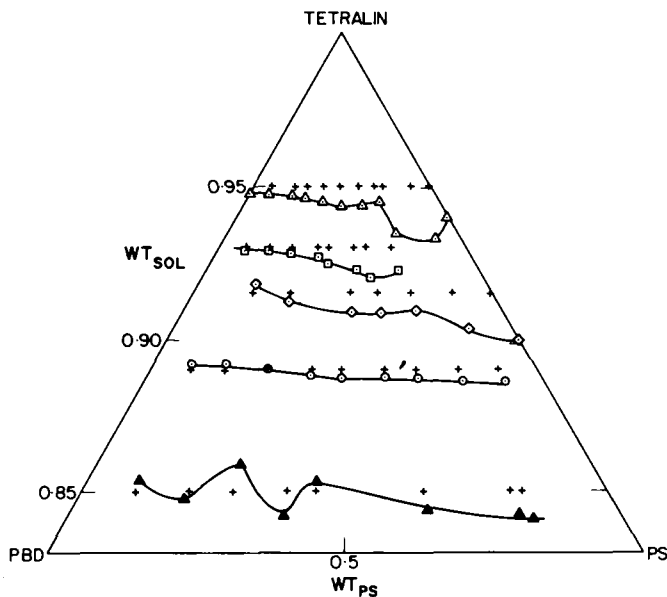


Fig. 1. Mix point compositions for polystyrene (PS)/polybutadiene (PBD)/tetralin mixtures. Actual compositions determined by weighing (+) are compared with the corresponding compositions determined by evaporation for mixtures of PBD2 ($\bar{M}_w = 161 \times 10^3$) with PS1 ($\bar{M}_w = 21 \times 10^3$), PS2 ($\bar{M}_w = 3 \times 10^3$), PS3 ($\bar{M}_w = 51 \times 10^3$), PS4 ($\bar{M}_w = 124 \times 10^3$), and PS5 ($\bar{M}_w = 200 \times 10^3$).

It was at first thought that the inability to remove the solvent completely rested in ceasing the drying operations and calculating the mix point composition when the drying reached a rate of weight loss of less than 0.0002 g/hr. To test the validity of stopping the drying at that point, many samples were

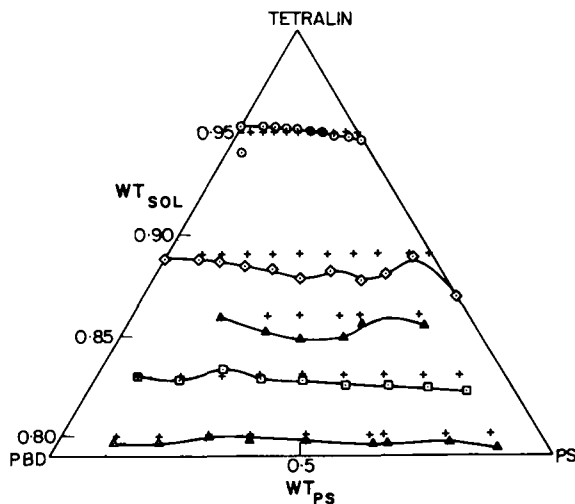


Fig. 2. Mix point compositions for polystyrene (PS)/polybutadiene (PBD)/tetralin mixtures. Actual compositions determined by weighing (+) are compared with the corresponding compositions determined by evaporation for mixtures of PBD4 ($\bar{M}_w = 333 \times 10^3$) with PS8 ($\bar{M}_w = 180 \times 10^3$) and for mixtures of PBD1 ($\bar{M}_w = 17 \times 10^3$) with PS1 ($\bar{M}_w = 21 \times 10^3$), PS2 ($\bar{M}_w = 37 \times 10^3$), PS4 ($\bar{M}_w = 124 \times 10^3$), and PS5 ($\bar{M}_w = 200 \times 10^3$).

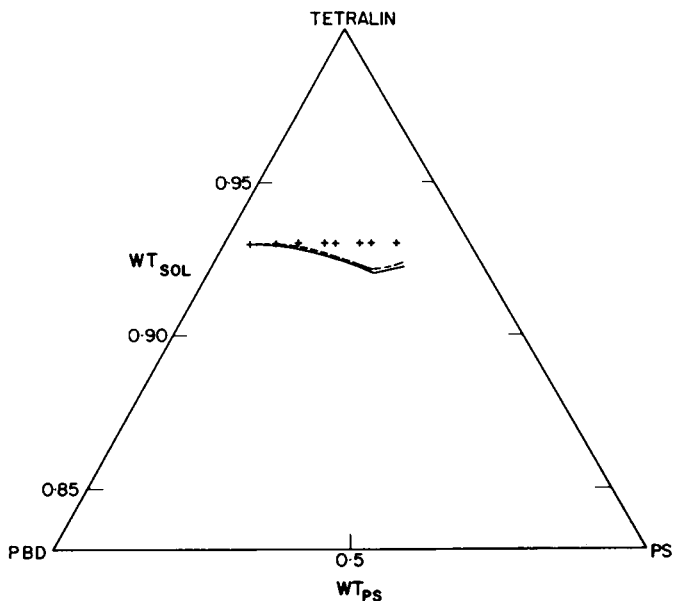


Fig. 3. Effect of prolonged drying on the mix point compositions for polystyrene (PS)/polybutadiene (PBD)/tetralin mixtures. Actual compositions determined by weighing (+) are compared with the corresponding compositions determined by evaporation to rate of weight loss less than 0.0002 g/hr (—) and rate of weight loss equal to zero (---) for the mixtures of PBD2 ($\bar{M}_w = 161 \times 10^3$) and PS4 ($\bar{M}_w = 124 \times 10^3$).

dried beyond the defined "complete dryness" endpoint, drying continuing until weight losses became immeasurably small over a 6-hr period. The results of one such test, for the system PS4-PBD2, are shown in Figure 3. In this instance, even at the final "dry" state the mix point compositions still

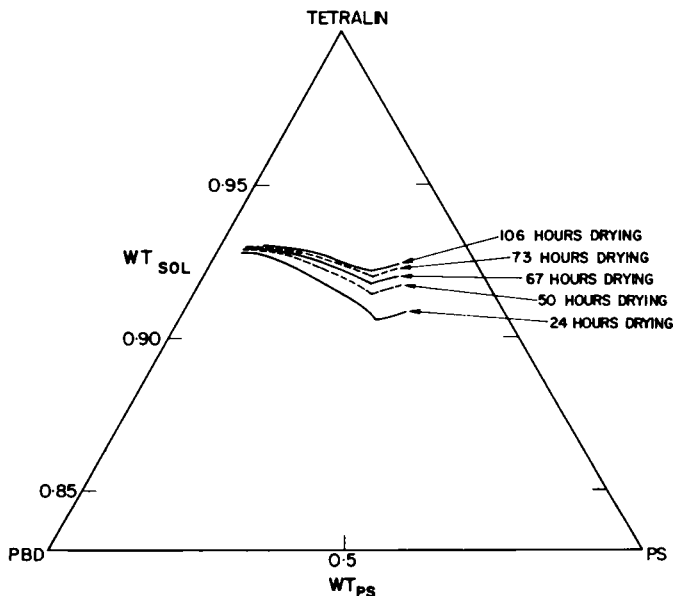


Fig. 4. Effect of drying time on the mix point compositions for polystyrene (PS)/polybutadiene (PBD)/tetralin mixtures. Compositions determined by evaporation to rate of weight loss less than 0.0002 g/hr are compared after various periods.

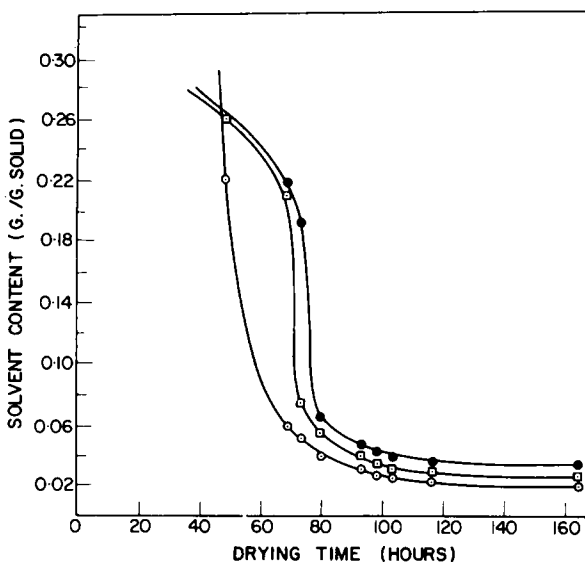


Fig. 5. Drying curves for polystyrene (PS)/polybutadiene (PBD)/tetralin mixtures. Solvent content in grams of solvent per gram of original polymer is plotted against drying time in hours for the mixtures PBD1 ($\bar{M}_w = 17 \times 10^3$) with PS1 ($\bar{M}_w = 21 \times 10^3$) (●-), PBD2 ($\bar{M}_w = 161 \times 10^3$) with PS1 ($\bar{M}_w = 21 \times 10^3$) (-□-), and PBD2 ($\bar{M}_w = 161 \times 10^3$) with PS2 ($\bar{M}_w = 36.6 \times 10^3$) (-○-). $T = 80^\circ\text{C}$, vacuum = 29 in. Hg.

show the excess in weight, which can probably be attributed to the presence of entrapped tetralin. The difference between the final "dry" composition and the defined "complete dryness" composition is shown to have a mean of 0.075% tetralin, with a standard deviation of 0.043% tetralin. These statistics are significantly smaller than the overall systematic difference value of -0.475% tetralin and a standard deviation of 0.654% tetralin, and thus premature ceasing of drying is eliminated as the major cause of the difference, although it has to be considered as a contributing factor.

Another factor was alluded to by Berens in his study on the desorption of vinyl chloride monomer from poly(vinyl chloride).¹³ He attributed a decreased rate of diffusion to an increase in the effective particle size. This conclusion would suggest in the present study that upon drying different particle sizes are being formed, particularly at intermediate compositions of the two polymers.

For comparison of the weight losses as a function time and composition, Figure 4 presents the mix points for the system PS4-PBD2 as they would be calculated at the times indicated on the graph. The differences in the corresponding mix points are found to depend strongly on the composition.

Figure 5 illustrates the drying curves for a few of the mixtures. The ordinate in this diagram is the solvent content defined as the grams of tetralin per gram of original solid polymer. The fact that none of the curves reaches the zero solvent content level emphasizes the fact that residual solvent remains in the polymer. If instantaneous slopes are taken either graphically or numerically in Figure 5 and plotted against the solvent content, the drying rate curves are obtained. This method was used to obtain the results shown in

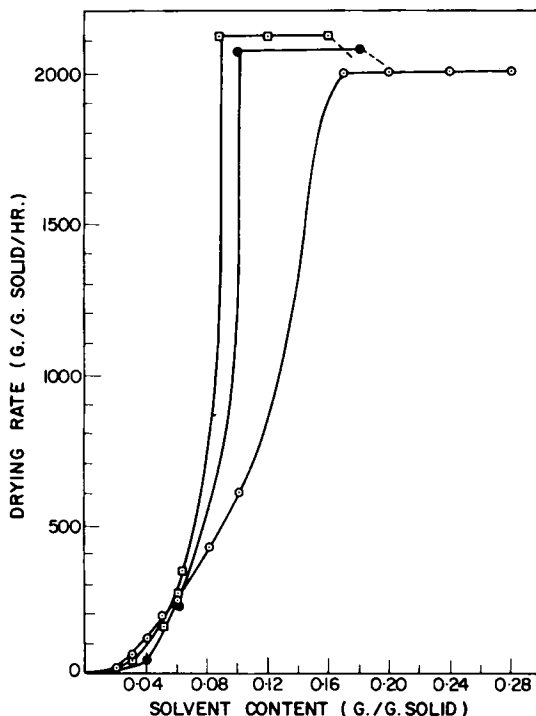


Fig. 6. Drying curves for polystyrene (PS)/polybutadiene (PBD)/tetralin mixtures. Drying rate in grams of solvent evaporated per gram of original polymer per hour is plotted against solvent content in grams of solvent present per gram of bone-dry polymer for the mixtures PBD1 ($\bar{M}_w = 17 \times 10^3$) with PS1 ($\bar{M}_w = 21 \times 10^3$) (—●—), PBD2 ($\bar{M}_w = 161 \times 10^3$) with PS1 ($\bar{M}_w = 21 \times 10^3$) (—□—), and PBD2 ($\bar{M}_w = 161 \times 10^3$) with PS2 ($\bar{M}_w = 36.6 \times 10^3$) (—○—). $T = 80^\circ\text{C}$, vacuum = 29 in. Hg.

Figure 6. The general shape of the curves closely resembles that given by Sherwood¹⁴ as the drying rate curve for a nonporous solid.

The approach taken above is that taken by chemical engineers in studying drying processes and further illustrates the inability to remove the solvent completely. The drying of nonporous solids has been found to entail shrinkage and casehardening of the solid which restrict the evaporation of the solvent.¹⁵

A further consideration with the entrapment of tetralin is the possibility that, upon drying and heating, crosslinking of one or both of the polymers occurred. Since it was observed that a condensing trap in the line between the vacuum oven and its pump managed to collect an amber-colored solution, it is possible to assume that the tetralin evaporated carried with it some of the antioxidant 2,6-ditertiarybutyl-4-methylphenol, the agent used to prevent the crosslinking of the polybutadiene. If this crosslinking did occur, then it is possible that interpenetrating polymeric networks⁷ (IPN), interpenetrating elastomeric networks^{16,17} (IEN), or some related network has formed. In both of these interpenetrating networks, polymers are deliberately crosslinked in the presence of a second polymer (or monomer) which itself may or may not be in turn crosslinked, in an attempt to overcome incompatibility problems when blending polymers to obtain desired properties. In fact, in their study of IEN's, Frisch and co-workers¹⁶ created their crosslinked net-

works by dissolving each polymer separately in a common solvent, mixing the two solutions and drying the mixture in an oven under vacuum to achieve crosslinking. In none of the work published on interpenetrating networks have direct measurements of the efficiency of solvent removal been made, but it is highly possible that solvent is entrapped, especially since Frisch and co-workers¹⁶ noted swelling of the network.

An additional consideration is the correlation, shown in Table III, between the time required to reach the defined "complete dryness" endpoint and the

TABLE III
Polymer Composition—Drying Time to "Complete Dryness"

Weight of polystyrene/ total weight of polymer	Time to "complete dryness," hr
A System PS1-PBD2	
.100	68
.201	68
.292	68
.392	68
.500	92
.705	92
.817	102
.841	102
B System PS1-PBD1	
.113	92
.205	72.5
.304	72.5
.392	78
.508	92
.645	92
.674	78
.801	140
.895	115.5
C System PS2-PBD2	
.103	78
.200	78
.301	78
.413	78
.494	78
.604	91
.696	91
.802	91
.906	91
D System PS8-PBD4	
.000	76
.102	76
.200	76
.300	76
.405	76
.500	76
.607	76
.699	82
.792	82
.898	82
1.000	82

(continued)

TABLE III (continued)

Weight of polystyrene/ total weight of polymer	Time to "complete dryness," hr
E System PS2-PBD1	
.099	92
.200	72.5
.302	102
.401	102
.498	102
.606	115.5
.707	102
.803	115.5
.890	140
F System PS4-PBD1	
.270	78
.400	78
.500	78
.617	97
.680	78
.857	78

fraction of total polymer which is polystyrene. A trend which is evident in a majority of cases is that the compositions rich in polystyrene take longer to reach a final dry state than do polybutadiene-rich mixtures. These results indicate that possibly altering the drying conditions to correspond to the polymer/polymer composition is advisable. When a polymeric solid is heated at a temperature greater than its glass transition temperature, the additional freedom of chain movement should more readily facilitate solvent escape and evaporation. Since the glass transition temperature of a mixture is dependent upon the composition, it may be best to assure that the drying temperature is greater than the glass transition temperature of the mixture.

Figures 1 and 2 show two interesting trends: one, that the residual tetralin is higher for higher proportions of polystyrene; and, two, that the proportions of residual tetralin is higher for higher molecular weight of polystyrene. When the curves of identical polystyrene molecular weight but different polybutadiene molecular weight are compared in Figures 1 and 2 and in Figure 5, it is evident that the molecular weight of PBD has little or no influence on the amount of tetralin entrapped. These findings are consistent with the earlier statement that the particle size was predominantly responsible for the liquid entrapment and reduced diffusion. A complete range of structure in the solid state of styrene-butadiene block copolymers, from micelles of segments of each polymer being dispersed in the other to intermediate rod-like and layered structures, has been discussed by Molau.¹⁸ The solubilizing or emulsifying effect of the block copolymer is not present in the system under study, however.

CONCLUSIONS

These experiments have pointed out some of the difficulties in removing completely a moderately high-boiling solvent by evaporation from polymer solutions. These difficulties appear to be increased when a solution of poly-

mers of limited miscibility is being evaporated. The result is the introduction of sizable inaccuracies when the drying technique is used as a laboratory technique and the entrapment of solvent, or extremely slow diffusion, in industrial applications. This entrapment may be considered disadvantageous if it is desired that the solvent be completely removed. On the other hand, this entrapment may be advantageous if it is desired to retain such components as plasticizers in vinyl polymers.

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