Rubber-Modified Polystyrene Impact as a Function of Flame-Retardant Additive Solubilization

W. E. SPRENKLE and J. H. SOUTHERN, *Monsanto Company, Indian Orchard, Massachusetts 01151*

Synopsis

Thermal optical analysis (TOA) is employed to study the solubilization of organic flame-retardant additives in high-impact polystyrene. The TOA approach (1) indicates the minimum temperature at which solubilization will occur; (2) yields information on how the composite will process; and (3) can be used to generate an equation that describes the kinetics of solubilization. Multiaxial impact strength increases proportionally as additive solubilization increases. The fundamental significance of the kinetic equation is discussed. Other applications of TOA are suggested.

INTRODUCTION

Methods currently available for measuring compatibility in polymer additive and polymer–polymer blends are after the fact (e.g., T_q, dynamic mechanical spectrometer, TEM, x-ray diffraction). The blend is or is not compatible at the processing conditions employed. But nothing further is learned, especially regarding extrapolation to another composition/processing combination. What is needed is a technique to follow the compatibilization event as it occurs.

High-impact polystyrene (HIPS) consists of a polystyrene matrix containing 0.1–10-μm-diam rubber particles, where the rubber contains both polystyrene occlusions and surface graft.[1] To increase flame resistance of HIPS, flame-retardant (FR) additives, such as decabromodiphenyl oxide (DBDPO), are included. The data presented here correlate the FR HIPS multiaxial impact with DBDPO solubilization. The degree of solubilization is shown via thermal optical analysis (TOA) to be a function of heat history. The application of thermal optical analysis represents a novel approach to defining quantitatively the solubilization phenomenon.

EXPERIMENTAL

The rubber-modified polystyrenes utilized herein are representative of commercially available HIPS and vary in weight-average molecular weight from 160,000 to 250,000, in heterogeneity index from 2.7 to 3.8 and in rubber level from 7.5 to 9.5%. Figure 1 defines the relevant Instron capillary rheometer viscosity versus shear rate curves (0.050-in. diam $\times$ 1.99-in. length capillary; data uncorrected for the Bagley[2] or Rabinowitch[3] factors). The 10% by weight decabromodiphenyl oxide,

MW = 960
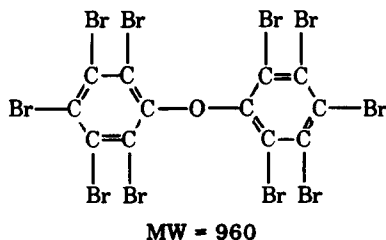
is added to the polystyrene samples examined herein. DBDPO is manufactured by Dow Chemical, Great Lakes, and Fine Organics, and has the following composition: % Br = 81–83,% H_2O ≤ 0.1, and % deca ≥ 85 with a decomposition temperature ≥ 425°C and a melting point of 295°C.

Samples were prepared for impact testing by extruding at 275°C (Killion −1 in. and National Rubber $1\frac{1}{2}$ in.) and injection molding at 265°C (1 oz Arburg).

The multiaxial impact test is ASTM D3029. A Bruceton staircase method is used to characterize a set of 30 100-mil chips. Each chip is struck once by a variable falling weight. The analysis leads to mean failure energy.

The thermal optical analysis[4,5] equipment consists of a hot-stage microscope, a photovoltmeter, and a readout instrument (du Pont 990). A beam of monochromatic light is passed through the sample. The fraction of the light transmitted by the sample is monitored versus time or temperature. When transmission is measured versus temperature, a solubilization temperature (T_s) is generated; when measured versus time (at a constant temperature greater than T_s), processing requirements are defined in detail. Samples can be microtomed (to 20 ±3 mil) to avoid variations due to thickness.

Figure 2 documents a typical percent transmission versus temperature curve (heating rate = 20°C/min). Optical micrographs of the sample quenched at points A and B show how percent transmission correlates with the solubilization process. It is assumed that (1) the baseline (λ_0) represents 0% solubilization, and (2) the maximum transmission (λ_{100}) represents 100% solubilization. Solubilization data presented herein are based on these premises, and fractional solubilization is assumed to be directly proportional to changes in light trans-
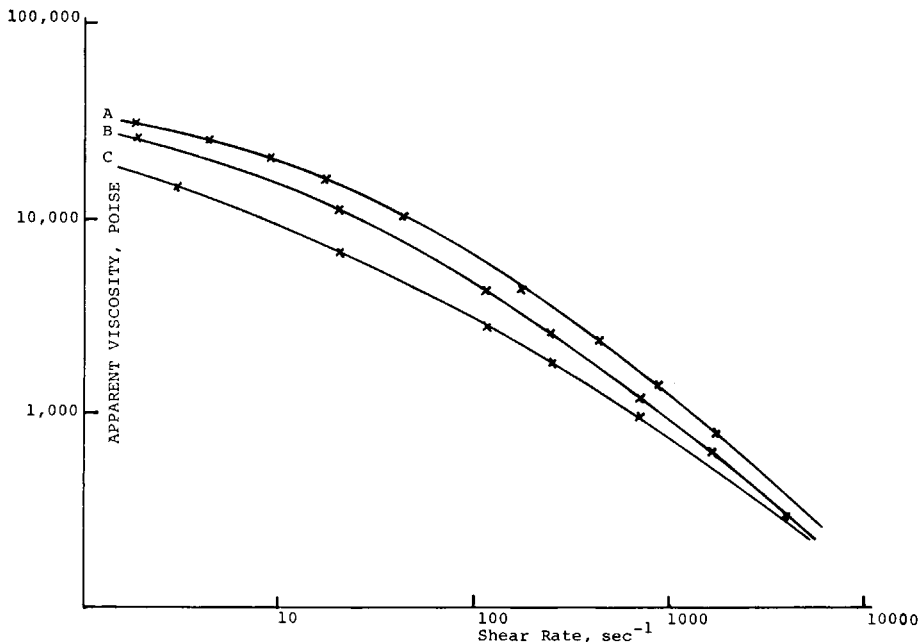

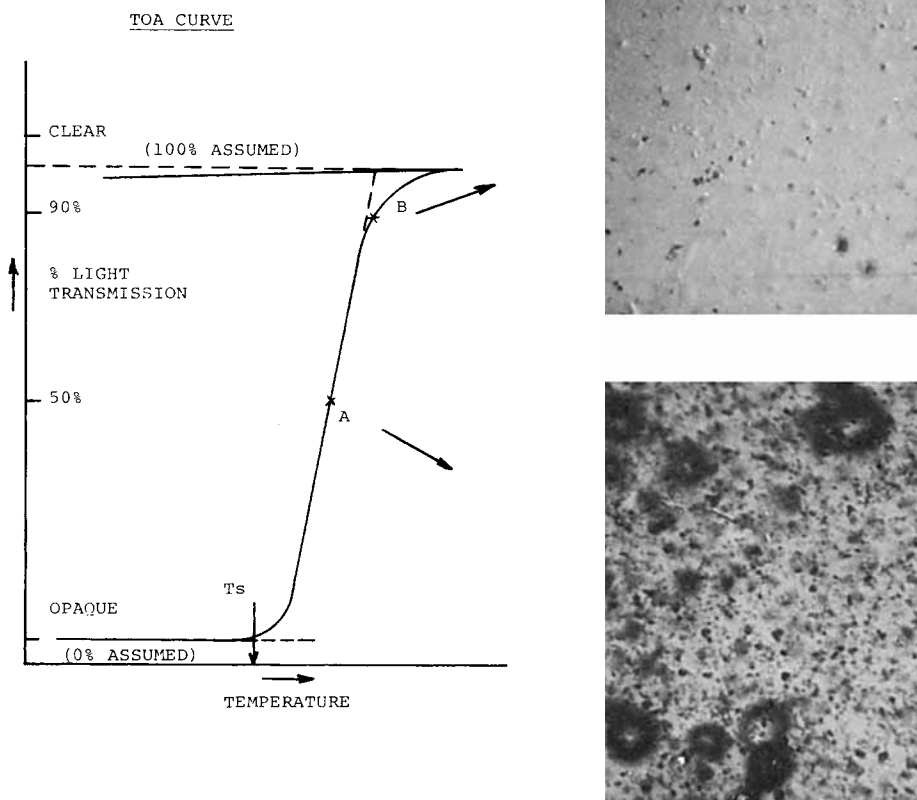Fig. 1. Apparent viscosity vs. shear rate for base HIPS at 450°F (505 K).

Fig. 2. DBDPO solubilization in TOA—Quench experiment. (A) 50% solubilization; (B) 90% solubilization. $\Delta T = 20°C/min$.

mission. As examples, per Figure 2:

$$50\% \text{ solubilization} = (\lambda_A - \lambda_0/\lambda_{100} - \lambda_0) \times 100\%$$

$$\text{or } \lambda_A - \lambda_0 = 0.5(\lambda_{100} - \lambda_0)$$

$$90\% \text{ solubilization} = (\lambda_B - \lambda_0)/(\lambda_{100} - \lambda_0) \times 100\%$$

$$\text{or } \lambda_B - \lambda_0 = 0.9 (\lambda_{100} - \lambda_0)$$

DISCUSSION

There are several subtleties hidden in Figure 2. Note that no solubilization will occur if heating is stopped at a temperature below T_s. Secondly, the solubilization is not instantaneous; it takes a finite amount of time to complete the solubilization at any temperature ($\geq T_s$). Also, not obvious from Figure 2 is that
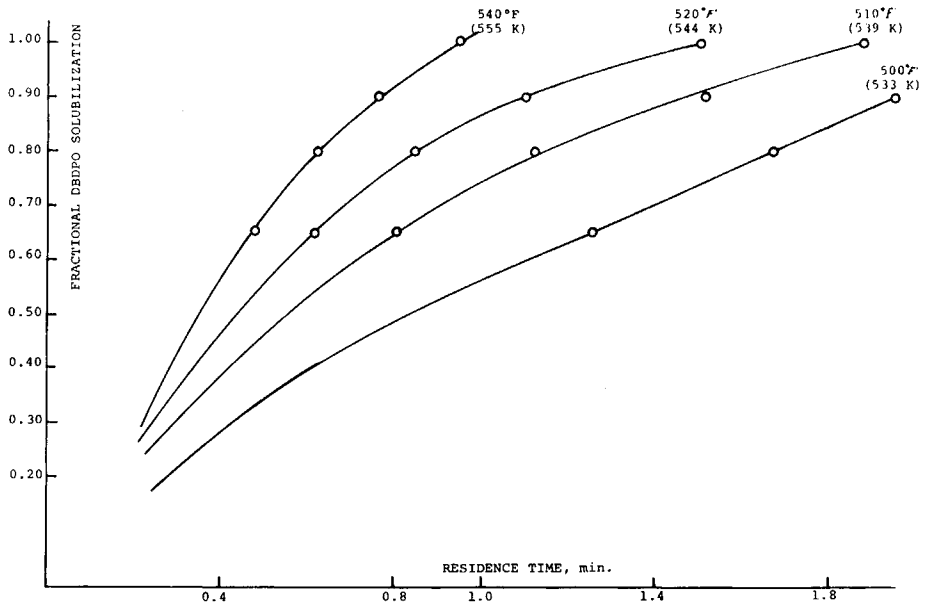
Fig. 3. DBDPO solubilization as function of thermal history.
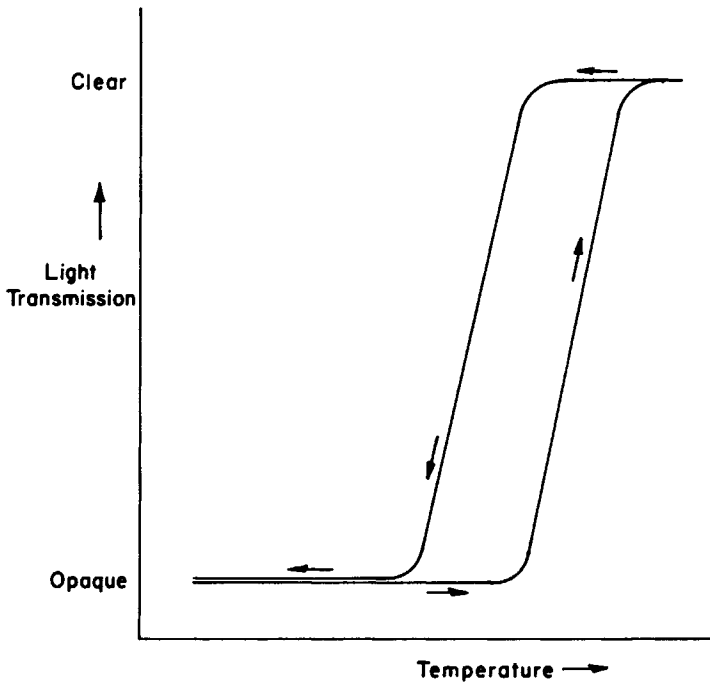
TOA – SOLUBILITY LIMIT EXCEEDED

Fig. 4. Two-phase hysteresis curve.
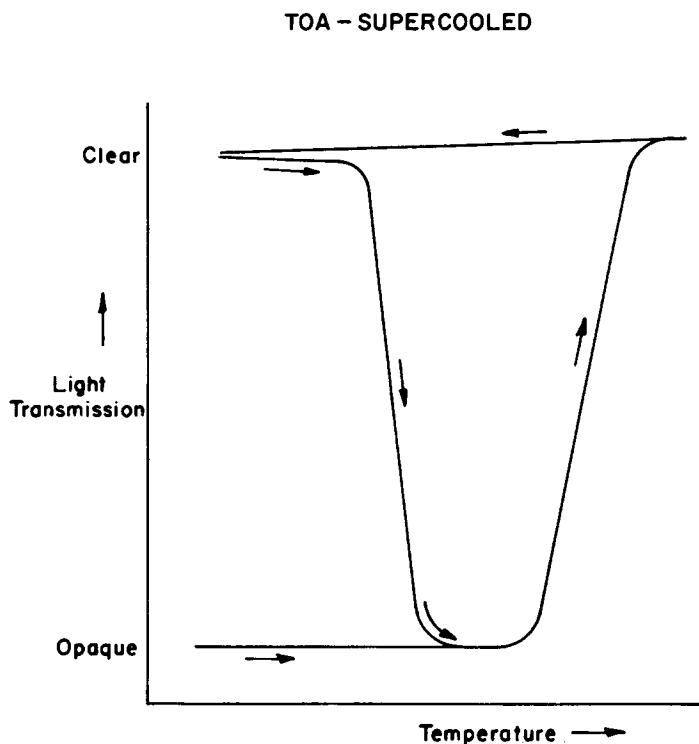
TOA − SUPERCOOLED

Fig. 5. TOA curve for a supercooled composite.

the time to complete solubilization decreases as temperature increases above T_s (also see Fig. 3). . Optical micrographs to the right of Figure 2 attest to the agreement of light transmission and the progress of the solubilization event. At 50% of the transmission scale, DBDPO particulates (dark in the picture) are plentiful; but at 90% of the transmission scale, DBDPO particulates are almost gone.

The shape of the TOA curve also yields valuable information on how the composite will behave in subsequent processing. The TOA curve shown in Figure 2 is ideal; T_s need only be achieved (and maintained for a finite time) once, and regardless of processing conditions in subsequent processing, the composite will remain one phase. However, if the solubility limit is exceeded, the TOA curve will have a different shape (Fig. 4). A hysteresis curve results and the composite will be *two* phases upon cooling, regardless of processing temperature. It is possible to supercool a composite that is near the solubility limit (Fig. 5). In this case, the composite can be one phase if it is cooled rapidly. But on reheating, the second phase again forms, and the solubilization event must again be completed to attain a single-phase composite. Residence times in commercial extrusion or molding equipment will rarely be long enough to allow resolubilization to complete. Note that these are profound bits of information that are not available through other testing techniques.

In the case of HIPS–FR additive compositions, additive solubilization increases with both time and temperature, as in Figures 3 and 6. Time–temperature superposition is achieveable using the following equation for DBDPO in HIPS at
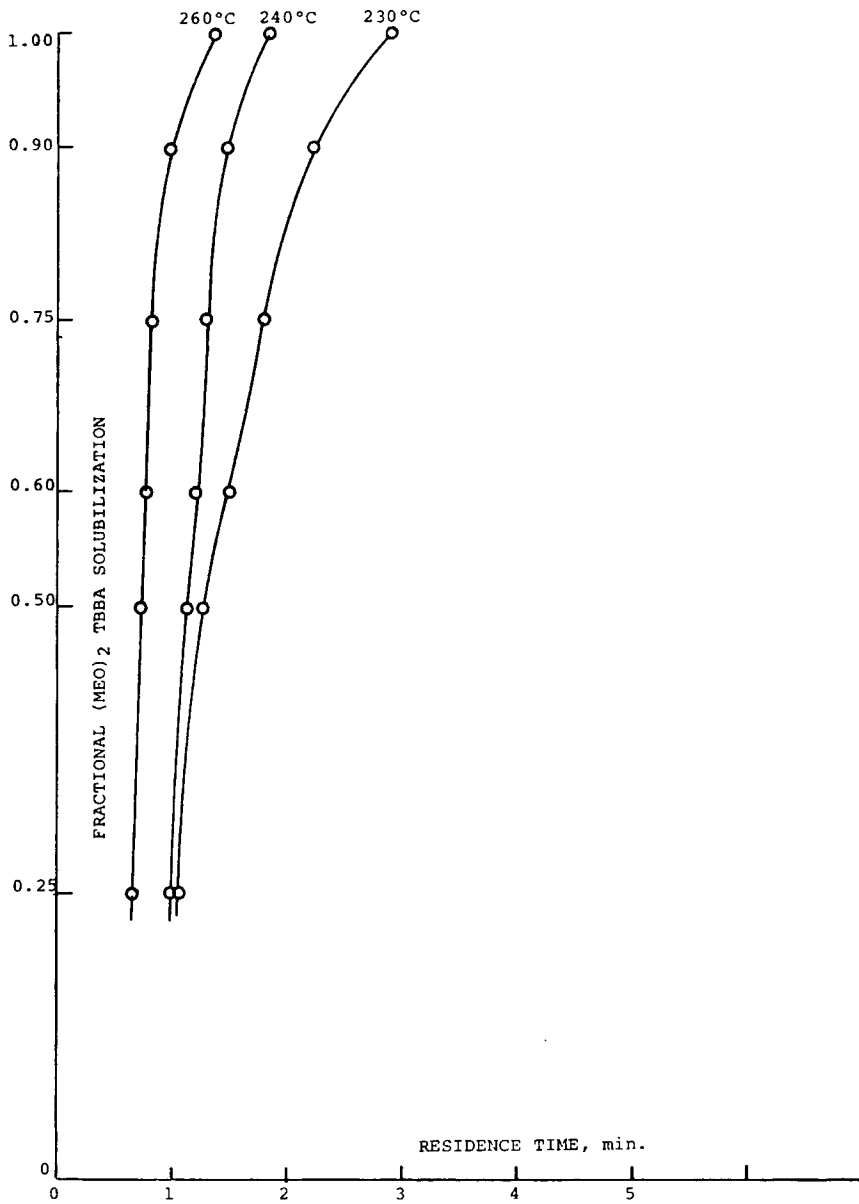
Fig. 6. (MeO)$_2$TBBA solubilization in HIPS, function of thermal history.

10% (Fig. 3):

$$1 - S = 1.91e^{[1120(t/R)(1/T-1/T_s)]}$$

where S is the fraction DBDPO solubilized; t is the time in sec (at T); R is the gas constant; T is the temperature, K, of processing; and T_s is the solubilization temperature of DBDPO in HIPS (522 K). Table I illustrates the excellent

TABLE I
Degree of Solubilization, DBDPO in HIPS, Measured vs. Calculated[a]

Temp, K	Time, sec	Measured % solubilized	Calc. % solubilized	% error
555	54.0	100	94	−6.0
555	45.6	90	90	−0−
555	37.5	80	83	+3.8
555	30.9	70	74	+5.7
555	25.5	60	63	+5.0
544	90.0	100	96	−4.0
544	66.0	90	89	−1.1
544	51.0	80	79	−1.2
544	40.8	70	68	−2.9
544	33.3	60	56	−6.7
539	113.	100	96	−4.0
539	86.4	90	90	−0−
539	68.4	80	81	+1.2
539	54.6	70	70	−0−
539	43.2	60	56	−6.7
533	117.	90	86	−4.4
533	101.	80	80	−0−
533	83.7	70	70	−0−
533	66.9	60	57	−5.0
			average	±2.4

[a] $1 - S = 1.91e^{[1120t/R(1/T-1/522)]}$.

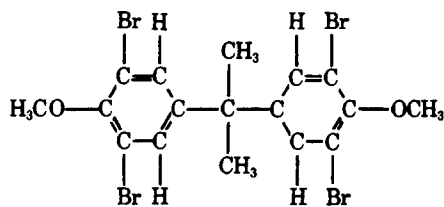agreement in comparing Figure 3 data with values predicted from this equation.

A second halogenated organic was similarly characterized to test the validity of the time–temperature superposition equation format. The dimethyl ether

TABLE II
Degree of Solubilization, Dimethyl Ether of Tetrabromo Bisphenol A in HIPS, Measured vs. Calculated[a]

Temp, K	Time sec	Measured % solubilized	Calc. % solubilized	% error
533	82.2	100	99	−1.0
533	59.4	90	90	−0−
533	49.2	75	72	−4.0
533	46.2	60	62	+3.3
533	43.8	50	52	+4.0
533	39.0	25	22	−12.0
513	111.	100	98	−2.0
513	88.8	90	89	−1.1
513	78.6	75	78	+4.0
513	72.6	60	67	+11.6
513	67.8	50	54	+8.0
513	58.8	25	17	
			average	±4.6

[a] $1 - S = 43.4e^{[965t/R(1/T-1/479)]}$

of tetrabromobisphenol A [Great Lakes Chemical; (MeO)$_2$TBBA]:

$$\text{Br H} \qquad\qquad \text{H Br}$$
$$| \;\; | \qquad CH_3 \qquad | \;\; |$$
$$C=C \qquad | \qquad C=C$$
$$H_3CO—C \qquad\qquad C—C—C \qquad\qquad C—OCH_3$$
$$C—C \qquad | \qquad C—C$$
$$| \;\; | \qquad CH_3 \qquad | \;\; |$$
$$\text{Br H} \qquad\qquad \text{H Br}$$

molecular weight = 572

shows a solubilization temperature of 206°C (479 K) in HIPS at a concentration of 10%. Again, fractional solubilization (see Fig. 6) reduces to a function of time and temperature incurred in processing and the following equation holds:

$$1 - S = A\, e^{[B(t/R)(1/T - 1/T_s)]}$$

where A equals 43.4, B is 965, and T_s = 479 K.

Table II shows values from this equation versus measured values from Figure 6. Thus, T_s appears to be of fundamental significance. Note that T_s changes slightly with additive concentration. These equations hold for compositions where the additive stays solubilized. Also note that the constant A is dimensionless, whereas B has units of cal/g mole sec. The magnitude of B, in both cases, is similar to values reported by Van Krevelen[6] for the heat of solution of additives in polymer bases; from these equations, B is positive, indicating an endothermic situation. However, the appearance of time in the denominator of B units prevents a direct comparison with heats of solution. The rate of solubilization is surface-area (of particles or domains) dependent, which is why B includes time in its units.

To define the sensitivity of multiaxial impact to additive solubilization, residence time and melt temperature were varied during extrusion compounding of HIPS–FR additive mixtures. In the relevant Figure 7 data, samples A, B, and C were single-pass compounded, and D, E, F, and G were double-pass compounded. All samples were processed at 269 ± 5°C stock temperatures. DBDPO solubilization was measured using thermal optical techniques. Figure 7 multiaxial impact retention is directly proportional to DBDPO solubilization (in the 50–100% range):

$$\% \text{ Impact Retained} = 1.05(\% \text{ Solubilized}) - 9.02\%$$

The embrittlement of ductile material such as impact polystyrene via particulate additives (acting as stress concentrators) has been well documented in the literature.[1] The Figure 7 data are consistent with this concept and provide a graphic demonstration of the importance of correct processing conditions for materials containing soluble additives.

There is some evidence that the melt viscosity of the base polymer influences the solubilization event. At first glance, one would expect that the higher the viscosity, the better. High viscosity will promote shear and mixing, and generates more surface area, all of which will aid molecular dispersion. Our experience, however, shows that there is an optimum viscosity, and at higher viscosities solubilization efficiency again falls off. The literature on bubble deformation and breakup in a sheared fluid cites such an optimum.[7] The analogy is clear in
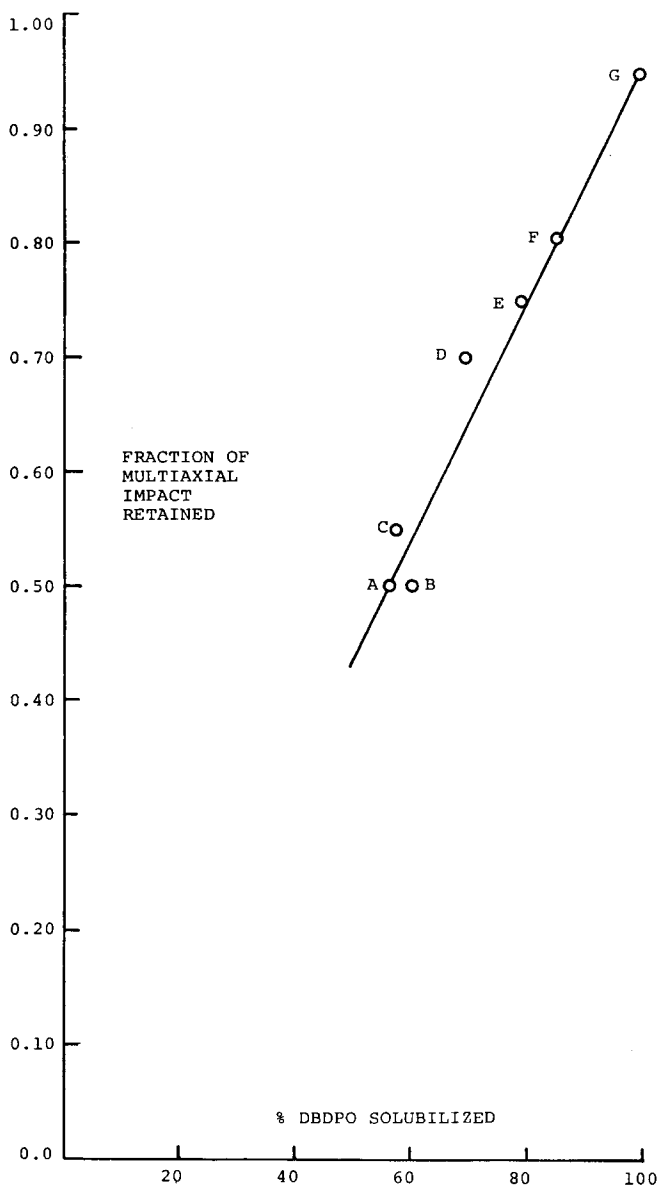
Fig. 7. Multiaxial impact retention vs. % DBDPO solubilized.

polymer–polymer blends. But it is not clear in polymer–particulate additive blends, since solubilization can occur as much as 50°C *below* the melting point of the additive. Polymer base viscosity accounts for some of the variation in impact strength retention noted in Figure 7 (particularly, samples D, E, and F).

There are many other studies that are amenable to TOA. Just as it was used to quantify compatibilization here, TOA could be used to quantify crystallization kinetics. The addition of polarized light may be helpful for crystallization studies, but not absolutely necessary. Phase diagrams can also be constructed with TOA, as Figure 8 shows for the DBDPO–HIPS system.
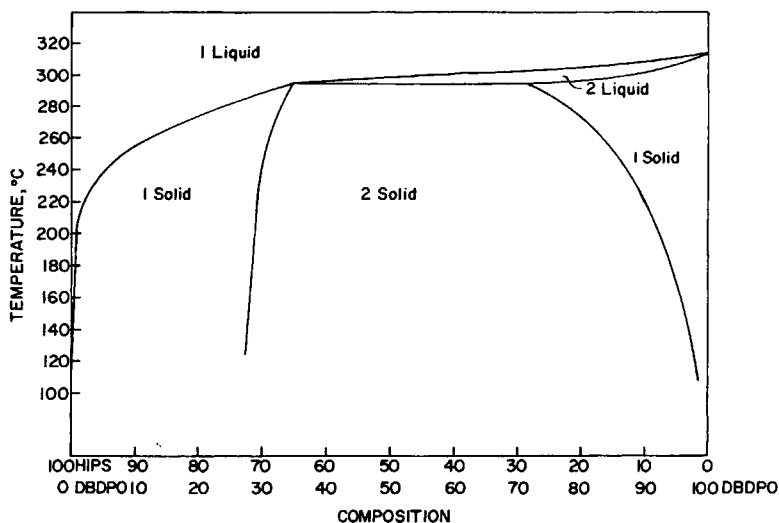
Fig. 8. Phase diagram DBDPO in HIPS.

The one obvious limitation of TOA is that the test is static; there is no mixing or shear other than thermal mixing. High shear, good mixing will promote solubilization, and the necessary residence times will be shorter than those predicted by TOA. Rates of solubilization will be dependent on surface area, of particulates, and at polymer–polymer interfaces, where mixing and shear assist. Also, there will be a limiting particle or domain size where TOA will no longer be meaningful; TOA may indicate a single phase, when there are actually two. Particulate additives as small as 0.8 μm were successfully studied here.

CONCLUSIONS

The thermal optical analysis data herein demonstrate increased solubilization with increased heat history for a flame-retardant additive (e.g., DBDPO) in impact polystyrene. The solubilization process is accurately described by a mathematical model based on time–temperature superposition. The importance of solubilization to flame-retarded polystyrene physical properties is exemplified by the multiaxial impact and solubilization correlation. Crystallization and phase diagram studies are also possible with TOA. Polymer–polymer blends should be viewed with caution.

References

1. C. B. Bucknall, *Toughened Plastics*, Applied Science, London, 1977.
2. E. B. Bagley, *J. Appl. Phys.*, **28**, 624(1957).
3. B. Rabinowitch, *Z. Physik. Chem. Abt. A*, **145**, 1(1929).
4. G. Claver, private communication, 1970.
5. I. Kirshenbaum, *et al. J. Polym. Sci., Polym. Lett. Ed.*, **2**, 897(1977).
6. D. W. Van Krevelen, *Properties of Polymers*, Elvesier, Amsterdam, 1972.
7. H. J. Karam, and J. C. Bellinger, *Ind. Eng. Chem. Fundam.*, **7**, (4), 576(1968).