Dynamic Mechanical and Thermal Properties of Fire-Retardant High-Impact Polystyrene

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Synopsis

The interaction of a series of fire-retardant additives with high-impact polystyrene (HIPS) has been inferred from their dynamic mechanical and thermal properties. High-melting additives phase separate and act as inert filler in both the rubber and polystyrene phases, while low-melting additives raise the T_g of the rubber phase and plasticize the polystyrene phase. Antimony oxide antiplasticizes the grafted rubber phase but acts as inert filler in the polystyrene phase. The impact strength of these fire-retardant HIPS's shows good correlation with the integrated loss tangent of the rubber T_g peak indicative of large energy dissipation in the rubbery region during impact causing the matrix to craze or flow. It is also suggested that additives which are compatible with, and localized in, the polystyrene phase help retain the impact strength of HIPS.

INTRODUCTION

Fire Retardancy in HIPS

In spite of the extensive fire retardancy studies on polystyrene,[1-4] there have been very few publications on the fire retardancy of HIPS. A priori, since over 90% of HIPS is polystyrene, fire retardants that are efficient in polystyrene can be extended over to HIPS, although Tousignant and Dickerson[5] have suggested that HIPS would require a greater amount of halogen than polystyrene.

One of the most effective ways of achieving fire retardancy in polystyrene or HIPS is by addition of halogen-bearing organics (e.g., Dechlorane) with a synergist like antimony oxide so that in the flame the two additives react to form volatile halides or oxyhalides of antimony which are believed to be the vapor-active species.[6] In order for the organic halides to be effective, they have to be stable at the molding temperature (~200°C). Also, they should evolve hydrogen halides at temperatures within 100°C below the combustion temperature of the polystyrene. Most of the fire retardants in this study satisfy such characteristics.

Mechanical Properties of HIPS

The toughening of glassy polystyrene to yield an impact-resistant thermoplastic (HIPS) is effected by dispersing rubber particles in the original glassy matrix. The presence of rubber averts brittle failure and permits enhanced

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energy absorption by facilitating the orientation and cold drawing of the glassy phase to form crazes.[7,8] The two-phase nature of HIPS is readily established by measuring the T_g due to the two phases by either dynamic mechanical or calorimetric properties. The effect of an additive on the glass and/or rubber phase can be studied by observing the shift in glass transition temperature of the component phases together with the change in other mechanical properties.

In developing a fire-retardant formulation for HIPS, it is important that care be taken not to impair any of the important physical performance properties such as impact strength, modulus, and mechanical strength and heat distortion temperature. Generally, compromise between mechanical performance versus flame retardation has to be considered.

The present studies examine the interaction of a series of fire retardants with the two phases of HIPS (the continuous polystyrene phase and the gel rubber phase) by dynamic mechanical spectroscopy and differential scanning calorimetry. Molecular distribution of the fire retardants in the two phases is inferred from the corresponding T_g shift in individual phases. Possible mechanisms that cause T_g shifts are presented and the impact properties of the samples are correlated with the distribution of the fire retardants in the two phases.

EXPERIMENTAL

All the samples in this study are based on Dow 492 Styron HIPS. The HIPS formulated samples are either (a) milled on a steam-heated Steward Bolling mill at 180°C for about 6 min or (b) milled, granulated, and dried at 80°C for about 20 hr and then injection molded on 204°C in an Eldorado molding machine in the form of ⅛-in. bars. Films about 5 mil thick were obtained by pressing the milled sheet on a Carver press at 180°C for ~30 sec under 10,000 lb pressure. Samples were removed from the press, cooled to room temperature, and used for the dynamic mechanical and thermal measurements. For the impact measurements, the ⅛-in. bar samples were annealed at 78°C for 92 hr to relieve or minimize any frozen strains during the injection molding cycle. In order to eliminate notch sensitivity, unnotched Izod impact values were obtained on an impact tester (Testing Machine, Inc., ASTM D256).

The chemical structures of the Dechloranes and four experimental fire-retardant additives (designated as EFR "A," "B," "C," and "D") are shown in Table I.
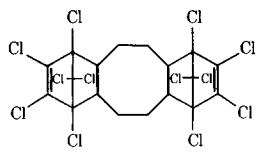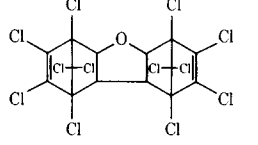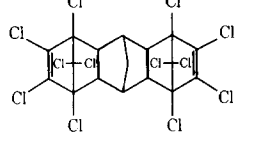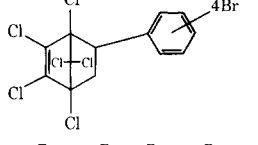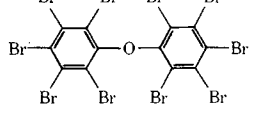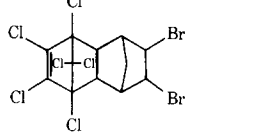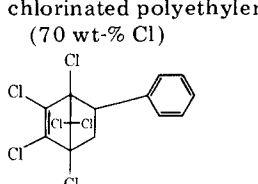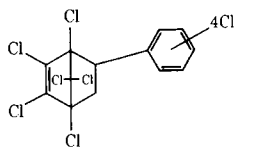
Dynamic Mechanical Measurements

Dynamic mechanical measurements were made at 110 Hz with a Rheo-Vibron Viscoelastometer (Toyo Company Model DDV-II) over the temperature range of −120° to 100°C. Sample dimensions used in these measurements are 0.005 × 0.1 × 1.2 in. The heating rate during the measurement was about 1°C/min. Readings were taken at every 4°C interval.

Differential Scanning Calorimetry

Thermal analyses were pursued on a Perkin-Elmer DSC-2 calorimeter. About 20–25 mg samples were placed in an aluminum pan with a lid. The heating rate was 20°C/min under a N_2 flow of 40 cc/min.

TABLE I
Chemical Structure of the Fire Retardant Additives

Fire-retardant additives	Structure
Dechlorane "A"	
Dechlorane "B"	
Dechlorane "C"	
Dechlorane "D"	
EFR "A"	
EFR "B"	
Chlorowax 70	chlorinated polyethylene (70 wt-% Cl)
EFR "C"	
EFR "D"	

Electron Spin Resonance

ESR spectra were recorded on a Varian E-4 spectrometer. The samples were packed into an open quartz tube (Wilmad 701-PQ) or evacuated to 10^{-3} mm Hg pressure for several hours at room temperature, sealed off, and transferred to the variable-temperature cavity; g values were determined (using DPPH; $g =$

TABLE II
Characterization of Dow Styron 492 HIPS

Polystyrene wt fraction	80%
Continuous phase	
Gel rubber phase wt fraction	20%
Polybutadienes	6%
Polystyrene	14%
Composition of polybutadienes	
1,4-*trans*	65
1,4-*cis*	25
1,2-vinyl	9
MW of extracted polystyrene	
$\overline{M}_w$	200,000
$\overline{M}_n$	55,000

2.0037) as the reference by the comparison method. Temperature of the cavity was calibrated with an iron–Constantan thermocouple.

Characterization of the Dow 492 HIPS

Separation of Phases.[9]   The separation of the gel phase from the rigid phase was carried out by high-speed centrifugation of a suspension of HIPS in 50/50 by volume of MEK/acetone. The suspension was obtained by adding 80 g HIPS pellets into 200 ml solvent with mild tumbling at 65°C for 6 hr. The suspension was then centrifuged at 25°C. The gel phase (16 g) was recovered by decanting it from the rest of the solution and vacuum drying at 65°C. The soluble rigid phase was recovered (~62 g) by MeOH precipitation of polystyrene from the clear supernatant. The extracted polystyrene has a $\overline{M}_w = 200,000$ and $\overline{M}_w/\overline{M}_n = 3.62$ as determined by GPC (Water Associates, Anapreg). After subsequent removal of free rubber from the gel phase by 2 × 200 ml heptane, the remaining gel phase was attempted to dissolve in THF. $\overline{M}_n$ and $\overline{M}_w$ of the soluble rubber portion are 79,800 and 103,000, respectively. The wt-% of the gel rubber phase in HIPS, as determined by the above extraction, is about 20%.

Characterization of the Gel Rubber Phase

Percentage of Rubber.   The rubber content in the gel phase was determined by NMR (Varian HA-100) using $CDCl_3$ as the solvent. The olefinic protons of the 1:2 vinyl isomer which resonate at ~5.03 ppm are hardly detectable. The ratio of the integrated areas under the aromatic protons (6.55 and 7.05 ppm due to polystyrene) versus those under the 1,4-*cis*- and *trans*-polybudiene olefinic protons (~5.40 ppm) of the polybutadiene was calculated; and after normalization by the number of protons, the gel phase contained about 30% of polybutadiene. This corresponds to about 6% of polybutadienes in HIPS.

Microstructure and Composition of the Polybutadienes

The microstructural characterization of the polybutadienes was determined by laser Raman spectroscopy (Spex-Ramalog-4). Raman bands at 1642, 1655, and 1668 cm^{-1} are assigned, respectively, to the 1,2-vinyl, 1,4-*cis,* and 1,4-*trans* C=C stretching vibration.[10]   The integrated areas under the corresponding
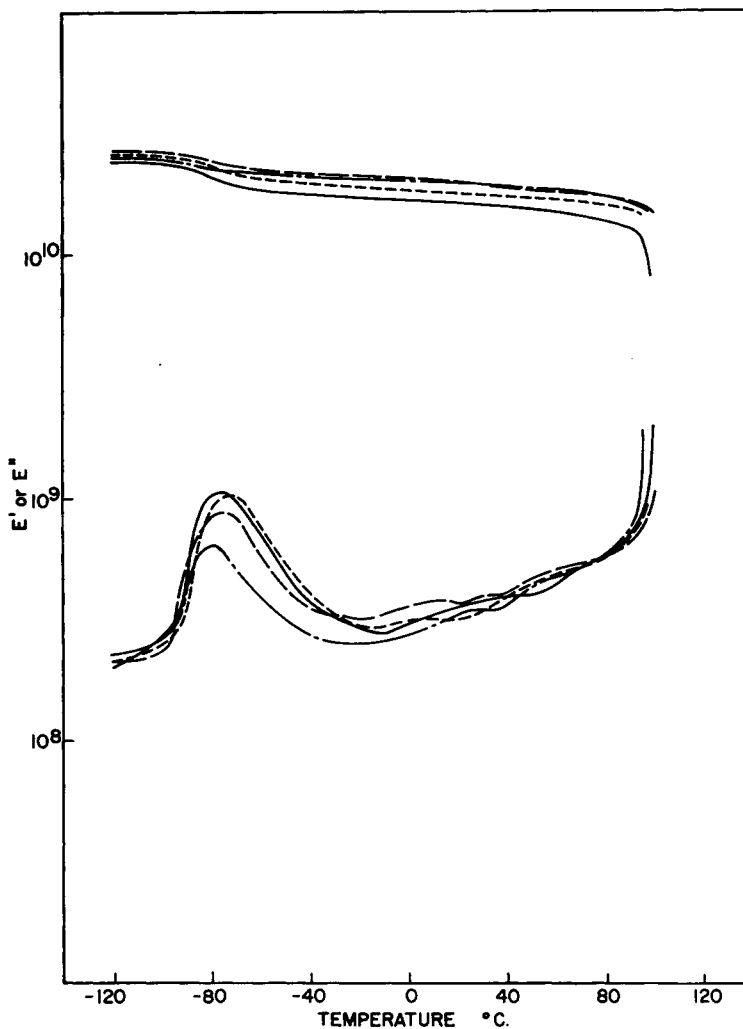
Fig. 1. Temperature dependence of E' and E'' for HIPS samples: (—) HIPS without additive; (— —) HIPS/Dechlorane "A" additive; (— · —) HIPS/Dechlorane "B" additive; (- - -) HIPS/EFR "A" additive.

bands were calculated and correspond to about 65% 1,4-*trans*, 25% 1,4-*cis*, and 9% 1,2-vinyl isomers. Table II summarizes the characterization of the HIPS.

RESULTS AND DISCUSSION

Dynamic Mechanical Properties of FR-HIPS

Inert Filler Fire Retardants

The temperature dependences of the dynamic storage modulus E' and loss modulus E'' for the samples of HIPS/15.8 wt-% Dechlorane "A" additive, HIPS/21 wt-% Dechlorane "B" additive, and HIPS/15.8 wt-% EFR "A" additive are shown in Figure 1. Compared with the control sample in all three cases, the
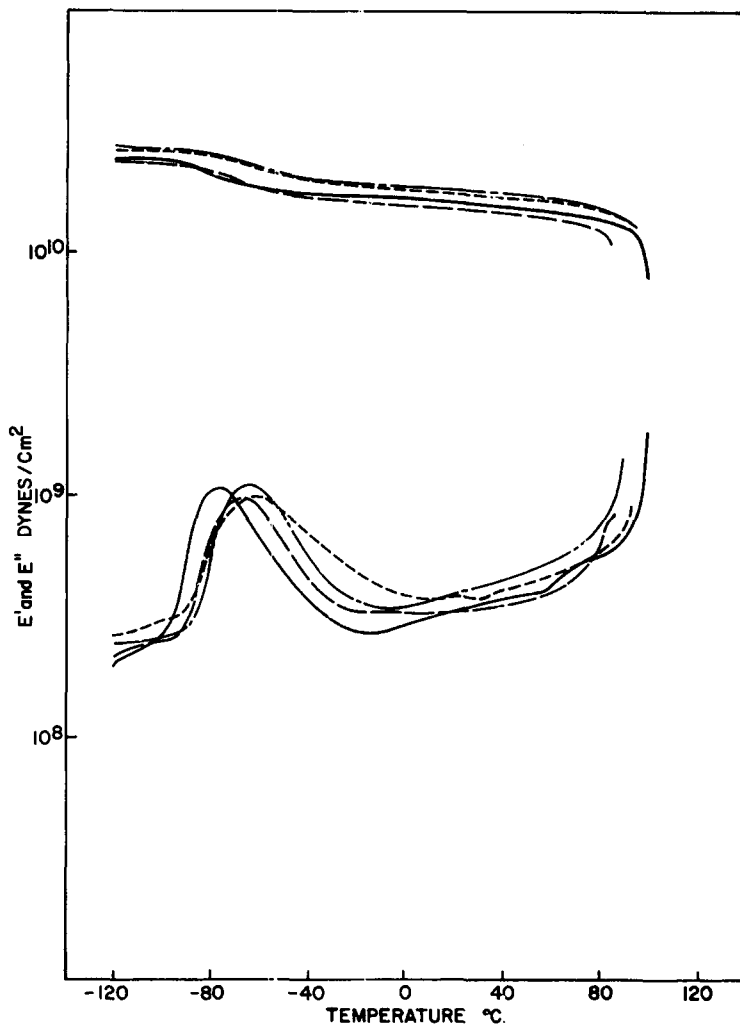
Fig. 2. Temperature dependence of E' and E'' for HIPS samples: (—) HIPS without additive; (—) HIPS/Dechlorane "D" additive; (— —) HIPS/EFR "B" additive; (- - -) HIPS/Chlorowax 70.

E' of the filled samples is raised, but the glass transition temperatures of the rubber and the polystyrene phases are hardly affected.

It has been pointed out previously in a separate paper[11] that additives which have melting points much higher than the processing temperatures usually phase separate from the polymer substrate. The very low or lack of interaction of the additives with the polymer phases results in an inert effect on the T_g shift; however, such fillers usually raise the modulus at high temperatures which lead to a higher heat distortion temperature.

Rubber Chain Stiffener–Polystyrene Plasticizer

A series of additives—Dechlorane "D," Chlorowax 70, and EFR "B"—show the unique characteristics of raising the T_g of the rubber phase but lowering the

T_g of the polystyrene phase. The temperature dependences of the E' and E'' for these samples are shown in Figure 2. The lowering in the T_g of the polystyrene phase can be attributed to the plasticizing effect of the additives which are melt blended at the processing temperature.

ESR studies on Dechlorane "D" and EFR "B" at temperatures comparable to the processing temperature (Table III) show a strong singlet indicative of radical formation. Such radicals (I) would either abstract an α-hydrogen atom on the polybutadiene chains or would add across the double bond as shown schematically below:
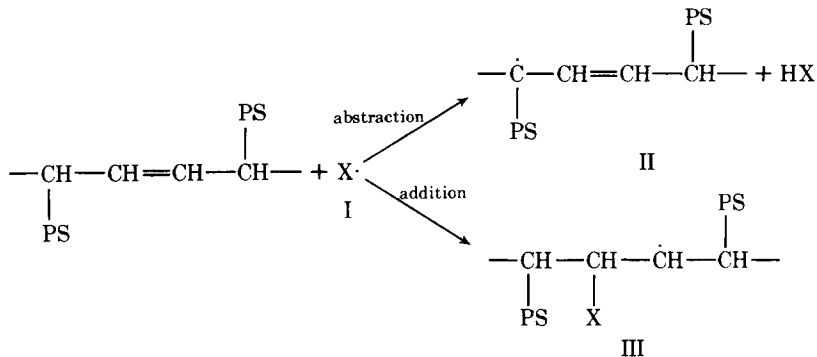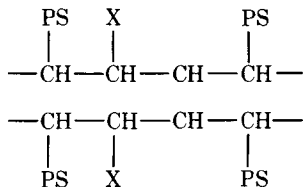
Both radicals II and III could combine with each other to form a crosslink in the following different ways. Processes 2(II) and 2(III) are probably not likely in view of the high kinetic chain length of polybutadiene crosslinking.[20] Such a crosslinked structure could be attributed to the elevation of T_g of the rubber phase:
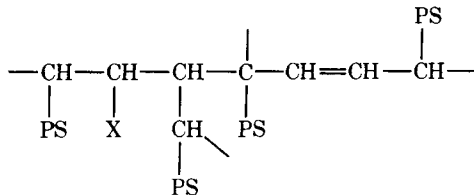
2 (II):
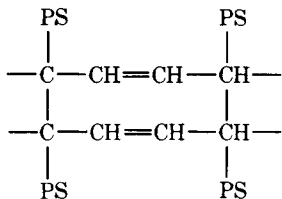
2 (III):

II + III:

TABLE III
ESR Data on Dechlorane "D" and EFR "B"

Sample	Pyrolysis temp., °C, and time	ΔH_{pp},[a] gauss	g	Atmosphere
Dechlorane "D"	203 (~60 min)	6.0	2.0039	open tube
	158	9.5	2.0026	10^{-3} mm
EFR-B	225 (~120 min)	7.0	2.0023	open tube

[a] Peak-to-peak separation in gauss.

Rubber Antiplasticizer

Antimony oxide constitutes a unique class of additive in FR-HIPS. It is used as a synergist with the Dechlorane additives. The effect of two grades of Sb_2O_3 (small particle size S, average ~0.5 μ, and large particle size L, average ~2.5 μ, were examined and compared in terms of their dynamic mechanical properties. The temperature dependence of E' and E'' for the two Sb_2O_3-filled HIPS's is shown in Figure 3. At temperatures below the T_g of rubber, the HIPS/Sb_2O_3-S, HIPS/Sb_2O_3-L, and the control HIPS samples have comparable E'; but at temperatures above -70°C, the reinforcing effect of the two grades of Sb_2O_3 is evident. At temperatures above 20°C, the reinforcing effect of the Sb_2O_3-S in the sample begins to taper off. The more pronounced T_g depressing effect of the Sb_2O_3-L is apparent for the E'' maximum plot. For the control sample, this occurs at -76°C, while that of HIPS/Sb_2O_3-S occurs at -92°C and that of HIPS/Sb_2O_3-S, at -96°C.

The increasing of E' but lowering of T_g has been referred to as the antiplasticizing effect[12–17] which has been observed with organic additives in PVC, polysulfone, and polycarbonate. The observation of similar effect in HIPS/Sb_2O_3 is quite surprising since Sb_2O_3 is inorganic and presumably insoluble in the rubber phase.

Table IV summarizes the dynamic mechanical and thermal results for the FR-HIPS samples.

Correlation between Izod Impact Strength with Dynamic Mechanical Data

Keskkula et al.[18] have previously indicated that the size of the rubber transition peak can be related to the toughness or impact strength within a family of similarly prepared polymers. It has been found in the present studies that the unnotched impact strength of a series of annealed FR-HIPS samples can also be correlated satisfactorily with the integrated loss tangent of the rubber glass transition peak (Fig. 4). The observed correlation indicates that the high impact strength of HIPS is associated with energy dissipation in the rubbery region causing the matrix to craze or flow. The intensity of such energy dissipation process can usually be inferred from the shape and intensity of the rubber damping peak which is dependent upon the interaction of the fire retardants with the rubber phase. It is noteworthy that among all the additives tested, Dechlorane "D" additive retains, while Dechlorane "B" additive reduces, the impact strength. It is further interesting to note that a 1:2 weight ratio blend of Dechlorane "B"/Dechlorane "D" additives shows a synergistic effect of yielding
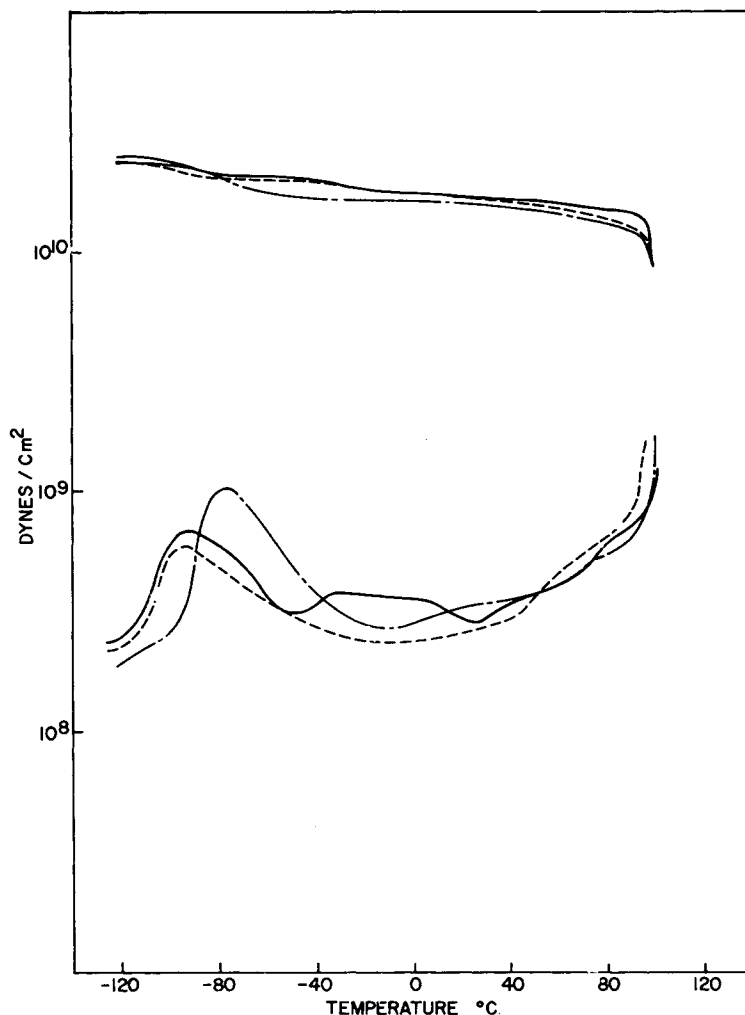
Fig. 3. Temperature dependence of E' and E'' for HIPS samples: ($\cdot$ —) HIPS without additive; (—) HIPS/Sb$_2$O$_3$ "S"; (- - -) HIPS/Sb$_2$O$_3$ "L".

the highest impact strength among all the fire-retardant samples. The mechanism for this synergism is presently obscure.

Correlation of Impact Strength with the Distribution of FR Additives in the Polystyrene and Rubber Phase of HIPS

Since the high impact strength of HIPS is dependent upon the morphology, amount, and type of the rubber phase and its coupling with the glassy polystyrene phase,[19] addition of FR, which inevitably changes such factors, would affect the impact strength. In the cases of inert fillers which phase separate, the general decrease in impact strength can be attributed to (1) the overall dilution of the rubber phase by the additive and (2) dewetting of the filler with the polymer matrices. For the fire retardants which melt blend and interact with the individual phases, their distribution in the polystyrene and grafted rubber phase

TABLE IV
Dynamic Mechanical and Thermal Properties of Dow 492 HIPS plus Additives

| Sample	Wt-% additive	Rubber T_g from E''_{max}, °C	ΔT_g, °C	Rubber T_g from DSC, °C	ΔT_g, °C	Polystyrene phase T_g from DSC, °C	T_g, °C	Inference	mp of additive, °C
Dow 492 HIPS (control)		−76		−88		99			
Dow 492/Dechlorane "A" additive	15.8%	−76	0	−88	0	100	+1	} filler	298.5
Dow 492/Dechlorane "B" additive	21%	−80	−4	−89	−1	99	0		300.0
Dow 492/EFR "A" additive	15.8%	−72	+4	−88	0	99	0		311.0
Dow 492/Sb$_2$O$_3$ (S)	15.8%	−92	−16	−106.5	−18.5	100	+1	} Rubber Antiplasticizer Polystyrene Filler	656.0
Dow 492/Sb$_2$O$_3$ (L)	15.8%	−96	−20						
Dow 492/Dechlorane "D" additive	15.8%	−64	+12	−80	+8	90	−9	} Rubber Immobilizer	181.5
Dow 492/Chlorowax-70	15.8%	−62	+14	−82	+6	93	−6	Rubber Immobilizer	70.0
Dow 492/EFR "B"	15.8%	−68	+8	−82	+6	87	−12	} Polystyrene Plasticizer	179.0
Dow 492/Dechlorane "B"/"D" additive (1:2)	15.8%	−68	+8	−81	+7	92	−7		

FR-HIPS ANNEALED
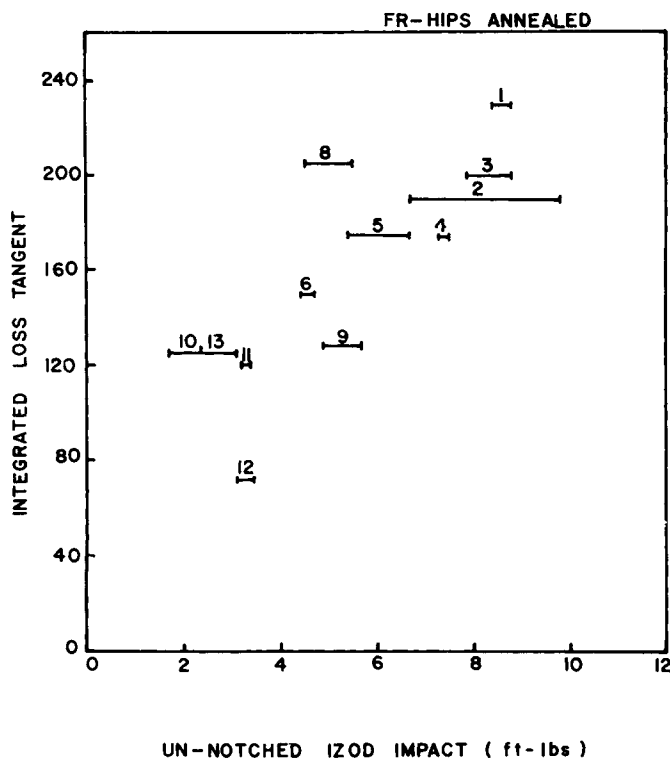
Fig. 4. Correlation of integrated loss tangent of the rubber T_g peak with unnotched Izod impact strength of HIPS samples: (1) HIPS without additive; (2) HIPS/Dechlorane "D" additive (80:15); (3) HIPS/Dechlorane "B" additive/Dechlorane "D" additive (80:5:10); (4) HIPS/EFR "B" additive (80:15); (5) HIPS/EFR "A" additive (80:15); (6) HIPS/Dechlorane "B" additive/EFR "A" (80:7.5:7.5); (7) HIPS/Dechlorane "B" additive/EFR "A" additive (80:15); (8) HIPS/Chlorowax 70 (80:15); (9) HIPS/Sb$_2$O$_3$ "S" (80:15); (10) HIPS/EFR "A"/Dechlorane "A" additive (80:7.5:7.5); (11) HIPS/Dechlorane "B" additive/EFR "A"/Sb$_2$O$_3$ (80:10:5.5); (12) HIPS/Dechlorane "B" additive (79:21); (13) HIPS/Dechlorane "A" additive (80:15).

would be an important factor. The distribution of the FR additives in the polystyrene phase of HIPS has been calculated by first determining the concentration dependence on T_g shift of the additives in the extracted polystyrene (Fig. 5). The T_g shift in the polystyrene phase observed from the HIPS/additive sample is then interpolated in Figure 5 to determine the concentration of the additive in the extracted polystyrene which yields the same T_g shift. For example, referring specifically to the EFR "A" additive, a depression of 12° in the polystyrene phase T_g was observed from the HIPS/EFR "A" sample. Such ΔT_g, when interpolated in Figure 5, would correspond to 10.1 g (74%) of EFR "A" additive in the continuous polystyrene or 11.8 g (87%) in the total polystyrene phase.

Using this T_g shift method, distribution of Dechloranes "B"/"D" (1:2 weight-ratio), Dechlorane "D", and Sb$_2$O$_3$ additives in polystyrene phase of HIPS, has been determined. The general trend of the results are shown in Table V. By correlating the distribution of additives in the polystyrene phase of HIPS with the unnotched Izod data, it can be seen that localization of the additive in the rigid PS phase helps retain the impact strength of HIPS. For the De-
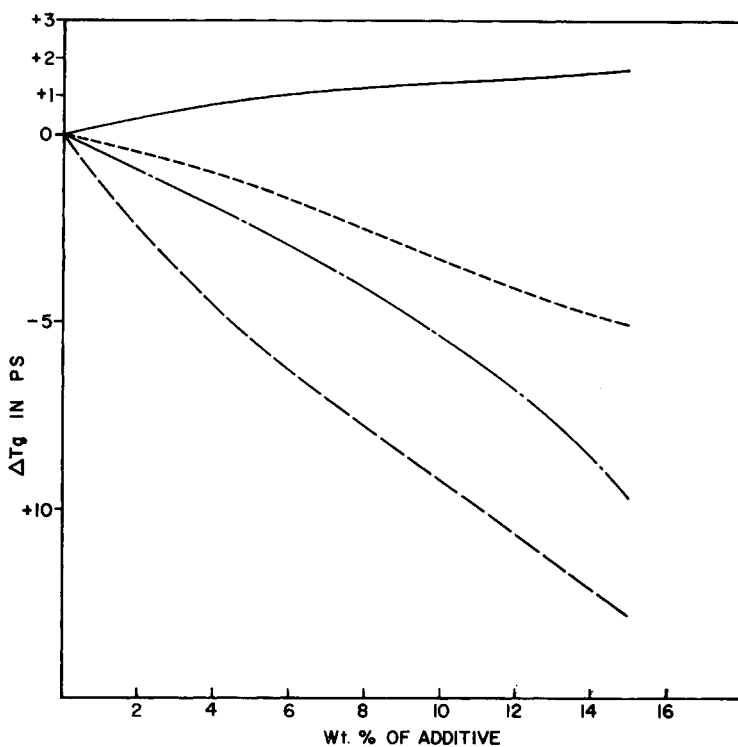
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Fig. 5. Variation in T_g shift of extracted polystyrene phase from HIPS with wt-% of additive (—) Sb$_2$O$_3$ "S", (- - -) Dechlorane "D"/EFR "A" (1:1), (— ·) Dechlorane "D", and (— —) EFR "B".

chlorane "B"/"D" blend additive, in spite of the impact reduction due to the Dechlorane "B" additive alone, the observed high impact value is due most probably to the contribution from the Dechlorane "D" additive. It is, therefore, interesting to note that for filler-type fire retardants which reduce the impact strength of HIPS, blends of such fillers with Dechlorane "D" additive could be employed to synergistically retain the high impact properties. The high percentage of Dechlorane "D" additive in the polystyrene phase is due most probably to its styrene derivative structure. Such hypothesis has also been tested and confirmed for two other styrene-derived experimental fire-retardant additives (EFR "C" and "D"). The localization of these two additives in the polystyrene phase correlates well with their observed reversed notched Izod impact strength (Table V). It is, therefore, suggested that additives which are compatible with and localized in the polystyrene phase help retain the impact strength of HIPS.

CONCLUSIONS

The present studies indicate that there are two important variables governing the interaction of additive with polymer matrix: (a) the melting point of the additive (T_m) in relation to the processing temperature of the thermoplastics (T_p), and (b) the compatibility of the additive with the polymer phases.

TABLE V
Correlation of Impact Strength with Distribution of Additives in the PS Phase

	HIPS Control	HIPS/ EFR"C" 15.8c%	HIPS/ Dechlorane "B"/"D" (1:2) 15.8	HIPS/ Dechlorane "D" 15.8	HIPS/ EFR"D" 15.8	HIPS/ EFR"A" 15.8	HIPS/ Sb$_2$O$_3$ 15.8
% of additive interacting with the continuous PS phase		99%	82%	72%	70%	67%	22.6%
Unnotched Izod[a] (ASTM D256)	8.6		8.4	8.2		7.4	5.3
Reversed notched[b] Izod (ASTM D256 Method E)	4.8	4.08			3.07		

[a] From injection-molded bars.
[b] From compression-molded bars.
[c] Weight % of additive.

Incorporating a high-melting fire retardant in a low temperature-processed thermoplastic $(T_m > T_p)$ results in phase separation of the additive. This gives rise to a rather heterogeneously dispersed filled sample which could be undesirable if we consider the heterogeneity of fire retardancy in the sample. Also, impact strength is reduced because of the imperfect wetting of the additive and the polymer matrix. However, possible reinforcing filler properties of such high-melting, insoluble additives could conceivably lead to higher heat distortion temperature and higher modulus of the sample.

On the other hand, melt blending is usually the result of incorporating a low-melting fire retardant in a polymer processed at a temperature comparable to, or higher than, the melting point of the additive $(T_m \lesssim T_p)$. The molecularly dispersed FR sample makes maximum homogeneity possible, but frequently plasticizes the higher T_g phase (e.g., polystyrene phase in HIPS). Such plasticizing action reduces the glass transition, which leads to a lower heat distortion temperature and modulus at elevated temperatures. Also, in view of the low melting temperature of the additive, decomposition or volatilization of the fire retardant at the processing temperature could be a problem.

It has been experimentally shown that styrene-derived fire retardants (Dechlorane "D" and EFR "C" and "D" additives) localize in the polystyrene phase of HIPS because of similarity in structure, and hence compatibility. Such localization in the rigid phase without perturbation of the elastic rubber phase helps retain the high impact strength. Also, filler-type Dechlorane additives which individually reduce impact can be blended with styrene-derived additives to retain high-impact properties.

The interaction of fire-retardant additives with high-impact polystyrene which determines the final properties of the product can hence be controlled and predicted to some extent by the melting temperature and structure of the additive. The impact strength of FR-HIPS is dependent upon the distribution of the additive in the two phases which can also be correlated with the ease of large energy dissipation process via backbone relaxation (T_g) of the rubber.

References

1. Robert F. Lindemann, in *Flame Retardancy of Polymeric Materials*, Vol. 2, W. C. Kuryla and A. J. Papa Eds., Marcel Dekker, New York, 1973, Chap. 1.

2. J. A. Rys, *Chem. Ind.* (London), **7**, 189 (1969).

3. P. Volans, *Plast. Inst., Trans. J., Conf. Suppl.*, **No. 2**, 47 (1967).

4. J. K. Jacques, *Plast. Inst., Trans. J., Conf. Suppl.*, **No. 2**, 33 (1967).

5. W. F. Tousignant and R. T. Dickerson (to Dow Chemicals) U.S. Pat. 1,094,723 (1967).

6. J. J. Pitts, P. H. Scott, and D. G. Powell, *J. Cell. Plast.*, **6**, 35 (Jan./Feb. 1970).

7. S. L. Rosen, *J. Elastoplast.*, **2**, 195 (1970).

8. S. Ktrella, *Appl. Polym. Symp.*, **7**, 165 (1968).

9. H. Keskkula and S. G. Turley, *Polym. Lett.*, **1**, 703 (1969).

10. S. W. Cornell and J. L. Koenig, *Macromolecules*, **2**, 540 and 546 (1969).

11. E. P. Chang, R. O. Kirsten, and R. Salovey, *Polym. Eng. Sci.*, **15** (10), 697 (1975).

12. N. Kinjo and T. Nakagawa, *Polym. J.*, **4**, 143 (1973).

13. L. M. Robeson and J. A. Fancher, *Polym. Lett.*, **7**, 35 (1969).

14. M. G. Wyzgorki and S. Y. Yeh, *Polym. J.*, **4**, 29 (1973).

15. W. J. Jackson, Jr., and J. R. Caldwell, *J. Appl. Polym. Sci.*, **11**, (1967).

16. W. J. Jackson, Jr., and J. R. Caldwell, *J. Appl. Polym. Sci.*, **11**, 227 (1967).

17. N. Kinjo, K. Nakamura, and T. Nakagawa, *Rep. Progr. Polym. Phys. Japan*, **14**, 329 (1971).

18. H. Keskkula, S. G. Turley, and R. F. Boyer, *J. Appl. Polym. Sci.*, **15**, 351 (1971).

19. B. J. Spit, *Polymer*, **4**, 109 (1963).

20. B. M. E. Van Der Hoff, *Appl. Polym. Symp.*, **7**, 21 (1968).