Halogen-Modified Impact Polystyrene. II. Evidence for Condensed-Phase Reactions by Thermogravimetry

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Synopsis

Blends of high-impact polystyrene with decabromodiphenyl oxide and/or antimony trioxide were characterized by thermogravimetry. The observed weight loss for the blends was compared with a calculated weight loss which was determined from a weighted sum of the weight loss of the individual materials in the blend. This comparison of observed and calculated weight loss provided a method to determine if condensed-phase reactions occur among the materials in the blend. Definite evidence for condensed-phase reactions was observed when polybutadiene (impact modifier), decabromodiphenyl oxide, and antimony trioxide were present simultaneously. In that case, the observed weight loss exceeded the calculated weight loss above 330°C. When one of the three materials was absent, the observed weight loss was less than or equal to the calculated weight loss. The condensed-phase reactions involving polybutadiene, decabromodiphenyl oxide, and antimony trioxide occurred in nitrogen as well as in air.

INTRODUCTION

The synergistic effect of antimony trioxide on the flame-quenching efficiency of organic halides, which has been recognized for 40 years, was reviewed in 1972.[1] More recently, the role of the polymeric matrix in the synergistic interaction of antimony trioxide and decabromodiphenyl oxide in high-impact polystyrene was described.[2] The present paper describes data obtained by thermogravimetry which indicate that the synergism originates with reactions that occur in the condensed phase and that involve decabromodiphenyl oxide, antimony trioxide, and polybutadiene. Condensed-phase reactions control the rate of fuel generation, and they must be in equilibrium with the consumption of the fuel in the gas phase to sustain combustion.[3] The condensed-phase reactions which occur in high-impact polystyrene that contains decabromodiphenyl oxide and antimony trioxide upset the equilibrium by flooding the gas phase with bromine-containing, flame-quenching molecules.[2]

EXPERIMENTAL

Materials

The impact polystyrene (IPS) was a commercial Union Carbide Corporation product. The decabromodiphenyl oxide (DBDPO) was supplied by the Dow Chemical Co. The antimony trioxide (Sb_2O_3) was Matheson, Coleman & Bell, reagent grade.
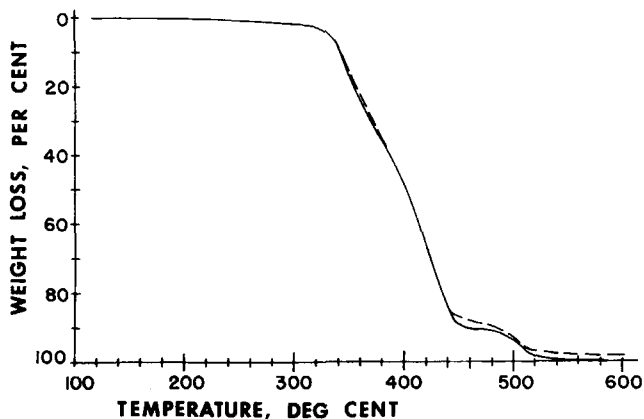
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Fig. 1. Thermogravimetry of 86/10/4 blend of IPS, DBDPO, and Sb_2O_3 (HM-IPS): heating rate, 10°C/min; atmosphere, air.

Blends containing IPS, DBDPO, and Sb_2O_3 were prepared on a compounding extruder. Blends of IPS and one of the other two components were prepared on a two-roll mill. Blends of DBDPO and Sb_2O_3 were dry blends mixed with a mortar and pestle.

Thermogravimetry

The thermogravimetric data were obtained with a Perkin-Elmer TGS-1 Thermobalance. The initial sample weight was approximately 2 mg. Samples were heated at 10°C/min with air or nitrogen flowing past the microfurnace at 30 cc/min.

Data were recorded on paper tape for subsequent analysis by computer.

RESULTS AND DISCUSSION

Impact Polystyrene Blended With DBDPO and Sb_2O_3

Impact polystyrene blended with DBDPO and Sb_2O_3 will be called halogen-modified impact polystyrene (HM-IPS). Figure 1 shows duplicate weight loss curves for HM-IPS when it is heated in air at 10°C/min. Rapid weight loss does not occur until the temperature exceeds 340°C.

The weight loss of HM-IPS in air is compared to the weight loss of IPS in air in Figure 2. Below 330°C, both materials have the same weight loss. Above 330°C, the weight loss of HM-IPS exceeds that of the IPS.

To determine the significance of the greater weight loss for HM-IPS relative to IPS, the weight loss of the individual materials in HM-IPS must be compared with the weight loss of HM-IPS. Therefore, a computer program was written to calculate the weight loss for a blend of materials from the weight loss curves for each of the materials in the blend:

$$W_{cal}(T) = \text{calculated weight loss of blend} = \sum_i \alpha_i W_i(T) \qquad (1)$$

where α_i = weight fraction of material i in the blend, and $W_i(T)$ = weight loss
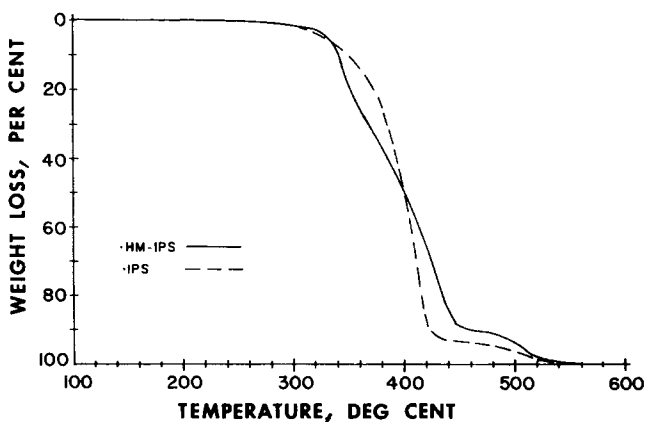
Fig. 2. Thermogravimetry of IPS and HM-IPS: heating rate, 10°C/min; atmosphere, air.
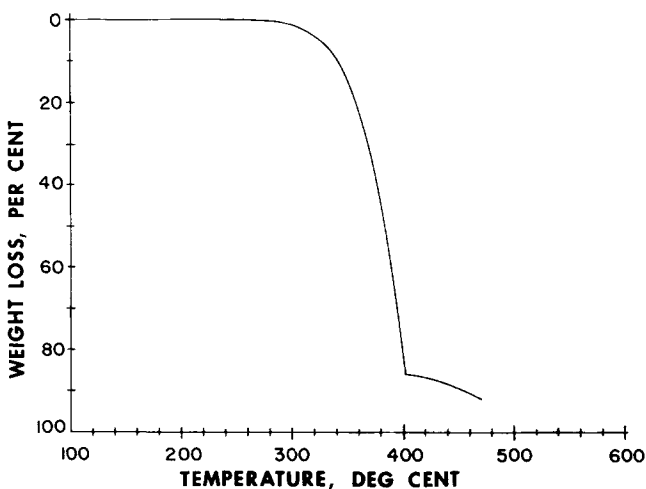

Fig. 3. Thermogravimetry of DBDPO: heating rate, 10°C/min; atmosphere, air or N_2.

of material i at temperature T. The calculated weight loss for the blend should be equal to the observed weight loss of the blend if the materials in the blend do not react among themselves.

Figure 3 shows the weight loss curve for DBDPO. This weight loss curve was the same in either air or nitrogen. Weight loss becomes detectable near 280°C and is accompanied by the formation of white crystals on relatively cool parts of the thermogravimetric apparatus. The melting temperature of DBDPO is approximately 300°C. The weight loss illustrated in Figure 3 most likely represents sublimation and voltalization rather than fragmentation.

Figure 4 shows the weight of Sb_2O_3 as a function of temperature. Weight loss is not detected until the temperature reaches 500°C. The weight loss is the same in either air or nitrogen until it amounts to approximately 20% near 550°C. The weight shows no further change above 550°C in air but continues to decrease in nitrogen.

Figure 5 illustrates that the weight loss observed for a blend of DBDPO and
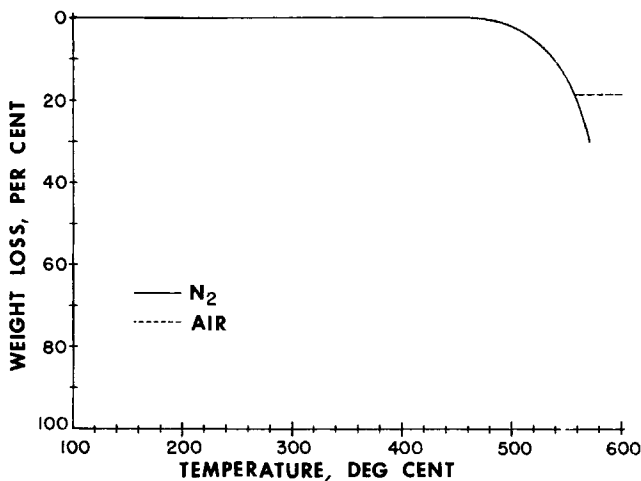
Fig. 4. Thermogravimetry of Sb_2O_3: heating rate, 10°C/min; atmosphere, air and N_2.
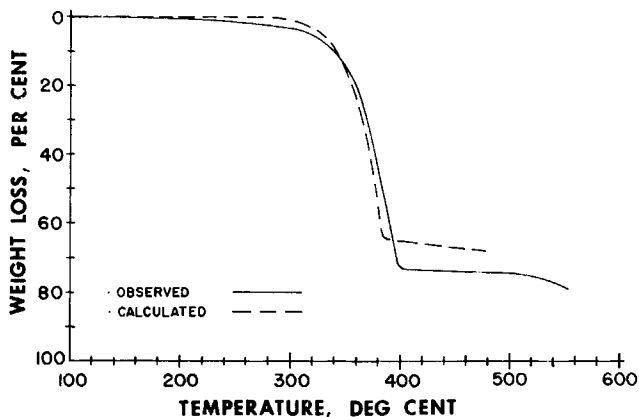

Fig. 5. Thermogravimetry of a 70/30 blend of DBDPO and Sb_2O_3 compared with calculated weight loss: heating rate, 10°C/min; atmosphere, air.

Sb_2O_3 is very similar to the weight loss calculated by eq. (1) from the individual weight loss curves of DBDPO and Sb_2O_3. The similarity of the observed and calculated weight loss curve in Figure 5 does not rule out the possibility that DBDPO and Sb_2O_3 react. If they do react, the reaction does not change the temperature dependence of the weight loss very much relative to what is expected for nonreacting materials.

Figure 6 compares the weight loss observed for HM-IPS in air with a calculated weight loss curve which was synthesized by eq. (1) from individual weight loss curves of IPS and a DBDPO/Sb_2O_3 blend in air. The observed weight loss of HM-IPS exceeds the calculated weight loss near 330°C. That is, the observed weight loss is greater than expected for a blend of nonreacting materials. Therefore, IPS, DBDPO, and Sb_2O_3 must interact above 330°C. Chemical reactions must occur in the condensed phase and generate products which volatilize above 330°C.
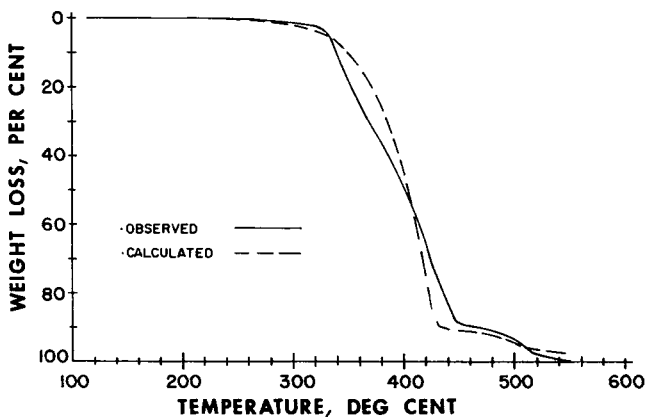
Fig. 6. Thermogravimetry of HM-IPS compared with calculated weight loss: heating rate, 10°C/min; atmosphere, air.
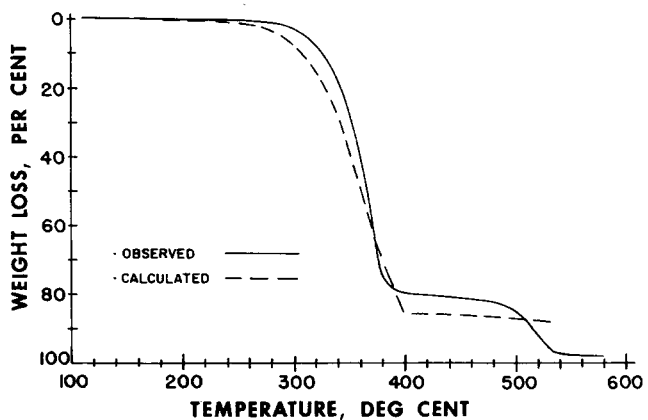
Fig. 7. Thermogravimetry of a 50/35/15 blend of polystyrene, DBDPO, and Sb_2O_3 compared with calculated weight loss: heating rate, 10°C/min; atmosphere, air.
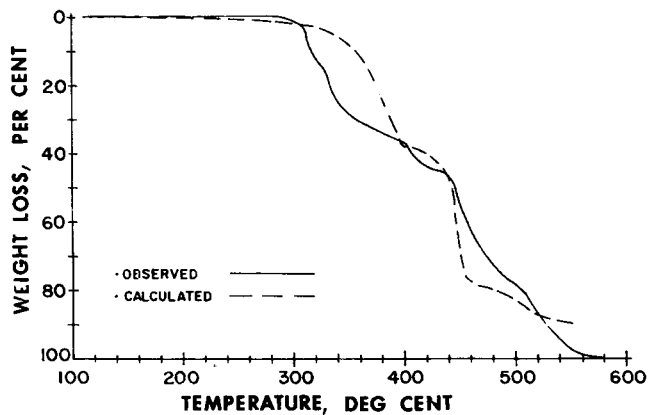
Fig. 8. Thermogravimetry of a 50/35/15 blend of polybutadiéne, DBDPO, and Sb_2O_3 compared with calculated weight loss: heating rate, 10°C/min; atmosphere, air.
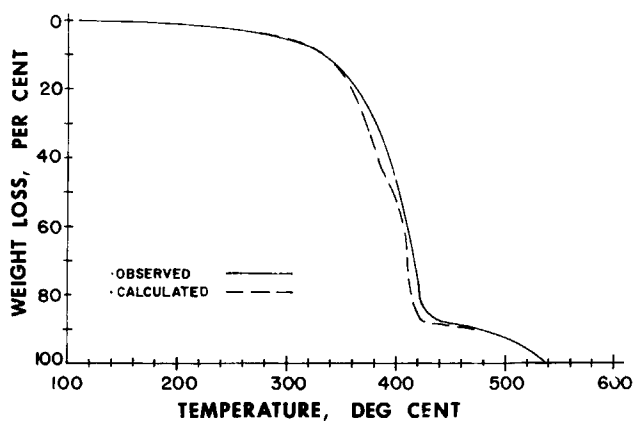
Fig. 9. Thermogravimetry of a 80/20 blend of IPS and DBDPO compared with calculated weight loss: heating rate, 10°C/min; atmosphere, air.
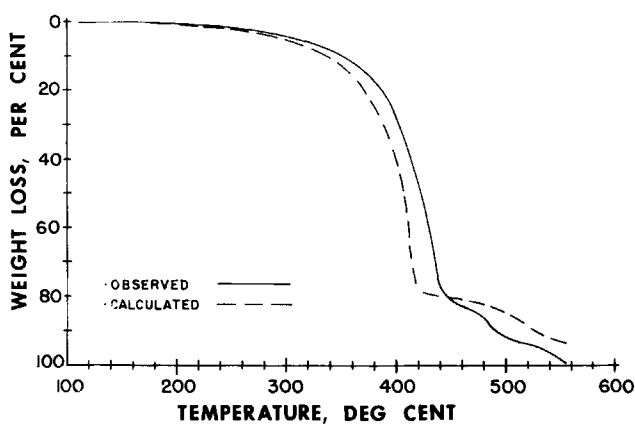
Fig. 10. Thermogravimetry of a 92/8 blend of IPS and Sb_2O_3 compared with calculated weight loss: heating rate, 10°C/min; atmosphere, air.
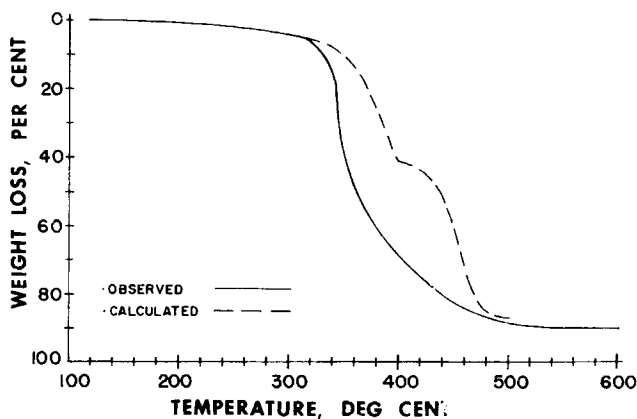
Fig. 11. Thermogravimetry of a 50/35/15 blend of IPS, DBDPO, and Sb_2O_3 compared with calculated weight loss: heating rate, 10°C/min; atmosphere, N_2.

Several additional blends were characterized to determine the necessary and sufficient conditions for the condensed-phase reactions to occur.

Polystyrene Blended With DBDPO and Sb_2O_3

The observed weight loss of a polystyrene/DBDPO/Sb_2O_3 blend is compared to its calculated weight loss in Figure 7. The observed weight loss is less than the calculated weight loss until the weight loss exceeds 70%. If the polystyrene, DBDPO, and Sb_2O_3 react, the reaction products are less volatile than the individual materials in the blend.

Polybutadiene Blended With DBDPO and Sb_2O_3

Polybutadiene is present in IPS as the impact modifier. Polybutadiene having the microstructure 35% *cis*-1,4, 55% *trans*-1,4, and 10% 1,2-addition was blended with DBDPO and Sb_2O_3.

Figure 8 compares the observed and calculated weight loss in air for a polybutadiene/DBDPO/Sb_2O_3 blend. In this case, the observed weight loss exceeds the calculated weight loss near 300°C. Therefore, the condensed-phase reactions are definitely indicated.

IPS Blended With Either DBDPO or Sb_2O_3 Separately

Figures 9 and 10 show the observed and calculated weight loss in air for IPS/DBDPO and IPS/Sb_2O_3 blends, respectively. The observed and calculated weight loss curves are similar for both blends, with the observed weight loss being less than the calculated weight loss.

Therefore, the observed weight loss exceeds the calculated weight only when polybutadiene, DBDPO, and Sb_2O_3 are present simultaneously. That is, a definite indication for condensed-phase reactions is observed only when all three materials are present.

Figure 11 compares the observed and calculated weight loss in nitrogen for an IPS/DBDPO/Sb_2O_3 blend. Even in nitrogen, the observed weight loss exceeds the calculated weight loss. Therefore, oxygen is not necessary for the condensed-phase reactions involving polybutadiene, DBDPO, and Sb_2O_3.

CONCLUSIONS

Synergism in the IPS/DBDPO/Sb_2O_3 system results from reactions that occur in the condensed phase and which require the simultaneous presence of polybutadiene, DBDPO, and Sb_2O_3.

The condensed-phase reactions do not require oxygen.

As described in an earlier paper,[2] the condensed-phase reactions are initiated by thermally generated polymeric free radicals which occur at lower temperatures for polybutadiene than for polystyrene.

References

1. J. J. Pitts, *J. Fire Flamm.,* **3,** 51 (1972).
2. E. R. Wagner and B. L. Joesten, *J. Appl. Polym. Sci.,* **20,** 2143 (1976).
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