Zinc–Borate Complex as Flame-Retardant Filler

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SYNOPSIS

Water-insoluble complexes have been prepared by reaction of boric acid, pentaerythritol, and metal salts i.e., acetates of zinc, cadmium, mercury, copper, nickel, cobalt, and manganese. The composition of these complexes has been established by determining metal content and by elemental analysis, and structural aspects have been studied by far-IR spectra. The heat-resistance data indicate that the zinc–borate complex is better than other metal–borate complexes, and, therefore, it has been selected for detailed study. The effect of 10–60 parts of zinc–borate complex on novel unsaturated polyester-7 (II) in respect of gel time, exotherm peak temperature, tensile strength, % elongation, nitroglycerine absorption, and flame retardance has been studied, and results have been discussed. Further, the zinc–borate complex also gives a synergistic effect in combination with antimony trioxide similar to other metal oxide fillers.

INTRODUCTION

The application of unsaturated polyesters and chloropolyesters for inhibition of double-base propellants has recently been reported.[1–5] The flame retardance of polymeric materials is one of the most desirable characteristics for their application as inhibitors for rocket propellants and is considerably improved

1. By introducing flame retardant elements like halogens, boron, phosphorous, etc., in the macromolecules.
2. By incorporating inert inorganic fillers like alumina trihydrate ($Al_2O_3 \cdot 3H_2O$), antimony trioxide (Sb_2O_3), molybdenium oxide, zinc borate, mica, asbestos, etc.

Inorganic fillers like antimony trioxide, alumina trihydrate, zinc–borate, etc., have been claimed to be effective flame-retardant additives[6,7] in polyesters, epoxy resins, and other polymers. The pentaerythritol–boric acid esters[8,9] have also been suggested as flame retardants for various polymeric materials. However, their use as flame retardants is limited due to their water solubility. Further, the intumescent properties of pentaerythritol and fire-quenching characteristics of fusible boron salts are incorporated by reacting these compounds with divalent metal salts of a weak acid, thereby producing insoluble complexes having flame-retardant characteristics. The synthesis and structures of some metal pentaerythritol–boric acid complexes have already been reported in the literature.[8,10–13] However, the influence of these complexes on properties of unsaturated polyesters has not yet been reported.

We report the synthesis, characterization, and evaluation of a zinc–pentaerythritol–boric acid complex as a flame-retardant filler for unsaturated polyester.

EXPERIMENTAL

Materials

The materials used for this work are

1. Boric acid (E. Merck, 99% pure), pentaerythritol (Aldrich: mp 255–259°C and purity $\approx$ 99%).

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2. Zinc acetate, barium acetate, cupric acetate, manganese acetate, mercury acetate, cadmium acetate, cobalt acetate (Robert Johnson, Bombay India, LR grade, purity ≈ 98%).

Novel unsaturated polyester-7 (II) [NUP-7 (II)] was synthesized as reported earlier.[14]

Methods

These metal–borate complexes were prepared by following method:

The required amounts of pentaerythritol (1.0 mol) and boric acid (1.0 mol) and water (2 L) were taken in a round-bottom flask equipped with stirrer, condenser, thermometer pocket, and gas bubbler and reacted at reflux temperature under nitrogen atmosphere and slow stirring. After 45 min, metal acetate solution in water was added slowly. The mixture was again heated to reflux temperature for $\frac{1}{2}$ h with slow stirring. On cooling to room temperature, a solid complex precipitated, which was washed with water and dried at 60°C for 48 h. These complexes were ground to a fine powder, sieved through (200 BSS), and again dried at 100°C for 24 h. The yield of these salts was ≈ 80–85%.

Characterization of Metal–Borate Complexes

Metal–borate complexes were analyzed for carbon and hydrogen by elemental analysis (Perkin-Elmer elemental analyzer), and metals[15] were determined gravimetrically. Far-IR spectra of these complexes were recorded on a Perkin-Elmer spectrophotometer, Model 283B, in cesium–iodide medium. Heat resistance, gel time, and exotherm peak temperature, tensile strength, % elongation, nitroglycerine absorption, and burning rate were determined by the methods reported earlier.[5]

Oxygen index (OI) was determined using an ONI flammability tester, Model CS-178B (Custom Scientific Instruments Inc., U.S.A.) by measuring the minimum concentration of oxygen in a slowly rising mixture of oxygen and nitrogen, which just supports candlelike burning.

Incorporation of Complexes

These complexes were mixed homogeneously in NUP-7 (II) by mechanical mixing followed by curing with MEK peroxide and cobalt naphthenate as catalyst and accelerator, respectively.

RESULTS AND DISCUSSION

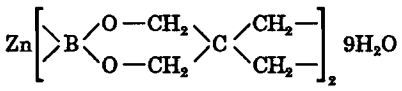
The elemental analysis of zinc–borate complex shows the presence of 28.5% C, 15.28% Zn, and 4.78% B, corresponding to the compositional/molecular formula $C_{10}ZnB_2$. Similarly, the general formula for other metal complexes is $C_{10}MB_2$, where M represents divalent metal atom, i.e., Zn, Ca, Hg, Mn, Ni, Cd, etc. It is therefore concluded that two pentaerythritol units and two boron atoms are present per atom of divalent metal atom.

The far-IR spectra of the zinc–borate complex further indicates the presence of −OH groups (3000–3500 cm^{-1}) and absence of the carbonyl group −C=O (1600–1700 cm^{-1}), indicating that metal is directly combining with the complex of boron and pentaerythritol and that acid is liberated. The presence of tetracoordinated boron and boron–oxygen linkages is indicated by the absorption bands at 980 cm^{-1} and 400–500 cm^{-1}, respectively. Based on el-

Table I Heat Resistance of NUP-7(II) Filled with Metal–Borate Complexes (40 phr) at 140°C

	Time (h)						
	1	2	3	4	5	6	7
Metal-Borate Complex	Weight Loss (%)						
Blank	0.13	0.14	0.15	0.16	0.17	0.17	0.17
Manganese	3.81	4.69	5.14	5.33	5.80	5.90	6.00
Cobalt	2.82	3.15	4.90	6.00	6.80	6.90	6.99
Nickel	3.11	4.08	4.51	4.83	5.04	5.20	5.31
Zinc	2.24	2.94	3.24	4.01	4.52	4.80	4.82
Cadmium	3.21	4.06	4.43	5.40	5.84	6.01	6.09
Mercury	3.56	4.50	5.01	5.50	5.90	6.28	6.30

emental analysis data and far-IR spectra, the structure of the zinc–borate complex may be proposed as



This structure is in close agreement with the structure of metal–borate complexes already reported in the literature.[10–13]

Heat Resistance

These metal-borate complexes were incorporated at 40 phr (40 parts of filler per 100 parts of resin) into NUP-7 (II), and their effect on heat resistance was studied at 140°C. Filled NUP-7 (II) samples were heated for 1–7 h at 140°C in a muffle furnace, and weight loss was recorded. It is observed that heat resistance is better in the case of the zinc–borate complex (Table I). It was therefore considered of interest to evaluate the zinc–borate complex further as a flame retardant for NUP-7 (II).

The effect of the zinc–borate complex on the following properties of NUP-7 (II) is described.

Gel Time and Exotherm Peak Temperature

Gel time and exotherm peak temperature data for NUP-7 (II) containing 10–60 parts of zinc–borate complex are given in Table II. It is seen that, as the quantity of the filler increases from 0 to 60 parts, the exotherm peak temperature decreases. As the quantity of filler increases, the quantity of unsaturated polyester, i.e., NUP-7 (II), decreases, leading to a decrease in the number of C=C bonds available in NUP-7 (II). These C=C double bonds are converted to C—C bonds during polymerization/curing, and heat is released. As the amount of NUP-7 (II) decreases with the increase in filler quantity, the exotherm peak temperature is expected to decrease, which is observed experimentally. Further, the addition of complex increases gel time of NUP-7 (II) as a result of hindered diffusion due to increased viscosity. This is in agreement with the findings of Agrawal et al.[3] in the case of unsaturated polyester and chloropolyesters.

Table II Variation of Gel Time and Exotherm Peak Temperature of NUP-7(II) Filled with Complex

Zinc–Borate Complex (phr)	Gel Time (min ± 5 s)	Exotherm Peak Temperature (°C ± 2°C)
00	30.8	60
10	37.1	56
20	40.8	54
30	46.8	50
40	57.6	48
50	—	—
60	—	—

Table III Variation of Tensile Strength and % Elongation of NUP-7(II) Filled with Complex

Zinc–Borate Complex (phr)	Tensile Strength (kg/cm^2)	Elongation (%)
00	80.0	25.0
10	141.8	27.9
20	240.5	14.0
30	293.4	10.7
40	384.7	8.9
50	401.4	8.1
60	425.0	7.7

Tensile Strength and % Elongation

The effect of the zinc-borate complex on mechanical properties of NUP-7 (II) is given in Table III. The tensile strength of NUP-7 (II) is 80 kg/cm^2, which increases to 240.4 kg/cm^2 on addition of 20.0 parts of zinc–borate complex as filler. It further increases with the increase in amount of zinc–borate complex from 20 to 60 parts due to the reinforcing action of the zinc–borate filler. The % elongation is accordingly lowered as tensile strength and elongation are interrelated.

Nitroglycerine Absorption

Table IV shows the influence of nitroglycerine (NG) on zinc–borate-complex-filled polyester. It is seen that the NG absorption decreases as the quantity of complex increases. This is due to the physical blocking of pores of the three-dimensional polyester network as a result of the addition of complex. This is supported by the fact that as the quantity of complex increases, NG migration decreases. The NG, being small in size, may otherwise diffuse into the cellular structure of the polyester.

Flame Retardance

Flame retardance in terms of burning rate and oxygen index (OI) is reported in Table V. Burning

Table IV Variation of Nitroglycerine Absorption of NUP-7(II) Filled with Complex Filler

Zinc–Borate Complex (phr)	Days					
	1	2	3	4	5	6
	Nitroglycerine Absorption (%)					
00	5.10	6.60	7.50	8.18	8.75	8.98
10	4.51	5.90	7.00	7.45	7.82	7.80
20	3.90	5.50	6.50	7.23	7.25	7.35
30	3.35	4.55	5.50	6.25	6.18	6.39
40	3.25	4.40	5.12	5.50	5.80	5.95
50	3.01	4.00	4.67	5.10	5.20	5.20
60	2.80	3.75	4.33	4.50	4.60	4.75

rate of NUP-7 (II) is 0.24 mm/s, which reduces to 0.10 mm/s on addition of 20% of zinc–borate complex. The addition of a higher quantity of this complex (30 parts and above) imparts a self-extinguishing property to NUP-7 (II) and proves it to be a potential flame-retardant filler. It is also seen that the addition of 10% Sb_2O_3 alone brings down the burning rate to 0.15 mm/s. But when this complex is added in combination of Sb_2O_3 (1 : 1), NUP-7 (II) becomes self-extinguishing (Table V). This shows that zinc–borate complex and Sb_2O_3 act as synergistic flame retardants.

The burning-rate data are further supported by the oxygen index (OI). OI data shows that NUP-7 (II) requires 16.2% oxygen for candlelike burning. On incorporation of complex, filled NUP-7 (II) requires 18.9% and 20.1% oxygen at 40 parts and 60 parts filler content, respectively. Similar to burning-rate data, the OI data also indicate that flame retardancy of NUP-7 (II) increases on the addition of zinc–borate complex filler.

Table V Variation of Burning Rate of NUP-7(II) with Different Parts of Zinc–Borate Filler

Zinc–Borate Filler (phr)	Sb_2O_3	Burning Rate (mm/s)	Oxygen Index (OI)
00	—	0.24	16.21
10	—	0.18	—
20	—	0.09	17.44
30	—	Self-extinguishing	—
40	—	Self-extinguishing	18.95
50	—	Self-extinguishing	—
60	—	Self-extinguishing	20.14
5	5	Self-extinguishing	—
—	10	0.15	—

The flame-retardant characteristics of this complex may be due to its endothermic decomposition and release of its water of hydration, which induces an overall cooling effect on the combustible unsaturated polyester and blanketing effect by residual constituents of the complex over NUP-7 (II). As a result of combined effects, flame does not propagate further and resin becomes self-extinguishing[16] at 30 parts filler loading.

CONCLUSION

The burning rate and OI data coupled with data on gel time, exotherm peak temperature, NG absorption, and mechanical properties suggest that this zinc–borate complex is a potential flame-retardant filler for unsaturated polyesters.

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