FLAME RETARDATION OF POLYPROPYLENE

BY

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C E R T I F I C A T E

This is to certify that the thesis entitled, "FLAME RETARDATION OF POLYPROPYLENE", being submitted by MR. ALOK CHANDRA MISRA, to the INDIAN INSTITUTE OF TECHNOLOGY, DELHI, for the award of the degree of DOCTOR OF PHILOSOPHY in the DEPARTMENT OF CHEMISTRY, is a record of bonafide research work carried out by him. Mr. Misra has worked under our guidance and supervision, and has fulfilled the requirements for the submission of the thesis.

The results contained in this thesis have not been submitted in part or in full, to any other University or Institute for the award of any degree or diploma.

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A B S T R A C T

A new series of Sb-halogen based flame retardants for polypropylene, viz., triphenylstibinedibromide and triphenylantimony(V) derivatives of tribromo-, trichloro- and pentachlorophenols, and of bisphenols viz., 2,2-bis(4-hydroxyphenyl)propane and 4,4-dihydroxydiphenyl sulfone were synthesized and characterized by elemental analysis, solution conductance, molecular weight, infrared and proton magnetic resonance spectroscopy, and thermal studies. Besides these organoantimony compounds, the performance of conventional flame retardants, Sb_2O_3 and $SbPO_4$ was also investigated after silanation with vinyltriethoxysilane and γ-aminopropyltriethoxysilane, in order to achieve better dispersion and adhesion of the filler in polymer matrix.

The flame retardancy of the filled polypropylene was evaluated by measuring limiting oxygen index (LOI), vertical flame test (UL-94), and smoke density. The pre-ignition interactions in the filled system were examined through thermogravimetric analysis, and the mechanism of flame retardation was proposed by analyzing the char obtained by isothermal treatment of flame retardant filled polypropylene at 450 and 500°C. Other properties studied were melt rheology, melting and crystallization behavior (by DTA), structural behavior (by XRD) and mechanical properties which included tensile, impact and flexural

strength. Attempt was also made to study the fracture mechanism with the help of scanning electron microscopy.

In general, the melt viscosity of the organo-antimony compounds filled polypropylene system was less than that of the virgin polypropylene, with a maximum drop in the (20 phr) pentachloro phenol derivative of triphenylantimony(V) filled polypropylene. On the other hand, addition of Sb_2O_3 and $SbPO_4$ increased the melt viscosity of filled polypropylene, but, the silanation of these fillers brought down the melt viscosity at 220°C, depending on the silane-filler interaction. The silane coupling agents improve the dispersion of filler in polymer matrix, which was confirmed by scanning electron microscopy.

The unit cell dimensions of polypropylene were not disturbed by the addition of these flame retardants, although the rate of crystallization and the percent crystallinity were affected, as evidenced by X-ray diffraction, and differential thermal analysis.

The mechanical properties of these systems were not much impaired even at 20 phr flame retardant loadings.

The LOI of filled polypropylene was increased to some extent by the addition of Sb_2O_3 and $SbPO_4$. The silanation of Sb_2O_3 and $SbPO_4$ resulted in a slight decrease in LOI of filled system irrespective of the silane-filler

combination. In contrast to $Sb_2O_3/SbPO_4$ filled system, the organoantimony compounds were found to be very efficient flame retardant for polypropylene even at low additive levels, i.e., the 5 phr of these organoantimony compounds increased the LOI of polypropylene to 23.0 or above and gave V-2 rating in UL-94 flame test.

Among the various flame retardant systems studied, the triphenylstibinedibromide at 10 phr additive level was found to be the best flame retardant for polypropylene, showing LOI of 31.5 with a V-2 rating in UL-94 test. However, for a V-0 rating a loading of 20 phr of these organoantimony compounds was required.

These halogenated organoantimony compounds seem to be vapor phase active as only very little amount of antimony was detected in the residue obtained by the isothermal treatment of filled polypropylene at 450°C for 1/2 hour. The basic mechanism of thermo-oxidative degradation of polypropylene was not changed by the addition of these flame retardants, although delayed.

In the last phase, ammonium polyphosphate and alumina trihydrate were used as flame retardants in conjunction with triphenylstibinedibromide, so as to explore the interactive behavior of Sb-halogen-phosphorus and Sb-halogen-aluminium systems. The ammonium polyphosphate at both 10 and 20 phr loading decreased the LOI of triphenylstibinedibromide (10 phr) filled polypropylene to 29.2 and 30.2 respectively. Whereas,

the alumina trihydrate at 20 phr loading increased the LOI of polypropylene filled with 10 phr of triphenylstibinedibromide to 32.3. Besides flame retardant action, ammonium polyphosphate and alumina were found to be smoke suppressant. The maximum effect was observed in the presence of alumina trihydrate, which decreased the smoke density of triphenylstibinedibromide (10 phr) filled polypropylene from 24.0 to 16.0.

The best performance of these systems is related to their dual phase activity, viz., triphenylstibinedibromide being active in the vapor phase, while ammonium polyphosphate and alumina trihydrate acts in the condensed phase.

C O N T E N T S

....(iii)

....(iv)

....(v)

CODES USED FOR VARIOUS POLYPROPYLENE FORMULATIONS IN THIS DISSERTATION

(A) $Sb_2O_3/SbPO_4$ Filled Polypropylene

Additives, phr	Code
- - PP before extrusion	P_0
- - PP after extrusion	P_1
Sb_2O_3(6)	P_2
Sb_2O_3- VTES(6)	P_3
Sb_2O_3- γ-APS(6)	P_4
Sb_2O_3- VTES(6) + Fe_2O_3(0.6)	P_5
$SbPO_4$(6)	P_6
$SbPO_4$- γ-APS(6)	P_7
$SbPO_4$- VTES(6)	P_8
Sb_2O_3(6) + PVC(19) + $CaCO_3$(10)	P_9
Sb_2O_3- VTES(6) + PVC(19) + $CaCO_3$(10)	P_{10}

PP, Polypropylene; VTES, Vinyltriethoxysilane; γ-APS, -aminopropyltriethoxysilane; PVC, polyvinylchloride.

(B) Organoantimony Compounds filled Polypropylene

Additives, (phr)	Code
- PP unextruded	P'_0
- PP extruded	P'_1
Ph_3SbBr_2(5)	P_{11}
" (10)	P_{12}
" (15)	P_{13}
" (20)	P_{14}
$Ph_3Sb(tbp)_2$(5)	P_{21}
" (10)	P_{22}
" (15)	P_{23}
" (20)	P_{24}
$Ph_3Sb(tcp)_2$(5)	P_{31}
" (10)	P_{32}
" (15)	P_{33}
" (20)	P_{34}
$Ph_3Sb(pcp)_2$(5)	P_{41}
" (10)	P_{42}
" (15)	P_{43}
" (20)	P_{44}

Ph_3SbBr_2, triphenylstibinedibromide; $Ph_3Sb(tbp)_2$ $Ph_3Sb(tcp)_2$ and $Ph_3Sb(pcp)_2$, derivatives of triphenyl-antimony(V) with tribromo-, trichloro- and pentachloro phenols, respectively.

(C) Ph_3SbBr_2/Ammonium Polyphosphate/Alumina trihydrate filled Polypropylene.

Additives, (phr)	Code
- unextruded PP	P''_0
- extruded PP	P''_1
Ph_3SbBr_2(10)	AP_1
APP(10)	AP_2
APP(20)	AP_3
Ph_3SbBr_2(10) + APP(10)	AP_4
Ph_3SbBr_2(10) + APP(20)	AP_5
ATH(10)	AP_6
ATH(20)	AP_7
Ph_3SbBr_2(10) + ATH(10)	AP_8
Ph_3SbBr_2(10) + ATH(20)	AP_9

Ph_3SbBr_2, triphenylstibinedibromide; APP, ammonium polyphosphate; ATH, alumina trihydrate.