Journal of Scientific & Industrial Research
Vol. 79, July 2020, pp. 582-585

Flame Profile Measurement of Cu (II) based Salen Complex Filled Thermally Stabilized PVC Sheets by Cone Calorimeter

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Received 22 August 2019; revised 16 January 2020; accepted 19 April 2020

This study deals with evaluation of Cu-based salen complexes as fire retardants in thermally stabilized PVC sheets. The complexes were prepared using salicylaldehyde/5-bromosalicylaldehyde, ethylenediamine and copper (II) acetate monohydrate are used in casting of PVC sheets. PVC sheets were subjected to cone calorimetric experiments and mechanical analysis. Copper based salen complexes filled PVC sheets have shown a decrease of 15.41 MJ/m^2 and 10.42 MJ/m^2 in total heat release in comparison to control sample. The complexes also enhanced tensile strength of the PVC sheets. A comparative account of PVC sheets for heat release rate, oxygen concentration and concentration of smoke is also presented.

Keywords: Flame retardants, Petrella's arbitrary scale, PVC, Salen complexes

Introduction

Flame retardants retard the ignition of polymeric materials and decrease flame spread, hence fire hazards and destruction of properties are minimized.[1] Flame retardants (FRs) are added on the basis of their chemical and physical states to improve the fire performance of polymeric materials.[2–4] The most effective, commercial fire retardant systems are based on halogen containing compounds. Due to the benefits of slowing down the flame spread, extensive research has been conducted on halogen based FRs being highly effective.[5,6] In order to tackle issues in conventional FRs such as high loadings, efficiency, toxicity etc., a new class of salen complexes is showing promising results when used as additives in polymers.[7] Recently, a series of metal based salen complexes have been synthesized and analyzed for different applications such as catalytic mimetic activities, dye sensitizer, antibacterial and antitumour properties.[8–14]

In this research contribution, Cu (II) based salen complexes have been synthesized and used in preparation of Poly (vinyl chloride) sheets. Fire retardant properties of Cu (II) based salen complexes filled PVC sheets have been evaluated using cone calorimetry. Heat release rate and total heat release were determined by using Petrella's arbitrary scale parameters under incident heat flux of 50 kW/m^2. A comparative analysis of non-halogenated Cu salen (Br0) and halogenated Cu salen complex (Br1) based PVC sheets have also been presented along with mechanical properties.

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Experimental

Materials and characterization

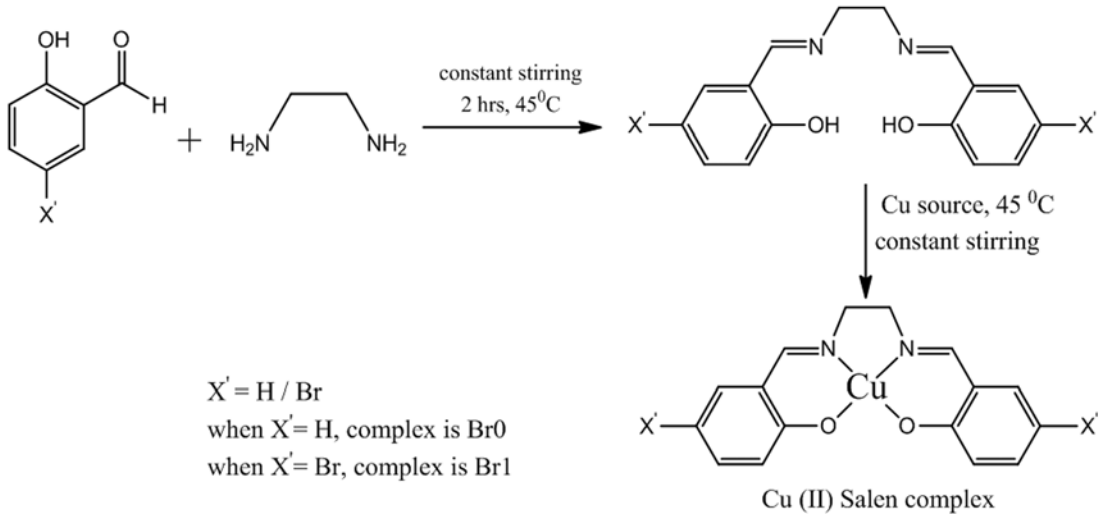
Salicylaldehyde (97%; Sigma Aldrich), 5-bromosalicylaldehyde (98%; Sigma Aldrich), ethylenediamine (99%; Thomas Baker), copper acetate monohydrate (98%; Qualigens), stearic acid (98%; Qualigens), calcium carbonate (98%; Qualigens) and dioctylpthalate (99%; Molychem) were used as received without further purification. Terephthalamide was used as thermal stabilizer, which was synthesized through depolymerization of Polyethylene terepthalate waste through ammonolysis reaction.[15]

Preparation of complexes

Cu (II) salen complexes were prepared as per procedure given in reference.[16] Two complexes namely (Br0) and (Br1) were obtained and used as additives in PVC formulations for casting sheets.

Casting of PVC sheets

PVC sheets were prepared in an internal batch mixer. The ingredients in the formulations were plasticizer, filler, terephthalamide stabilizer (TP), processing aids etc. (Table 1). Two PVC sheets were



Scheme 1 — Synthesis of Cu (II) Salen complexes

Table 1 — Composition of PVC sheets

Formulation	PVC resin (phr)	$CaCO_3$ (phr)	DOP (phr)	Stearic acid (phr)	Zinc oxide (phr)	Wax (phr)	TP (phr)	Br0 (phr)	Br1 (phr)
Control sample	100	15	50	1	2	1	10	—	—
PBr0	100	15	50	1	2	1	10	1	—
PBr1	100	15	50	1	2	1	10	—	1

prepared comprising Br0 and Br1 designated as PBr0 and PBr1. All the ingredients expect plasticizers were mixed thoroughly at 60–70°C. The required amount of plasticizer was then added to the mixer and then mixed again. During mixing, the temperature was raised up to 110°C. PVC formulations were processed by two roll mill at the temperature of 144°C for roll 1 and 146°C for roll 2. Finally the PVC sheets were prepared by compression moulding by keeping temperature of compression plates lower and upper 142°C and 145°C respectively with holding time of 1.5 minutes and cooling time of 1 minute[16].

Cone calorimetric analysis of sheets

Flammability test of PBr0 and PBr1 sheets were performed by cone calorimeter III C31SO5660-1. Flat samples with size .01000m^2 were tested with radiation flux of 50 kW/m^2 and heater temperature of 757.2°C. Samples were kept at the distance of 25 mm from the lamp and tested for 6.8 minutes.

Mechanical properties

Tensile strength and percentage elongation values were determined with the help of universal testing machine as per standard ASTM D638. All the tests were performed at the room temperature, at testing rate speed of 28 mm min^{-1}. The sheets were cut into dumbbell-shaped specimens. Three specimens from each sample type were tested and average value was reported. Hardness was determined using Durometer as per standard ASTM D 2240 (Shore-A).

Table 2 — Comparative fire parameters

S.No.	Parameters	TP-10	PBr0	PBr1
1.	Total Heat released (MJ/m^2)	44.01	28.60	33.59
2.	Average heat generation at 60°C (kW/m^2)	273.23	213.91	219.91
3	Average heat generation at 180°C (kW/m^2)	169.42	133.42	160.81
4	Average heat generation at 300°C (kW/m^2)	130.00	87.29	107.05
5.	Peak heat Generation rate (kW/m^2)	366.03	297.41	288.61

Percentage elongation = $\frac{final\ length - intial\ length}{intial\ length} \times 100$

Tensile strength = $\frac{value\ of\ load}{thickness} \times 100$

Results and Discussion

Flame profile of Sheets

Fire retardant properties of PVC sheets filled with Cu (II) based salen complexes have been studied with the help of cone calorimeter data obtained at incident radiation flux of 50 kW/m^2. The total heat released and average heat generation rates have been calculated by using equations given in reference.[16] The comparative

data of the parameters have been reported in Table 2, along with TP 10 sheet calorimetric data.[17]

On close inspection of the data, it was revealed that the amount of heat released by TP-10 sheet (control sample) is more than Cu-salen based complex filled PVC sheets. The difference of 15.41 MJ/m^2 and 10.42 MJ/m^2 was observed in total heat released of TP-10 sheet and PBr0 and PBr1 respectively. Average heat generation data at temperatures 60°C, 180°C and 300°C is also reported in Table 2. TP-10 sheet is generating more heat at these temperatures in comparison to PBr0 and PBr1 sheets. Maximum heat generation was observed for TP-10 sheet at 60°C (273.23 kW/m^2) and minimum average heat generation was observed for PBr0 sheet at 300°C (87.29 kW/m^2). These results suggest that incorporation of Cu-salen based complexes in PVC sheets is enhancing fire retardance properties.

The formulations were comprised of only 1 phr of synthesized complexes and showed marked difference in peak heat generation rates. The PVC sheet consisting of brominated complex has shown lowest value of peak heat generation rate (288.61 kW/m^2). Hence, it can be concluded that complexes Br0 and Br1 can be used as fire retardant materials in fabrication of PVC sheets. The data indicates that with increase in amount of complexes, fire retardance properties will also improve.

Heat release rates of PBr0 and PBr1 sheets as a function of time have been plotted in Fig. 1. Concentration of smoke (Fig. 2) was found relatively low for PBr1 sheet with respect to PBr0 sheet, therefore it leads to less smoke obscuration, which makes it a little less toxic. In Fig. 3 curves for oxygen concentration for PBr0 and PBr1 sheets are shown. Lowest oxygen percentage values observed are 20.25 and 20.28 for PBr0 and PBr1 sheets respectively.

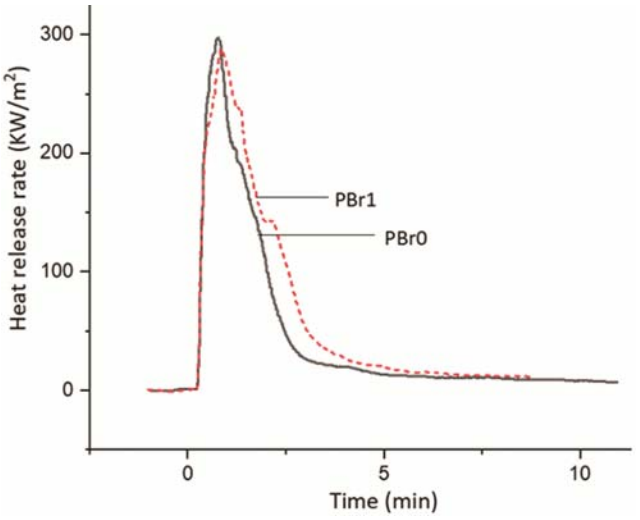


Fig. 1 — Heat release rate v/s Time

Mechanical properties

Tensile strength, elongation at break and hardness values of thermally stabilized PVC sheet (TP-10), PBr0 and PBr1 are presented in Table 3. Tensile

Table 3 — Mechanical properties of PVC Sheets

Samples	Tensile strength (N/mm^2)	Percentage Elongation (%)	Hardness
TP-10	11.92	140.23	88
PBr0	12.72	135.20	89
PBr1	12.96	133.62	89

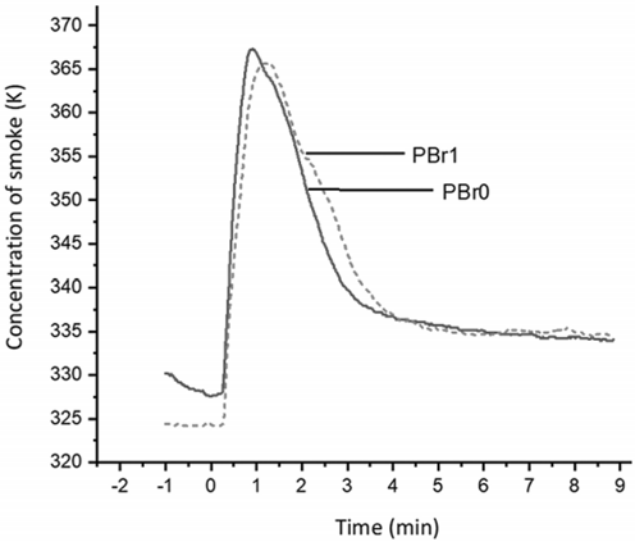


Fig. 2 — Concentration of smoke v/s Time

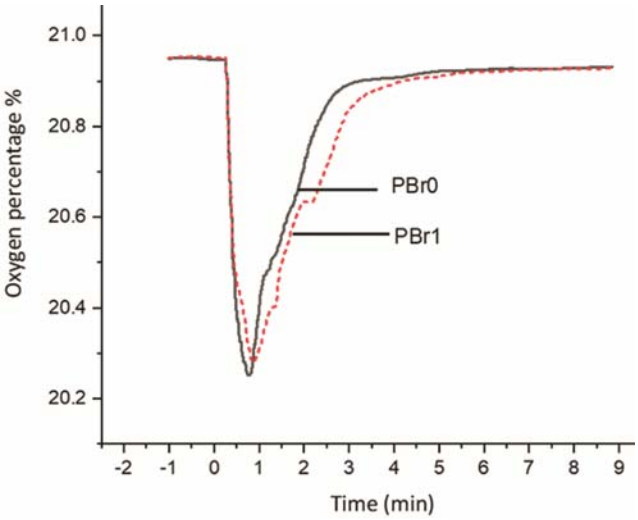


Fig. 3 — Oxygen concentration v/s Time

strength values of PBr0 and PBr1 are 12.72 and 12.96 N/mm^2 respectively which are higher than control sample, however elongation at break values of Cu (II) based salen complexes filled PVC sheets were found to decrease.

Conclusions

Thermal behavior of terephthalamide stabilized Cu (II) based Salen complexes filled Poly vinyl chloride sheets have been investigated using cone calorimeter. The data obtained has been compared with TP-10 sheet and the order of fire retardant properties was found as PBr1>PBr0>TP-10. The complexes are improving fire retardance of PVC sheets only at 1 phr concentration. A decrease of 15.41 MJ/m^2 in total heat released was observed in PBr0 and of 10.42 MJ/m^2 in PBr1 sheets with respect to TP-10 sheet. Mechanical properties of PBr0 and PBr1 sheets were also determined and compared with TP-10 sheet. Incorporation of complexes has increased tensile strength values but lowered elongation. Future work will focus on optimization of concentration of Cu (II) based salen complexes as a function of fire retardance and desired mechanical properties.

Acknowledgement

The authors thank Prof. Y Matsubara, Ms Satitaphorn Sriphuttha, and Ms Yanyang Deng at Department of Global Fire Science and Technology, Tokyo University of Science for assistance of measurements.

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