Salen Type Copper (II) Complexes as Flame Retardants for PVC Sheets

Meenu Teotia¹, Anjali Verma¹, Takashiro Akitsu², Shinnosuke Tanaka², Tomoyuki Haraguchi², and RK Soni¹*

¹Department of Chemistry, Chaudhary Charan Singh University, Meerut-250005, Uttar Pradesh, India
²Department of Chemistry, Tokyo University of Science, 1-3 Kagurazaka, Sinjuku-ku, Tokyo 162-8601, Japan

Received 06 February 2018; revised 17 September 2018; accepted 03 December 2018

Salen type copper (II) complexes have been synthesized by the reaction of salicylaldehyde, 5-bromosalicylaldehyde and 3,5-dibromosalicylaldehyde with ethylenediamine and copper(II) acetate monohydrate. The synthesized complexes were used in poly(vinyl)chloride (PVC) formulations and examined for flame retardant properties. The casted sheets were analyzed through simultaneous TGA and DTA thermal techniques. The combustion points of PVC sheets with Br0, Br1 and Br2 complexes were determined and found higher by 9.43, 10.67 and 6.03 °C, respectively, in comparison to control sample. Furthermore, the mass spectrometry results suggest that bromine substituted copper (II) complexes are environmentally safe and can be used as effective flame retardants in PVC formulations. The casted PVC sheets may find applications as fire retardant polymers in cables, panels, doors, windows, furniture etc.

Keywords: PVC sheets, TGA, DTA thermal techniques

Introduction

Polyvinyl chloride (PVC) is the most versatile polymeric material. Ignition temperature of PVC is very high and its chlorine content also provides it good fire retardant properties. However, smoke released by burning of PVC contains hydrogen chloride gas which gets condensed to give liquid hydrogen chloride in presence of water. Therefore, burning of PVC shows highly adverse effects on human body as well as on environment. Hence, the use of flame retardants in PVC formulations has become the basic requirement. Flame retardants are the chemicals which inhibit or lower the ignition temperature of materials when added to a material. In present study, flame retardant property of PVC is improved using bromine which is one of commonly used flame retardant. The bromine-based flame retardant used in this study is a bromine-substituted salen type copper (II) complex synthesized for use in dye-sensitized solar cells. These complexes were used as additives in PVC formulations and investigated for flame retardant properties. It was investigated, whether the flame retardancy was improved by the number of bromine atoms in the synthesized complex. Thermogravimetric analysis and differential thermal analysis (TG-DTA) of PVC sheets were carried out. Also, bromine-based flame retardants resulted in environmental pollution.

In order to investigate the substances contained in the gas discharged, TG-DTA-MS was entrusted to OFMGT, Material Science and Technology Promotion Foundation Analysis Evaluation Department.

Experiment

Materials and characterization

Salicylaldehyde, 5-bromosalicylaldehyde and 3,5-dibromosalicylaldehyde were of Sigma Aldrich and used as received. Ethylenediamine (Thomas Baker), copper acetate monohydrate (Qualigens), methanol (Qualigens), stearic acid (Qualigens), calcium carbonate (Qualigens), and Dioctyl phthalate from (Molychem) were used as received without further purification. Terephthalamide was used as thermal stabilizer, which was synthesized through depolymerization of polyethylene terephthalate waste through ammonolysis reaction.

Preparation of complexes

Three complexes were synthesized as per the procedure given below. The structures of the synthesized complexes are shown in Figure 1.

Complex Br0:

Salicylaldehyde (1 mmol) was dissolved in methanol (10 mL) then ethylenediamine (0.5 mmol)
was added dropwise. The reaction mixture was stirred for 2 hrs at 40 °C to produce a yellow coloured solution of ligand. Copper(II) acetate monohydrate (0.5 mmol) was added in the resultant yellow solution and stirred again for 2 hrs to synthesize complex Br0. The crude complex was filtered and recrystallized from methanol.

**Complex Br1**
Solution of 5-bromosalicylaldehyde (1 mmol) was prepared in methanol (10 mL). In this solution ethylene diamine (0.5 mmol) was added dropwise and the resultant reaction mixture was stirred for 2 hrs at 40°C to prepare ligand solution. Copper(II) acetate monohydrate (0.5 mmol) was added in the ligand solution and stirring was continued further for 2 hrs to synthesize complex Br1. The resultant complex was filtered, dried and recrystallized from methanol.

**Complex Br2**
3,5-dibromosalicylaldehyde (1 mmol) was dissolved in methanol (10 mL). Ethylenediamine (0.5 mmol) was added in this solution then resultant reaction mixture was stirred for 2 hrs at 40 °C. Copper (II) acetate monohydrate (0.5 mmol) was added in the reaction mixture and stirred further for 2 hrs to synthesize complex Br2. The synthesized complex was isolated by filtration, dried and recrystallized from methanol.

**Preparation of PVC sheets**
Compounding of PVC was done in an internal batch mixer by adding plasticizer, stabilizer, filler, flame retardant and processing aids. All these ingredients, except plasticizer were mixed at 70-80 °C. Then plasticizer was added in requisite amount and mixed further at 110 °C. After mixing, PVC compounding was processed using two-roll mill at constant temperature 140 °C of both rolls. Final forming of PVC sheets was done using compression moulding machine by keeping the temperature of compression plates at 145 °C and pressure 70 kg/cm² with 1.5 min holding time and cooling time was kept for 1 min. Each formulation contains fixed amount of PVC resin (100 phr), plasticizer DOP (50 phr), filler CaCO₃ (15 phr), stabilizer terephthalamide (10 phr), and lubricant stearic acid (1 phr). The sheets were prepared using Br0, Br1 and Br2 complexes (0.5 phr). One control sample was also prepared without the synthesized complexes.

**Thermogravimetry and differential thermal analysis (TG-DTA)**
In TG-DTA, measurement of PVC / PVC + Br0 / PVC + Br1 / PVC + Br2 was carried out and sheets of PVC / PVC + Br0 / PVC + Br1 / PVC + Br2 were measured in TG - DTA-MS. Thermogravimetry and differential thermal analysis were conducted using Bruker AXS MS 9610 / DSC 3200 A / TG-DTA 2010 SA. The measurement temperature range was 25-450 °C and the temperature rise rate was 5 °C/ min.

**Results and Discussion**
**Thermal weight and the results of differential thermal analysis**
Figures 2 and 3 show graphs of TG-DTA measurement results. All the sheets followed single step decomposition and the maximum weight loss was observed in the range 250-450 °C. The burning points of the samples based on these results are shown in Table 1. The combustion point for PVC+Br1 formulation (277.26 °C) was found highest which is higher by 10.67 °C from control sample. Table 2 shows the degree of weight reduction for each sample with increasing temperatures for PVC, PVC+Br0, PVC+Br1 and PVC+Br2 sheets. At 250 °C, the copper (II) complexes incorporated sheets showed somewhat higher weight reduction percentages in comparison to control sample (by 3-4 %), however with increasing temperatures no significant difference was observed.

**MS results**
The intensities of H₂O, Cl₂, CO₂ and C₆H₆ evolved during TGA experiments discharged around 280 to 295 °C, where the weight change of the complex was severe have been summarized in Table 3. If Table 3 is verified here, hydrogen and chlorine inside the sample

![Fig. 1 — Structure of salen type copper (II) complexes with different substitution number of bromine.](image-url)
gasify, which is considered to have resulted in a mass reduction greatly. Increasing the number of substitution of Br increases the degree of weight reduction at this point, because Br is an electron-withdrawing atom, so that the leaving group is more easily dislodged. However, gasification of Br was not confirmed in the result of mass spectrometry at any temperature. Therefore, it is unlikely that the bromine-
was not evolved at any temperature suggesting that synthesized salen type copper(II) complexes are environmentally safe and can be used as effective flame retardants.

Acknowledgement

This work was partly supported by Centre for Fire Science and Technology, Tokyo University of Science, Japan. The authors thank to Ms. Nanami Fujisawa (Tokyo University of Science) for her help in experiments.

References