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Studies on Flame Resistance of PVC Sheet Stabilized with Copper Salen Complex and Sb_2O_3

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In the present work, thermal stability behavior and flammability properties of Poly Vinyl Chloride (PVC) sheets filled with copper salen complexes and Sb_2O_3 have been studied through differential scanning calorometry, thermal conductivity measurement, Limiting Oxygen Index (LOI), discoloration, and Congo red test. Surface morphology of PVC sheets have also been studied through scanning electron microscopy analysis. The thermal stability of PVC sheets having Sb_2O_3 in conjunction with Cu-salen complex was found more than the Cu-salen complexes filled PVC sheets at 200°C observed through Congo Red test results. No change in colour of PVC sheets was observed even at 200°C and 300°C comprising 10 wt% of Sb_2O_3 with 1 phr Cu-salen complex. Limiting oxygen index values showed a hike of 5.9% with respect to limiting oxygen index value of control sample. The data obtained from experimental investigations reveal that copper salen complex and Sb_2O_3 in conjunction are depicting excellent synergy and efficiently retarding the flammability of casted Poly vinyl chloride sheets. The formulations may find suitable applications in construction, automobile, medical, and packaging materials.

Keywords: Antimony oxidem, Copper salen complexes, Flame retardants, Limiting oxygen index, Poly vinyl chloride sheets

Introduction

Poly Vinyl Chloride formulations have wide spectrum of applications in construction, automobile, medical, wire and cable, packaging, and clothing products.[1–3] Due to changes in climatic conditions, increase in global warming the overall temperature of globe has increased significantly over the years.[4,5] Thermal stability and fire resistive properties have become more and more prominent in order to enhance the workability of polymer products in real time environment.[6] Flame resistance in polymer is crucial today for safety across various industries, for protecting of workers in hazardous environments like oil, gas, and electrical sectors. With rising wildfire incidents due to climate change, fire-resistant gear is vital for firefighters and residents in high-risk areas. In transportation, aviation, and consumer products, flame-retardant materials help to prevent fire-related accidents. As urbanization and industrial activities grow, flame-resistant technologies play a key role in reducing fire hazards and saving lives.[7–9] Numerous flame retardants, including compounds of antimony, tin, zinc, copper, iron, aluminum, magnesium, and molybdenum, have been investigated to enhance fire resistance in polymers. Various polymers such as poly (vinylalcohol)[10], acrylonitrile butadiene styrene, poly(butylene terephthalate), poly(3-hydroxy-butyrate-co-3-hydroxyvalerate), poly(butyleneadipate -co-terephthalate)[11,12] have been investigated for fire resistive properties with Sb_2O_3 and metal based compounds.[13] However, very little research has been conducted on the synergistic fire-resistive properties of PVC polymer. Baggaley *et al.*[14] investigated the use of $ZnSn(OH)_6$ as a synergistic flame retardant in combination with other flame retardants. Recently, Bin *et al.*[15] investigated the synergistic effect of Zinc Borate (ZB) and antimony trioxide (Sb_2O_3) on PVC, while Zhang *et al.* studied the combination of stannic oxide (SnO_2) and ZB with Sb_2O_3.[16] Their findings indicated improved flame retardancy and smoke suppression in PVC sheets using 20% (by weight) additives. Over the years the demand of PVC based products has increased with an alarming rate due to versatile applications in different commercial sectors. Hence research investigations to achieve excellent mechanical performance along with specified application based properties are the current state of art. In previous studies Cu-salen complexes have been investigated for flame resistance properties[17] at 1 phr. In this series to achieve superior flame resistance in PVC formulations, the synergistic effect of copper salen complex and Sb_2O_3 at low concentration is thoroughly investigated as high concentration affect mechanical properties adversely. The research focuses on evaluating

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thermal degradation behavior, thermal conductivity, Lee Disc apparatus[18,19] and Limiting Oxygen Index (LOI) data to assess the effectiveness of this novel flame-retardant system. By systematically analyzing the interactions between copper salen complexes and Sb_2O_3, this study seeks to provide insights into the development of more efficient, environmentally friendly, and high-performance flame-retardant PVC materials. The findings of this research may have significant implications for industries requiring advanced fire-resistant polymeric materials, contributing to enhanced fire safety standards and sustainable material development.

Experimenital

Material

The chemicals, namely 5-bromosalicylaldehyde and salicylaldehyde (Sigma Aldrich), copper acetate monohydrate (Qualigens), calcium carbonate (Qualigens), stearic acid (Qualigens), dioctylphthalate (Molychem), PET waste, liquid ammonia (Sigma Aldrich), and ethylenediamine (Thomas Baker) were used without any additional purification.

Methods

Preparation of Cu-Salen Complex

In 10 mL of methanol, 1 mmol of 5-bromosalicylaldehyde was dissolved, and then 0.5 mmol of ethylene diamine was added dropwise. The reaction mixture was subjected to continuous stirring at 40°C for a span of two hours, leading to a ligand solution with yellow appearance. The resulting yellow solution was stirred again for two hours while 0.5 mmol of copper (II) acetate monohydrate was added to obtain Cu-salen complex Br1 (CuBr1) The crude complex was separated and recrystallized with methanol.[17,20,21] The structure of the synthesized complex is shown in Fig. 1.

Preparation of Terephthalamide (TP)

Soni *et al.* and Teotia *et al.* has worked extensively on the synthesis of aromatic amides through deploymerisation reaction of PET waste.[22,23] Terephthalamide[24,25] has been synthesized through ammonolysis of PET waste at ambient condition without the use of catalyst with aqueous ammonia in the ratio of 1:10 (w/v) and used in PVC formulations as thermal stabilizer.

Fabrication of PVC Sheets

PVC sheets were fabricated following the previously reported procedure by Soni *et al.*[26] The copper salen complex (CuBr1) was used as flame retardants in the PVC formulations for casting of PVC sheets. Seven PVC sheets with a thickness of 30 mm were prepared as per Table 1 and designated as A, B, C, D, E, F, and G.

Evaluation of Thermal Stabilizing Efficiency of PVC Sheets

Congo Red Test

In this experiment, the time required for HCl emission at a stable temperature is employed as a measure of heat capacity. Despite the absence of a direct association between the extent of dehydrochlorination and any alterations in colour, this methodology proves highly advantageous in the development of innovative thermal stabilizers. It encompasses the measurement of the time it takes for HCl to evolve and the subsequent emission rate, all at a consistent temperature. Both PVC powder and PVC cuttings are suitable for this test. The measuring

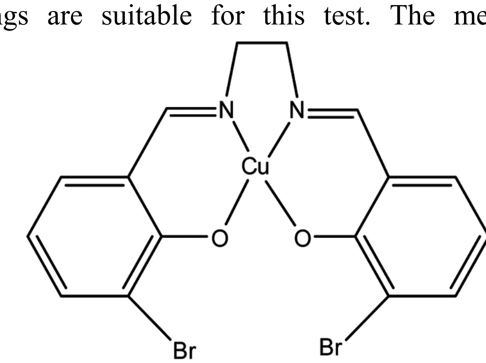

Fig. 1 — Structure of Cu-salen complex (CuBr1)

Table 1 — Composition of formulations of casted PVC sheets

Designation	PVC Resin (phr)	$CaCO_3$ (phr)	DOP (phr)	Stearic acid (phr)	Zinc oxide (phr)	Wax (phr)	TP (phr)	Sb_2O_3 (phr)	Cu-Br1 (phr)
A	100	15	50	1	2	1	10	—	—
B	100	15	50	1	2	1	10	—	1
C	100	15	50	1	2	1	10	2	1
D	100	15	50	1	2	1	10	4	1
E	100	15	50	1	2	1	10	6	1
F	100	15	50	1	2	1	10	8	1
G	100	15	50	1	2	1	10	10	1

device operates at a consistent temperature, and it records the timing of HCl gas evolution. To perform the test, the casted PVC sheets were fragmented into small pieces and heated within an oil bath at 225°C. The sample's thermal decomposition resulted in a colour change in the wet Congo red test Paper placed above the test tube. This time measurement is useful for the evaluation of thermal stability. The extended time taken for the sample in colour change is referred to have better thermal stability.

Discoloration Test

Determination of the extent of discoloration of PVC sheets as a degradation function is also very helpful to investigate the thermal stability. It can be determined by visually observing the thermally treated samples at various time intervals. Casted PVC sheets with approximately 1mm thickness were cut to size about 15 mm × 20 mm and transferred to aluminum foil paper in a temperature-controlled oven. The PVC sheets were heated at 200°C and 300°C and were removed every 10 minutes for colour change analysis. The effect of an increasing amount of Sb_2O_3 in PVC sheets was compared through the colour change of heated PVC sheets.

Thermal Conductivity of PVC Sheets

A material's capacity to conduct heat is determined by a characteristic known as thermal conductivity, or k. If a solid medium has a temperature gradient, conduction will occur. When nearby molecules collide, energy is transferred from more energetic to less energetic molecules. Since a greater temperature is connected with a higher molecular energy, conductive heat flow happens in the direction of a lower temperature.[15] Conduction heat transmission is described by Fourier's Law as:

$$H = \frac{\kappa A\left(T_2 - T_1\right)}{\chi} \qquad \ldots (1)$$

Here, 'x' represents the thickness of the sample, 'A' denotes the cross-sectional area of the sample, 'κ' stands for thermal conductivity, 'H' represents the rate of heat transfer, and (T_2-T_1) signifies the temperature difference across the sample thickness 'x'.

The temperature generally affects the thermal conductivity. Different material classes have varying k values and k/T dependency. The basic theory that at high temperatures, k decreases with temperature is often followed by crystalline polymers. In amorphous polymers, k finally becomes significantly less than the crystalline phase as the degree of crystallinity declines, and k rises as temperature rises. For investigation of thermal conductivity of casted sheets, a set of seven samples with control samples were prepared. Thermal conductivity of casted PVC sheets from 'A' to 'G' was investigated using Lee disc apparatus. With the use of a steam boiler, which was nearly half filled with water and heated to make steam, steam was produced for the purpose of measuring the thermal conductivity of cast sheets. The thickness of the sample and the diameter of the disc were measured using a Vernier caliper, the weight of the lower disc was determined using a weighing balance, and its specific heat was determined from a constant value (Thermal conductivity (k) of PVC is 0.17 W/mk (25°C)), and finally, the outlet of the boiler was connected to the inlet of the upper disc at room temperature. The sample was then placed between the two discs in order to obtain steady-state temperatures across the sample. The steady-state temperatures T_1 and T_2 were recorded after a 10-minute break. The steam chamber was then taken out, along with the sample. The steam chamber was then placed on the bottom disc to further warm it up until it reached a temperature of T_1+7°C. Lower disc was to be heated evenly for two minutes after the steam chamber was removed.[19,20] Furthermore, data obtained from the above procedure, time v/s temperature (cooling curve) was plotted in order to determine slope dT/dt at steady temperature T_1. The rate of cooling at T_1 is indicated by dT/dt, while the quantity of heat emitted per second is given by in Eq. 2.

$$H = mS\, dT/dt \qquad \ldots (2)$$

Now equating (1) and (2), we get k as –

$$\kappa = \frac{ms\left(\frac{dT}{dt}\right)x}{A\left(T_2 - T_1\right)} \qquad \ldots (3)$$

LOI of PVC Sheets

The LOI (Limiting Oxygen Index) is the minimum amount of oxygen, within a flow of oxygen and nitrogen, required to fully combust a material for a minimum of 30 seconds. This measurement was obtained using a modified procedure as outlined in NFT 51–07 and with the corresponding apparatus.

DSC Analysis of PVC Sheets

The DSC thermogram was obtained using DSC 7020 Thermal Analysis System (HITACHI) in nitrogen atmosphere. Thermograms were recorded using samples weighing 2 mg, sealed in an alumina crucible within temperature range of 30– 400°C keeping heating rate of 10°C /min.

Scanning Electron Microscopy (SEM)

SEM (scanning electron microscopy) was performed to investigate the morphology of the thermally stabilized PVC sheets using JEOL, Japan SEM, operated at 9 kV accelerating potential.

Results and Discussion

Congo Red and Discoloration Test of PVC Sheets

The thermal stability of casted PVC sheets *A to G* was determined through Congo red test method. The time required to change the colour of Cogo red test paper from sheet 'A' to 'G' is 89, 92, 104, 126, 135, 145, and 150 respectively. There is an increment of 3 minutes from sheet A to B in time taken for release of HCl molecules from PVC polymer. This increment is attributed to presence of 1 phr Cu-salen complex (Fig. 2). However, marked increase in thermal stability is observed in sheet C having 2 phr of Sb_2O_3. A difference of 9 minutes was seen in sheet C which was further enhanced to 22 min. in sheet D alongwith consistent increment in time further (Fig. 3). Atimony oxide in conjuction with Cu-salen (CuBr1) complex is converted to antimony halide that acts in gas phase and enhances thermal stability of the PVC sheets.[27,28] From this data, it is clearly evident that antimony oxide is enhancing the thermal stability effectively in synergism with Cu-salen complex.

Casted PVC sheets were observed for discolouraton by keeping at 200°C and 300°C temperatures. The change in colour was recorded before and after heating at time intervals of 10 minutes. The photographs of thermally heated sheets at 200°C and 300°C are given in Table 2. There is a gradual improvement in thermal degradation from sheet A to G in terms of time required to initiate dehydrochlorination as well as charring of the sheet. After 100 minutes of heating at 200°C, the control sample (sheet A) undergo charring however no charring was observed in sheet G and F after 100 mintues of heating. These results supports congo red test data and indicates the effective synergistic effect of Sb_2O_3 and Cu-salen complex.

Thermal Conductivity of the Casted Sheets

The thermal conductivity of casted sheets was found to decrease with an increase in the concentration of Sb_2O_3 in comparison to the control sample. The thermal conductivity data of the casted PVC sheets is summarised in Table 3. It was observed that there is gradual decrease in thermal conductivity values as the concentration of Sb_2O_3 is increased from 2 phr to 10 phr. The thermal conductivity values were found in the range 0.00028-0.000157 Cal/cm sec°C. The data clearly indicates that antimony oxide is preventing thermal conduction in PVC sheets.

LOI Test of PVC Sheets

Limiting oxygen index test data is plotted in Fig. 4. The value ranges between 23.9% to 29.8% from sheet

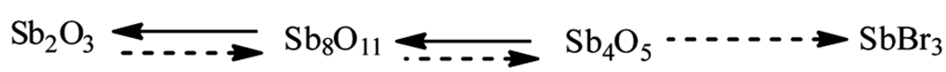

Fig. 2 — Formation of $SbBr_3$ in the mixtures of Sb_2O_3 and metal complex

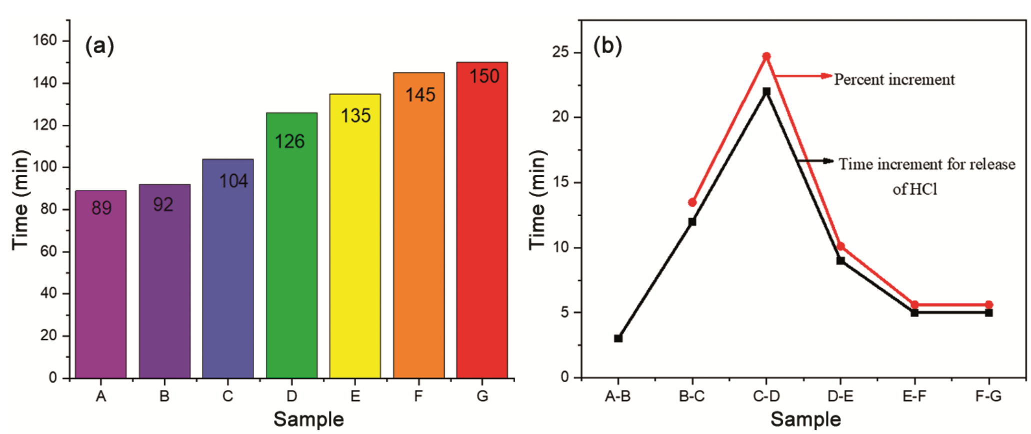

Fig. 3 — (a) Congo Red test results of Sb_2O_3 filled PVC sheets, (b) Overall time and percentage increment for release of HCl

Table 2 — Discoloration with time (min) and temperature of PVC samples filled with Sb_2O_3 and Cu-salen Br1

Sample | Sheets at 200°C | Sheets at 300°C

No Heat, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 | 10, 20, 30, 40, 50

A, B, C, D, E, F, G

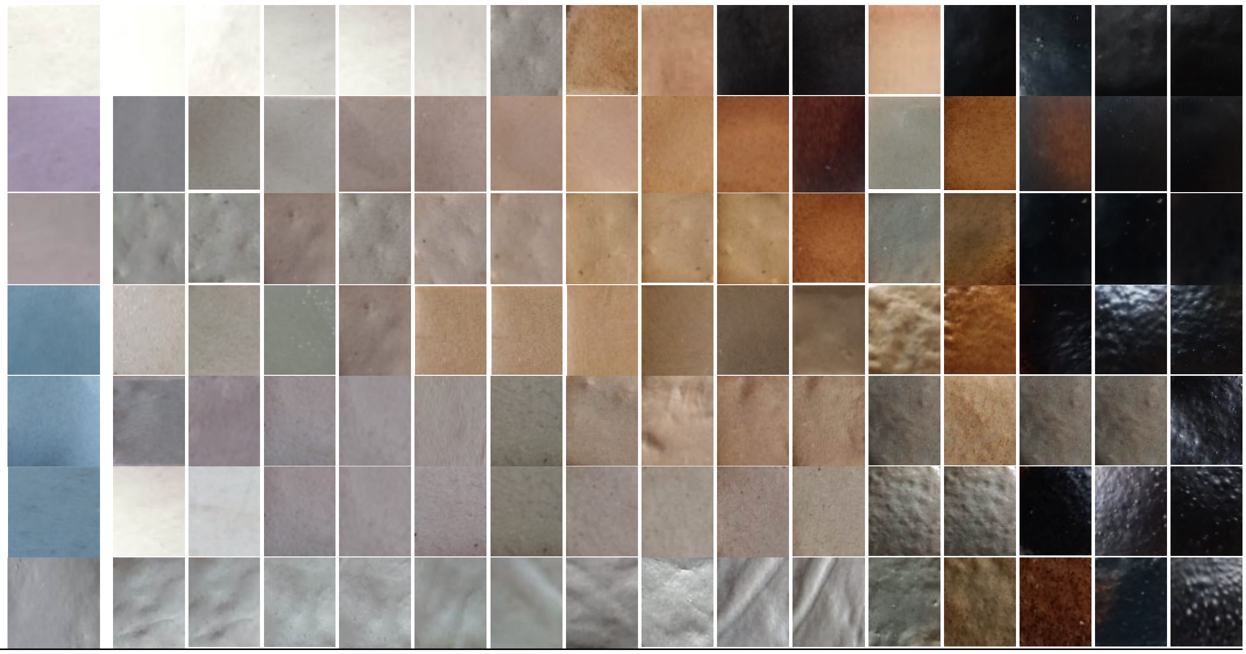

Table 3 — Thermal conductivity of casted PVC sheets

Samples	Thermal conductivity of Sheets (Cal/cm sec°C)	Heat dissipated (Joules)
A	0.00028	3.43
B	0.00027	3.30
C	0.000268	3.28
D	0.000268	3.22
E	0.00026	3.1
F	0.000153	1.92
G	0.000157	1.96

A to G. An increment of 5.9% in LOI value is observed depicting fire resistive properties with increasing amounts of Sb_2O_3.

Differential Scanning Calorimetry analysis

DSC Thermograms of sheets A to G are overlayed in Fig. 5. No sample was decomposed upto 300°C i, e the final temperature of the DSC experiment. An endothermic peak of melting of the sheet was observed around 260°C. This peak becomes broader and broader as the concentration of Sb_2O_3 is increased from sheet B to G. This indicates that Sb_2O_3 is contributing amorphous nature to the sheets and there is no lowering of melting point.

SEM Analysis

SEM micrographs were recorded for all sheets and shown in Fig. 6. No cracks and pores are seen in sheets A and B which do not have Sb_2O_3, however the pores and cracks are being intensified as the concentration of antimony oxide increases from sheet B to G. These may affect the mechanical properties of the sheets. Hence there is requirement of an optimum concentration of Sb_2O_3 where a proper balance of thermal stability, fire resistance and mechanical properties is obtained.

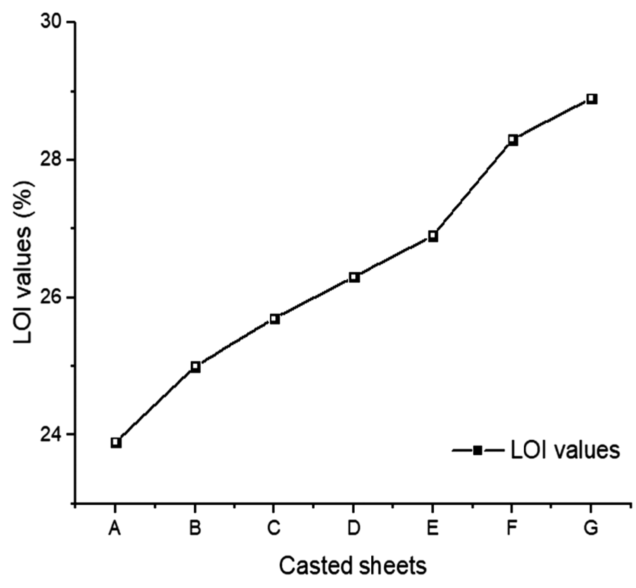

Fig. 4 — Limiting Oxygen Index values of casted

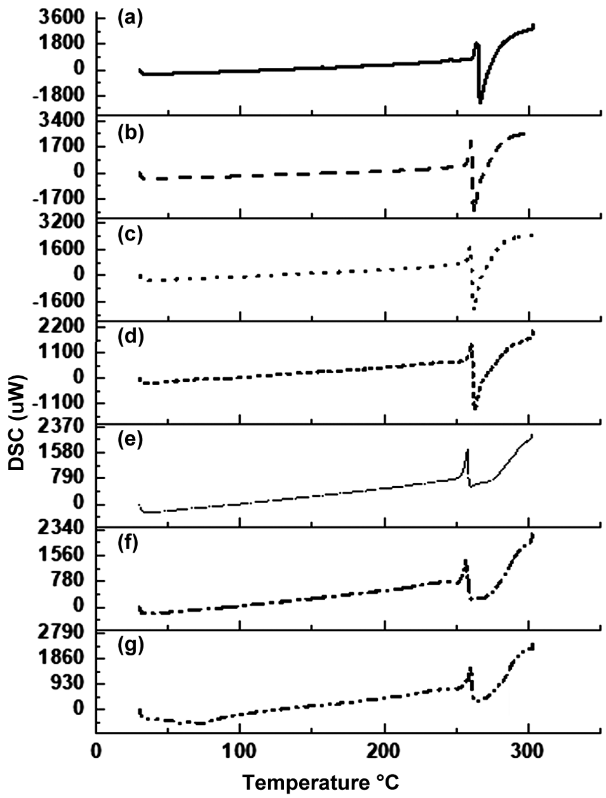

Fig. 5 — Overlayed DSC thermogram of PVC sheets PVC sheets

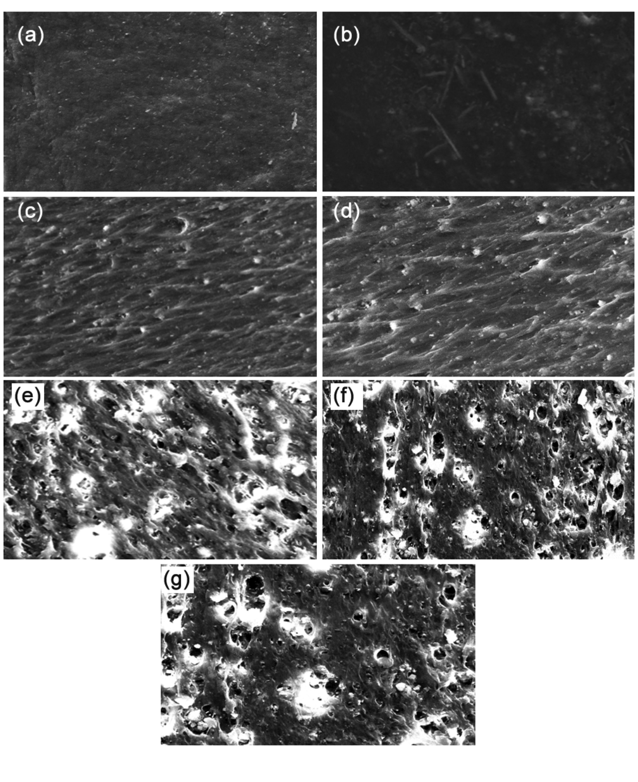

Fig. 6 — SEM images of Sb_2O_3 filled PVC sheets

Conclusions

Thermal stability behaviour and flammability properties of PVC casted sheets filled with copper salen complex and Sb_2O_3 have been studied through DSC, Thermal conductivity, LOI, discoloration test, and Congo red test. Experimental findings reveal that PVC sheets filled with Cu-salen complex along with Sb_2O_3 are depicting excellent thermal stability and flammability properties. Time of 61 minutes was found to increase for initiation of release of hydrogen chloride from sheet A to G. Limiting oxygen index values shown promising results with an increment of 5.9% from sheet A to G. The data obtained from all thermal stability and fire retardants (LOI) reveals positive synergism of Cu-salen complex and Sb_2O_3. Future work envisages the evaluation of mechanical properties and optimization of Sb_2O_3 concentration for improved final properties of PVC products.

Conflict of interests

The authors declare that there is no conflict of interest.

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