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TGA Decomposition and Flame Profile Measurement of Terephthalamide Stabilized PVC by Cone Calorimeter

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TGA decomposition and flame profile of terephthalamide stabilized PVC sheet have been investigated using simultaneous TGA/DTA and cone calorimeter respectively. PVC sheet was casted through compression moulding technique using terephthalamide as thermal stabilizer and obtained through depolymerisation of PET waste with ammonia. PVC has been considered as low fire risk material under flashover heat flux of 20 kW/m^2 and effects of accidental fire are not so prone. Flame profile of PVC sample was analyzed using Petrella's arbitrary scale parameters under incident irradiance heat flux of 50 kW/m^2. The use of terephthalamide in PVC sheet enhanced its thermal stability but contributed significantly to peak heat generation rate and also the gross heating value. The corresponding increase in its flashover propensity suggests high risk level for the sample however total heat released indicates an intermediate risk level.

Keywords: TGA, PVC, Cone Calorimeter

Introduction

Polyvinyl chloride (PVC) is the most commonly used plastics. It has good fire retardance properties because of its chlorine content and high ignition temperature (455 °C). Upon ignition, PVC releases HCl gas and smoke, HCl condenses in presence of water to give liquid HCl and get combined with smoke which is more alarming hazard to the use of PVC products in people's daily lives[1]. Hence, the study of fire behaviour of such building materials is essentially required before their practical applications. Cone calorimeter and thermogravimetric analysis are effective tools for the evaluation of fire risks of various materials[2-5]. In the present work, fire retardance property of terephthalamide stabilised PVC sheet has been investigated by calculating Petrella's arbitrary scale parameters through the cone calorimetric data and thermal gravimetric analysis.

Experimental

Materials and characterization

Post consumer PET bottles were used for synthesis of terephthalamide. Aqueous Ammonia (40%), Stearic acid and Calcium Carbonate were of Qualigens and used as received. Dioctyl phthalate was procured from Molychem and used as received without further purification.

Synthesis of terephthalamide

Soni *et al*. have worked on synthesis of aromatic amides through depolymerisation of PET waste using ammonolysis[6-7] and aminolysis[8-10] reactions. Terephthalamide was synthesized and characterised by depolymerising PET flakes through ammonolysis at ambient conditions without the use of catalyst[8] with aqueous ammonia in the ratio 1:10 (w/v) and used in PVC formulation as thermal stabilizer.

Casting of PVC sheet

PVC compounding was prepared in an internal batch mixer by taking plasticizer, filler, stabilizer, processing aids etc. with PVC resin. All the ingredients except plasticizer were mixed thoroughly at 60-70 °C. The required amount of plasticizer was then added to the mixture and mixed again thoroughly. During mixing, temperature was raised up to 110 °C. Formulation comprises PVC resin 100 phr, DOP 50 phr, $CaCO_3$ 15 phr, stearic acid 1 phr and terephthalamide 10 phr. PVC formulation was processed by two roll mill at the temperature of 144 ^{0}C for roll 1 and 146 °C for roll 2. Finally the PVC sheet was prepared by using compression moulding machine by keeping temperature of compression plates at 142 °C (lower) and 145 °C (upper) with holding time of 1.5 minutes and cooling time of 1 minute.

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TGA/DTA and cone calorimetric analysis of PVC sheet

Simultaneous thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) thermograms of PVC sheet were recorded on Bruker AXS.MS9610/DSC3200A/TG-DTA 2010SA under nitrogen atmosphere in the temperature range of 25-450 °C at heating rate of 20 °C/ min.

Flammability test was performed using the Cone Calorimeter III C3 ISO5660-1. Flat sample with size 10×10 cm and thickness 2.5 mm was tested with radiation amount of 50.00 kW/m^2 and heater temperature of 761.2 °C. Sample was kept at a distance of 25 mm from cone and tested for 753 seconds (12.54 min).

Results and Discussion

Thermogravimetric analysis

Simultaneous TGA/DTA thermogram of the casted PVC sheet is shown in Figure 1. No significant weight loss was observed upto 150 °C, however maximum weight loss was observed between 250-300 °C with DTG peak value of 285.56 °C corresponding to 55.01% weight loss. It shows that terephthalamide is very efficiently stabilizing PVC. The thermogram reveals single step degradation of PVC sheet with 25.71% char residue at 450 °C. DTA curve is almost smooth showing a very broad and weak endothermic hump in the range 260.21-290.04 °C with peak temperature of 272.57 °C(-5.345μV) corresponding to nearly 38.30% weight loss and extending to an exothermic slope 400 °C onwards showing decomposition of the sheet.

Table 1— Data obtained from TGA/DTA of terephthalamide based PVC sheet

S.No.	Temperature (°C)	Weight loss (%)
1	150	0.14
2	200	1.44
3	250	11.68
4	300	60.19
5	350	65.60
6	400	67.67
7	450	74.29

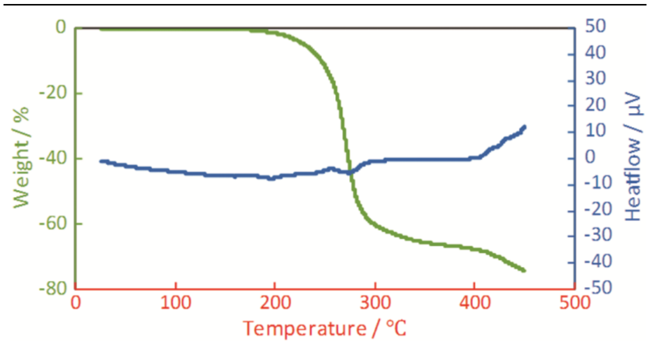

Fig. 1 — TGA of injection moulded terephthalamide based PVC sheet

Flame profile of PVC sheet

Fire hazard assessment of PVC sheet was performed through combustion with the help of cone calorimeter. An incident radiation heat flux of 50 kW/m^2 was applied to measure the concentrations of oxygen, carbon dioxide, carbon monoxide, maximum heat generation rate, gross heating value and average heat generation rate. The total heat released (gross heating value, in MJ/m^2) was calculated by the equation 1 and average heat generation rates; T60, T180 and T300 (kW/m^2) were calculated using equations 2-4 respectively. Table 2 summarizes the calculated results of these parameters.

$$THR = \int_0^{\infty} HGR(t)dt \qquad ... (1)$$

$$\bar{T}_{60} = \frac{1}{60}\int_{tig}^{tig+60} HGR(t)dt \qquad ... (2)$$

$$\bar{T}_{180} = \frac{1}{180}\int_{tig}^{tig+180} HGR(t)dt \qquad ... (3)$$

$$\bar{T}_{300} = \frac{1}{300}\int_{tig}^{tig+300} HGR(t)dt \qquad ... (4)$$

Ignition time for the PVC sample was found to be 22.6 seconds. Petrella[11] proposed arbitrary scale parameters based on 50 kW/m^2 incident heat flux for flashover propensity (x) and THR (y) given by equations 5 and 6 respectively. The x and y values are helpful in determining the risk factor of the materials to thermal and flashover contribution under fire hazards.

Table 2 — Calculated results of some important thermal parameters

S. No.	Parameter	Value
1.	Total heat released(THR)	44.01 MJ/m^2
2.	Av. Heat generation rate in 60 seconds ($\bar{T}_{60}$)	273.23 kW/m^2
3.	Av. Heat generation rate in 180 seconds ($\bar{T}_{180}$)	169.42 kW/m^2
4.	Av. Heat generation rate in 300 seconds ($\bar{T}_{300}$)	130.00 kW/m^2
5.	Peak heat generation rate	366.03 kW/m^2

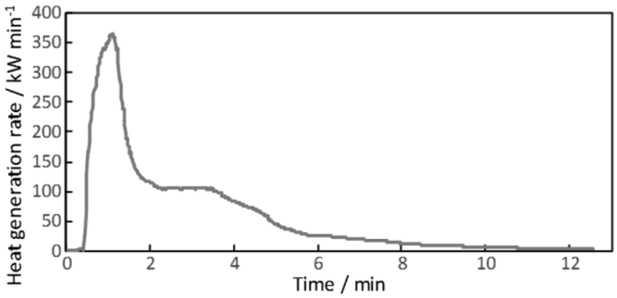

Fig. 2 — Heat generation rate versus time

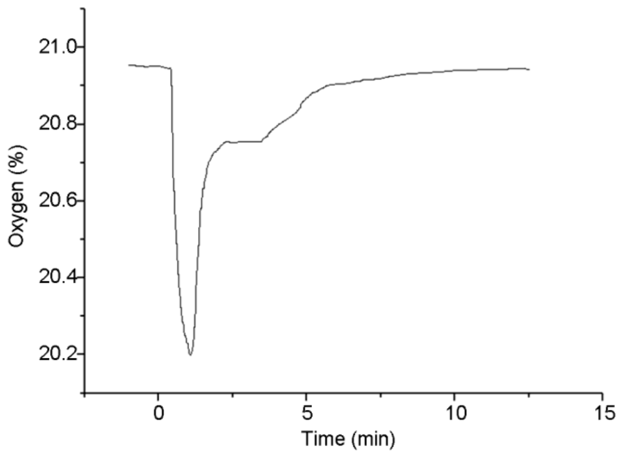

Fig. 3 — Oxygen concentration versus time

$$x = \frac{peak\ (HGR)}{t_{ig}} \quad \text{... (5)}$$

$$y = THR = \int_0^\infty HGR(t)dt \quad \text{... (6)}$$

The calculated values of *x* and *y* are 16.19 kW/m^{2}s and 44.01 MJ/m^2 respectively which characterized the terephthalamide stabilized PVC sheet as high risk material for flashover propensity, however for the parameter *y*, the sheet showed intermediate risk level. On comparing the results with the test results of Xu *et al.*[4], where flashover propensity for the PVC wall panels was found in the range 5.21-5.70 kW/m^{2}s and THR was 18.65-21.66 MJ/m^2, it was observed that the calculated values are much higher than previous findings. The significant increase in the values is due to the presence of terephthalamide in the sheet which is contributing to the heat generation rate and also total heat released. Figure 2 shows heat generation rate versus time plot, which is similar to PMMA[12], but PMMA possess high ignition time and hence characterized as intermediate risk material. Figure 3 and 4 show curves for oxygen concentration in percentage and

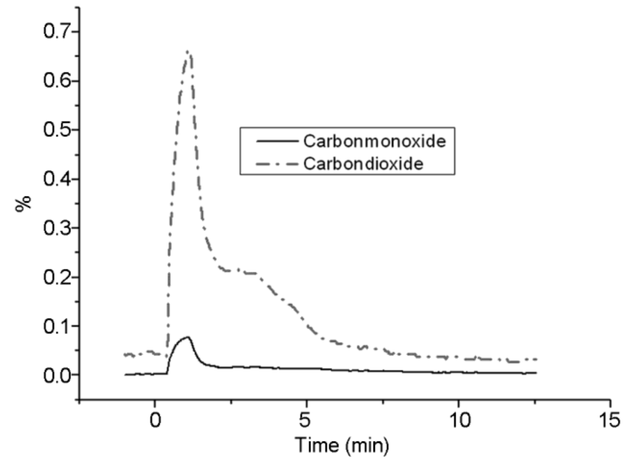

Fig. 4 — Carbondioxide and carbon monoxide concentration versus time

carbon monoxide & carbon dioxide concentrations in percentage of dry air respectively.

Conclusion

In this paper, cone calorimeter data and thermogravimetric analysis has been used to investigate the thermal behaviour of terephthalamide stabilized PVC sheet under irradiation heat flux of 50 kW/m^2. PVC sample undergoes single step thermal degradation with peak maxima at 285.56 °C. The sample shows high value for flashover propensity which indicates high level of risk however the total heat released suggests intermediate level of risk. The PVC sheet was well stabilized thermally and hence efforts should be made to overcome the problem of heat release to convert PVC sheet to be safe for construction applications.

Acknowledgement

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