

東京理科大学「火災安全科学研究拠点」

Tokyo University of Science “Research Center for Fire Safety Science”

■研究成果概要報告書/ Report for Outline of Research Results

研究課題 Research Topic		Development of new flame retardant and thermal stabilizers for polymers Especially used in buildings and construction applications	実施年度
			2016
研究代表者 Research Leader	所属 Affiliation	Department of Chemistry, Chuadhary Charan Singj University, Meerut, India	
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受入担当責任者 Organization	氏名 Name	Takashiro Akitsu	
<p>1. 研究の背景および目的/ Background and Aim of Research</p> <p>The objective of this ongoing research project was to prepare new thermal stabilizers for PVC (polyvinyl chloride) which shall be heavy metal free and shall be fire resistant and generates low smoke. PVC is commodity plastic which is used in the building as cables/ doors/windows etc. The PVC compounding force us to add heavy metal compounds such as Lead or cadmium compounds which generates heavy metal dangerous compounds on heating or burning. It is necessary to find alternative thermal stabilizers which should be free from heavy metals or does not produce toxic compounds during burning or heating. The principal investigator was interested to prepare new thermal stabilizers which should be heavy metal free and generates less toxic gases on heating or combustion. The research project was adopted for the financial year 2016-17.</p>			

## 2. 利用施設及び利用日/ Facility and Schedule

- ●●装置 (2016年--月--日～ --月--日) 1.4.2016
- ●●装置 (2016年--月--日～ --月--日) 31.3.2017

The following facilities of Department of Chemistry, Chaudhary Charan Singh University, Meerut were utilized:-

1. Two roll mill
2. Compression Molding press
3. Tensile Strength Testing Machine
4. Differential Scanning Calorimeter
5. FTIR
6. HPLC
7. Reaction assembly

The following facilities of Tokyo University of Science were used:-

1. TGA
2. Cone Calorimeter
3. Reaction facility

In addition the samples were sent for testing to M/S Hitachi High tech Laboratory situated in Tokyo, Japan. Prof Akitsu and Prof. Soni visited twice their laboratory but due to breakdown of the instrument the required testing of evolved gas analysis could not be made. On receipt of these results, another research paper will be completed.

3. 実験方法・研究成果、および考察（申請時の計画に対する達成度合いも含む）

※継続課題の場合は、前年度との関係性、進展度合いについても記載すること。

/ Method, results, and conclusions (degree of achievement compare to application)

In the first year of the project Prof. R. K. Soni visited Tokyo University of Science to conduct research work in collaboration of Prof T. Akitsu twice. Prof. Soni prepared several aromatic amides in his laboratory in Charan Singh University, Meerut, UP India by the reaction of ammonia and amines with PET waste. Different aromatic amides prepared by Prof Soni and his team are as follows:-

**Synthesis and Characterization of NN' substituted terephthalamides**

N,N' bis-methyl terephthalamide, N,N' bisaminoethyl terephthalamide, N, N' bis-hydroxyethyl terephthalamide, N, N'-bis-n-butyl terephthalamide and terephthalic dihydrazide have been synthesized through aminolysis of PET waste with methyl amine, ethylenediamine, ethanolamine, butyl amine and hydrazine hydrate at ambient conditions of temperature and pressure. The aminolysates have been characterized through different spectroscopic and other analytical techniques.

**Determination of Calorific Value of Terephthalamides**

Calorific values of terephthalamides have been evaluated to suggest another application of these aminolysed end products by complete burning of a unit mass of the amide with oxygen at constant volume process. The heat of combustion of terephthalamides have been determined using Scientech digital Bomb calorimeter (an adiabatic system) calibrated with benzoic acid. Standard calorific values of benzoic acid, ignition thread and wire were used to calculate the water equivalent, whose value was used to determine the calorific values of different terephthalamides by measuring the temperature rise on combustion.

**Calculation of Calorific values**

Bomb calorimeter was standardize with benzoic acid and water equivalent (W) was determined using standard calorific values of the nichrome wire and cotton thread; 350 cal/gm and 4200 cal/gm respectively. Calorific values of different aminolysates were calculated by using the recorded Δt values using the following expressions:

$$W = \frac{6319 \times \text{weight of benzoic acid} + (E_1 + E_2)}{\text{Temperature rise}}$$

.....Eqn 1

$$\text{Calorific value} = \frac{WX\Delta t - (E_1 + E_2)}{\text{Sample weight}} \dots\dots\dots \text{Eqn}$$

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Where 6319 cal/gm is the calorific value of benzoic acid, E<sub>1</sub> (Standard CV of wire X weight of wire consumed) and E<sub>2</sub> (Standard CV of thread X weight of cotton thread consumed) are the calorific values of wire and cotton thread. W was calculated (2538.78 cal/°C) and used to calculate the calorific values of terephthalamides through equation 2.

### 3 MS and TGA Characterization

Simultaneous TGA/DTA thermograms were recorded on Perkin Elmer, Diamond TG/DTA at 20.00 °C/min in nitrogen atmosphere from 40 to 700°C. MS spectra were recorded on Waters, Q-TOF Microma SS (LCMS) mass spectrometer.

These prepared aromatic amides were used in the preparation of PVC sheets. All aromatic amides were successfully used as thermal stabilizers and smooth PVC sheets filled with different aromatic amides were casted with the help of two roll mill and Compression Moulding press.

#### 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<sub>3</sub> 15 phr, stearic acid 1 phr and terephthalamide 10 phr. PVC formulation was processed by two roll mill at the temperature of 144 °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.

Prof Soni brought all the PVC sheets to Tokyo University of Science during his first visit and it was planned to test these PVC sheets for TGA and burning experiments. During this visit, Prof. Akitsu and his team prepared few complexes designated as Br0, Br1 and Br2 and given to Prof Soni for the preparation of PVC sheets. These complexes were also used successfully and PVC sheets filled with these complexes were prepared by Prof. Soni in this laboratory. The PVC sheets were also tested for

their mechanical properties at CCSU Meerut, India.

### **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<sup>2</sup> 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).

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<sup>2</sup>. 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.

Prof. Soni and Prof Akitsu also visited Hitachi Laboratory in Tokyo for conducting experiment for evolved gas analysis. The PVC samples were handed over to Mr. Obuko for testing. Unfortunately the testing could not be completed for break -down of the instrument.

During second visit of Prof Soni to TUS Tokyo, Japan, the PVC sheets(Br0, Br1 and Br2) prepared in his laboratory were handed over to Prof. Akitsu for testing by TGA and for burning experiment. Prof Soni and Prof akitsu visited Hitachi laboratory and Research Center for Fire Safety Science for conduct of experiment. The TGA and burning experiment were conducted on PVC sheet filled with TP10. A research paper was also written which has been accepted for publication in Journal of Scientific and Industrial Research.

**During first year of project, all the objectives were achieved however all the PVC sheets could not be tested due to shortage of time and non-availability of the instruments.**

4. 今後の展望（今後の発展性, 見込み等についても記述） / Future Perspectives

In the next year 2017-18, more PVC sheets will be prepared by adding different aromatic amides and Br complexes. Such PVC sheets will be tested for burning experiments and evolved gas analysis. The mechanical properties of these sheets will also be determined. Such PVC sheets will be tested for flame resistance and smoke generated during burning of the samples. It will also be evaluated for toxic gases.

5. 成果の公表状況（学会への発表, 学術誌への投稿等を記述。予定も含む）

/ Publishing (presentation, paper, etc. incl. plans in the future)

In 2016, we have carried out some preliminary experiments and will publish one book chapter (whole research concept) and at least two original research papers.

[Book chapter] T. Akitsu, R. K Soni *et al.*, “Dual Purpose Bromine-containing Schiff base Cu(II) Complexes for DSSC Dyes and Polymer Flame Retardants” in Hybrid Systems: Performance, Applications and Technology, Nova Science Publishers, Inc (NY, USA), in press.

Research Papers:- The following two research papers are prepared out of the research work conducted in the last year. One research paper has been communicated to the journal for publication and the other research paper is under preparation.

1. T. Akitsu, R. K Soni *et al* “TGA decomposition and Flame profile measurement of Terephthalamide stabilized PVC by Cone calorimeter” **Accepted for publication in Journal of Scientific and Industrial Research.**
2. T. Akitsu, R. K Soni *et al* “*Studies of aromatic amide stabilized PVC sheet*” ***under preparation.***

6. 経費の使用状況/ Usage of Budget

expendables · Meeting · Printing		Travel expense		Personnel expenses	
Contents	Cost	Contents	Cost	Contents	Cost
Chemicals	15,752	Airfare,	286,080		0
Book	2,160	Accommodati			
Experimental		on,			
material	196,008	Road Travel			
Subtotal	213,920	Subtotal	286,080	Subtotal	0
Burden of Tokyo University of Science / Total Yen500,000 yen					
Burden of _____ / Total Yen					