Fume Toxicity and Combustion Behavior of Different Polymers and their Health Hazard

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Abstract

The risk of fire is a significant problem in today's society. When a material burns, a number of components are liberated, and poisonous gases are produced as well. Carbon dioxide and carbon monoxide are the two main gases released during a fire, along with hydrochloric acid, nitrogen oxide. Some polymers like polyamides, wool, or silk also release cyanide. These gases can cause a variety of lung diseases, hypoxia, respiratory diseases, fevers, stomach ulcers, and metal diseases due to certain organo-irritants. In this article, we talk about issues relating to the toxicity of textile fumes, such as those from polyester, nylon, aramide fabrics and various polymers like PU, PVC, Fluoropolymer, Styrene etc. Here, the impacts of conditions on the combustion reaction and their burning behavior are described in detail, along with the toxicity of combustion products and assessment of combustion toxicity. The fume toxicity has been studied for different polymers using method NCD 1409.

Key words

Toxicity, combustion, NCD 1409, PVC, PU

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1.0 Introduction

One important consideration in the choosing of polymer for diverse applications is the fire risk posed by the materials. Building materials, as well as those used in automobiles, trains, hotels, and home appliances, must meet specific fire performance standards. A flammability test is used to determine a material's flame resistance. The substance degrades thermally in three different ways: through oxidative pyrolysis, anaerobic pyrolysis, and ultimately through flame burning. Below 400 °C, many materials, especially polymers, begin to degrade thermally, releasing poisonous and combustible gases.[2]

Due to their versatility, affordability, and ease of use, polymers are now favored over traditional materials like metals and ceramics in many applications. However, there are concerns due to a larger flammability risk than with traditional materials.[2]

Many polymers have hydrocarbons as their backbones, which makes them more combustible and increases the risk of fire. Polymer shows self-sustaining combustion upon ignition in air. The properties, combustion products, and burning behavior of various polymers vary. According to the material's composition and the fire's temperature, a variety of hazardous chemicals with varying compositions are present in fire smoke.[2]

Ignitability, flammability of volatiles, total heat and its release rate, flame spread, smoke generation, and fume toxicity are the main hazardous aspects of fire. In the table below, a number of polymers are mentioned along with information about how they are used in most sectors and the gases they emit. (Table1)

Table 1 - Polymers their applications and combustion product

Sr. No	Polymers	Applications	Gas evolved during combustion
1	Polyurethane	Expanded rigid boards, sprayed insulation, flexible foams, elastomers, window treatments, resin flooring, gaskets and thermoplastics rubbers and elastic fabrics.	CO_2 and CO, HCN, NO and NH_3. HCN
2	Fibre reinforced polymers	Aerospace, marine and automotive industries, furniture, bathroom cabins	CO, CO_2 and Nox and dangerous inhalable fibers, Particulates
3	PVC	piping, window frames, low-voltage cables, insulating sheathing, carpets and PVC coated fabric for seat covering, Artificial wool	CO_2, CO and HCL
4	Fluoropolymers	Wires and cables, insulator coatings of wires	low and unsteady yields of CO_2 and CO

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Sr. No	Polymers	Applications	Gas evolved during combustion
5	Polyester	Fabrics (clothing, curtains, and carpets) , bottles and as composites in furniture and appliances	CO, H_2O and CO_2,benzene, acetaldehyde, formaldehyde and different kinds of hydrocarbons
6	Polyamide	Flammable interior furnishings and decorative materials particularly textiles), fabrics and consumer and industrial applications. Aliphatic polyamides (nylons) are used in textiles and are important engineering plastics. Aromatic polyamide (aramid) is used mostly in advanced composites	Heavy hydrocarbons, CO, CO_2, NH_3, HCN and NOx; furans, isocyanates
7	Polystyrene	As an insulating material, Fire retardant polystyrene foam	Soot, CO, CO_2 and H_2O, aromatic compounds

2.0 The impact of environmental factors on the start and spread of fire

Major factors impacting fire include temperature, pressure, water, amount of oxygen present, and ventilation. Evaluation of the combustion products is required since the results of material combustion are greatly influenced by the fire conditions. When a fire starts, the temperature raises, the oxygen level drops, and the concentration of combustion products rises.

Fire fume Toxicity is assessed using a variety of techniques; CO concentration is the primary factor, followed by the development of other harmful gases with lower concentrations. Pyrolysis, charring of the substance and thermal degradation are only a few of the several conditions and stages of fire. First, a solid material is transformed into a gas, and then the material's surface chars, using less energy.

3.0. Health impacts and combustion product analyses.

Only a small portion of fire-related deaths and injuries are caused by the heat and flames; many victims die as a result of the hazardous fire effluents and poor visibility of smoke generation. However, this is dependent on the individual's inhalation rate, exposure period, and proximity to the fire. Because the vast majority of the fire's by products are regarded as toxic.[3]

The Table 2 lists and provides information on the numerous gases that are typically produced during fire incidents, along with any associated health risks.

Table 2 - Combustion product and their effect on human and environment

Sr. No	Combustion product	Effect on human	Effect on environment
1	Carbon Dioxide	Nausea ,vomiting, rapid breathing, rapid heart rate	The fire effluents may or may not make an impact on environment depending up on the duration of exposure. Effects to the environment are destroying homes, natural habitat and timber, polluting the air with emission of carbon dioxide. Disrupt transporattion, communications, power and water supply, deterioration of the air quality, Release soot particles to the environment. Hazardous chemical are released into the environment through fire plume, figherfighting operations, air and water contamination
2	Carbon monoxide	Fatigue, headaches confusion and dizziness due to less O2 delivery to brain	
3	Nitrous Fumes	Breathing problems, Headache, reduced lungs function, Eye Irritation, loss of appetite. bronchitis	
4	Hydrogen cyanide	Lungs disorder, harmful to blood vessels.	
5	Ammonia	Burning of the eye, nose, throat and respiratory tract	
6	Hydrogen chloride	Gastritis, bronchitis, dermatitis .Eyes nose irritation	
7	Phosgene	Coughing, burning sensation in the throat and eyes difficulty in breathing nausea and vomiting	
8	Sulfur dioxide	Respiratory tract infection, coughing, asthma.	
9	Formaldehyde	Burning sensation in the eyes, nose, throat, skin irritation	
10	Hydrogen sulfite	Dizziness, Headache, Stomach upset, irritation to eye.	
11	Phenol	Irritation to eyes, nose, throat, skin irritation, muscle ache, skin burn	
12	Hydrogen fluoride	Body pain, eye irritation	
13	Acrylonitrile	Weakness, headache, vomiting, dizziness.	
14	Formaldehyde	Burning of the eye, nose, throat ,coughing and nausea	

4.0 Analytical approach

By using GCMS, pyrolysis gas chromatography/mass spectrometry (PGC/MS), simultaneous thermal analysis (STA), and pyrolysis-combustion flow calorimetry, it is possible to determine the composition of smoke and other fire products (PCFC).[4]
Small amounts of sample are needed for these procedures. By using infrared polarisation spectroscopy, it is possible to monitor the ongoing generation of HCl during combustion tests (IRPS)[4]

These techniques are effective fire-safe material screening tools for recently synthesized materials. They involve injecting a sample to the GC to separate the mixture's components based on several characteristics, such as boiling point and polarity.[4]

Each developed country has its own set of textile fire testing standard methods which together with those defined by other national and international bodies. ASTM E 662, ISO 5959-2, NF-X 70-100 are different methods for determination of smoke/fume toxicity in US, UK, France etc. In India NCD 1409 is mainly used for the determination of fume toxicity using colorimetric gas detection tubes.

5.0 Test Method:-

The toxicity of fumes is only briefly mentioned in a few mandatory standards. These standers do not include any requirements; instead, they examine the product or material based on its fire qualities.[5]

A minimum amount of fabric or test material is burned for the toxicity index test in a volume of air that produces a maximum toxic concentration of each gas developed during burning. The test technique can be used to specify a raw materials or product's quality because a single test is ineffective for determining the overall fire risk of a product under actual fire situation. This test can be used to compare a variety of synthetic and natural materials' specific combustion characteristics.

The toxicity factor of 14 specific (hazardous) gases produced by complete combustion of the substance in air under a predetermined test environment is added up and assessed using the NCD 1409 test technique. These variables are obtained from the calculated amount of each gas that would be produced when 100g of the substance were burned in air in a volume of 1m3, with the concentration of the resulting gas being expressed as a factor of the concentration fatal to man at 30min. exposure time.[5]

For the detection of harmful gas effluents from fires, colorimetric tubes are usually required. Each gas of interest is captured and analyzed using a separate tube. The majority of the tubes are available in a variety of concentration ranges, and the detectable concentration range may sometimes be altered by the quantity of pump strokes used. Colorimetric tubes are simple to use and can deliver reliable results when used with a single known gas.

Colour change and Cf value for the colorimetric gas detection tube are given in Table3 below.

The concentration of measured gases is the only parameter used to calculate the toxicity index. Using the provided formula, the Concentration of each gas produced is determined.

$$C8 = \frac{C \times 100 \times V \quad ppm}{m}$$

Where's C=Conc. of gas in test chamber ()

m=Fire test mass (g)

V = Volume of test chamber (m3)

C8 for all detected gases are used to calculate the Toxicity index.

$$\text{Toxicity Index} = \frac{C_8 1 + C_8 2 + C_8 3 + \text{-----}\ C8n}{Cf_1 + Cf_2 + Cf_3 + \text{-------}\ Cf n}$$

Cf = concentration of gas considered fatal to mass for 30min exposure time (ppm).

Cf values for various gases are given in the standard.[5]

Table 3 - Colour change and Cf value for the colourimetric gas detection tube.[5]

No.	Name of the gas	Colour change	Value of CF
1	Phosgene (COCl2)	White to Red	25
2	Hydrogen Fluoride (HF)	Yellow to Purple	100
3	Hydrogen Chloride (HCl)	Yellow to Pink	500
4	Hydrogen Bromide (HBr),CF=0.8	Yellow to Purple	150
5	Phenol (C6H5OH)	Yellow to Grey	250
6	Sulphur Dioxide (SO2)	Greenish Black to Yellow	400
7	Hydrogen Sulphide (H2S)	White to Brown	750
8	Hydrogen cyanide (HCN)	Yellow to Red	150
9	Acrylonitrile (CH2CHCN)	Yellow to Red	400
10	Formaldehyde(HCHO)	Yellow to Red	500
11	Carbon Monoxide (CO)	White to Brownish Green	4000
12	Carbon Dioxide (CO2) -(%)	Blue to off white	10000
13	Nitrous Fumes (NO+NO3)	White to Yellow	250
14	Ammonia (NH3)	Yellow to Blue	750

6.0 Experimental Data:-

In this paper toxicity studies of PVC coated sheet and the other PU foam, are shown.

6.1.1 In the case of PVC sheet out of 14 hazardous gases as mentioned in the standard, only three gases namely Hydrogen chloride, Carbon monoxide and carbon dioxide are found. The figure 1 shows the colour change in the detection tube.

Table 4 - Toxicity data for the PVC sheet.

No.	Name of the Gas	Concentration of Gas Generated in ppm (Gas Conc-Blank)	Value of C8 = CX100X0.94/MASS	Toxicity Value of Gas C8/Cf
1	Hydrogen Chloride (HCl)	100	2346.94	4.69
2	Carbon Monoxide(CO)	20	469.39	0.117
3	Carbon Dioxide (CO2)	0.7	164286	1.64
Toxicity Index				6.45

6.1.2 When PU foam was burned the gases evolved mainly are hydrogen cyanide, carbon monoxide, carbon dioxide, and nitrogen oxides (NOx).The other gases were not detected. Only the measured gases are used to construct the toxicity index. Results are shown in Table 5; the figure 2 shows the colour change in the detection tube.

Table 5 - Toxicity data for the PU foam.

No.	Name of the Gas	Concentration of Gas Generated in ppm (Gas Conc-Blank)	Value of C8 = CX100X0.94/MASS	Toxicity Value of Gas C8/Cf
1	Hydrogen Cyanide (HCN)	5	111.76	0.745
2	Carbon Monoxide(CO)	5	111.76	0.0279
3	Carbon Dioxide (CO2)	0.5	111766	1.11
4	Nitrous Fumes (NO+NO3)	1	22.35	0.089
Toxicity Index				1.97

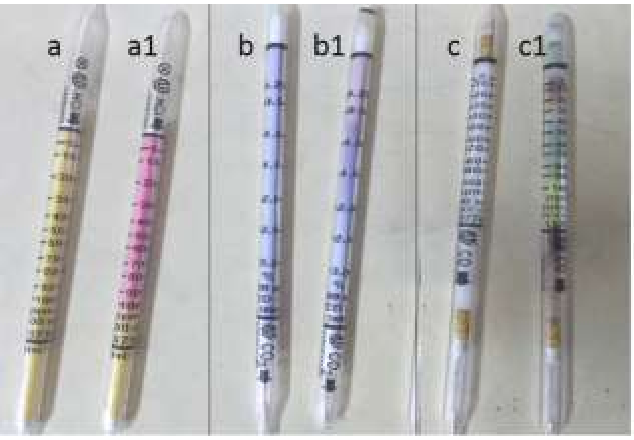

Figure -1:-Change in colour before and after test. Colour change after test is noted by no. 1

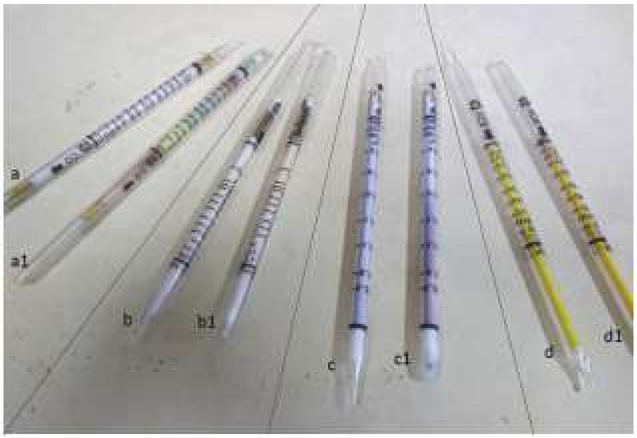

Figure-2:-Change in colour before and after test.

7. Conclusion:

The fume toxicity index value of PVC and PU foam is presented in this study. HCL is found in PVC in the higher concentration, followed by CO and CO2. In case of polyurethane foam in addition to CO and CO2, HCN and NOx (NO+NO2) were also found. For vitiated combustion of N-containing materials, there is often increased generation of HCN and NOx. Toxicity index of 1 is acceptable for a given volume, but in the situations mentioned above, the index value is greater than 1, which is caused by the high concentration of HCl and HCN found in PVC and PU respectively. Isocyanates and halogenated gases primarily arise during the initial stages of the fire and this causes major health hazard to the fire victim.

Therefore, in order to meet the current environmental need, new environmentally friendly flame retardants must be developed in order to replace halogenated ones, isocyanate, and N-containing polymers.

The further toxicity studies on different polymer will be presented in the upcoming paper.

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New Testing Facilities at High Performance Fibre Facility, BTRA, Mumbai

Dynamic Mechanical Analyzer (DMA) and **Thermo-mechanical Analyzer (TMA)** are very sophisticated type of equipments used to study the mechanical/physical/thermal behavior of a wide range of solid materials subjected to various modes. Both of these equipments are now installed in the “High-Performance Fibre Research Laboratory” at The Bombay Textile Research Association (BTRA). The brief introduction and importance of these equipments in material characterization are stated below:

DMA machine:

DMA machine is used to study the visco-elastic behavior of the polymers under the solid state for the determination of Glass transition temperature, Creep resistance behavior, structural integrity at various temperatures, Stress-relaxation, mechanical behavior, Fatigue behavior on a specific temperature and master curve of polymers in very less time than other conventional mechanical characterization machines. DMA measures these responses in the form of complex modulus (E*) (total strength of the material), Storage Modulus (E') (Strength of Elastic region), Loss Modulus (E") (Strength of viscous/rubbery region) and Tan (delta) (ratio of E" to E') which is extremely difficult to measure by conventional mechanical testing machines/ UTM. The DMA machine installed at BTRA has the capability to study the whole visco-elastic region of polymers and makes it a part of essential equipment required for various applications such as:

1. Tg measurement of polymer, especially pressure-sensitive adhesives and sealants under the pre-loaded condition to simulate a real-application environment.
2. Frequency response on glass-transition of polymer-based diaphragms.
3. Effect of Plasticizer and Filler content on polymer property.
4. Polymer blends compatibility.
5. Characterization of virgin polymer (under powder form) for quality control.
6. Characterization of soft materials and foams.
7. Characterization of single fibre as well as bunch of fibres.
8. Creep behavior and Accelerated Creep behavior (Creep TTS) of Polymers to be used in various applications such as Geo-textile grids, packaging films, conveyors etc.
9. Most importantly the material performance and lifetime prediction using the Time-Temperature Superposition principle.
10. And so on……..

TMA Machine:

Similar to DMA, the TMA facility available at High-Performance Fibre Research Laboratory, BTRA is also capable of studying the thermo-mechanical response of the material in the form of dimensional changes at various temperatures. This equipment gives us an understanding of how a material reacts to its environment which is more important from the application point of view. The TMA facility at BTRA can be used for the various measurements of the materials such as:

1. Determination of coefficient of linear expansion of various materials in the various forms (films, solids, fibres, irregular shape solids etc)
2. Shrinkage/Expansion in the films and fibres.
3. Softening of the material
4. Determination of Glass transition temperature
5. Creep behavior of the material.

And so on……..

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