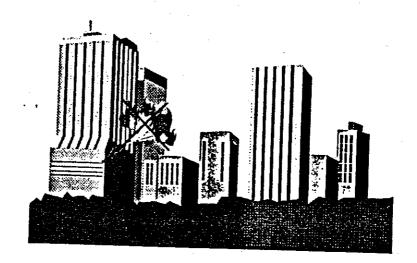
SEMINAR ON

FIRE PROTECTION FOR BUILDINGS & FACTORIES

09.03.1996





ORGANISED BY
THE INSTITUTION OF ENGINEERS (INDIA)
GHAZIABAD, LOCAL CENTRE



उच्चस्तरीय दूरसंचार प्रशिक्षण केन्द्र गाजियाबाद - २०१००१ ADVANCED LEVEL TELECOM. TRAINING CENTRE, GHAZIABAD- 201001.

POLYMERS IN BUILDINGS-FIRE HAZARDS AND THEIR MITIGATION

ABSTRACT

Polymers have entered the building industry in a big way. The various advantages they offer, can not be negated. However, being organic in nature, they are likely to catch fire. The main hazards associated with polymers during fire are flammability and smoke generation which are the main causes of fatal injury. Flame retardancy has been the area of interest since the 18th century, however smoke suppression has received attention recently. During the last three decades much work has been done in this area. Some of the important smoke suppression techniques are discussed in the present communication.

INTRODUCTION

Polymeric materials have, to some extent been able to bridge the widening gap between the demand and supply of building materials required to meet the need of millions of houses today. While the availability of conventional building materials continues to be scares, the annual world production of plastics has increased exponentially. During the last three decades, use of plastics in buildings has increased steadily mainly because of practicity, comfort, convenience and energy saving. Plastics are valueable, often indispensable, auxiliaries to other materials, verstile materials for non structural applications and can make possible new and ingenious structural and non structural forms when employed as composites. In buildings they are being used for, almost every application viz. roofing, flooring, doors, furnitures, insulation, domestic appliances and objects of utilitarian or decorative values etc. The various desirable properties of polymeric materials such as non-toxic, non-irritant, economical, easy processibility and little change in chemical and physical properties over their useful lives, have made them increasingly valuable to the construction. engineering and furniture industries. However, their use in buildings is always overshadowed by the possible hazards in the event of fire. Smoke from polymers is considered to be their main drawback in general accaptance as building materials.

CLASSIFICATION OF PLASTICS

Plastics are actually synthetic polymeric materials with additives such as plasticizers, fillers etc. They are generally categorised in two classes- thermoplastics and thermosets. Thermoplastics, on exposure to heat, soften or melt and start to flow generating the phenomenon called dripping, whereas thermosets tend to cure further due to their 3-D crosslinked molecular structure. Flowing and dripping of thermoplastics comes handy as these properties may prevent ignition by subtracting themselves from the ignition source before catching fire.

The most commonly used thermoplastics in buildings are vinyl polymers (PVC, PVDC), styrene polymers (PS, ABS), polyolefins (PE, PP), polyacrylates (PMMA) and polycarbonates. Among thermosets, unsaturated polyester is by far the

most common material in buildings while phenolic, urea and melamine are largely used as auxiliaries in resin bonded wood (particle board, plywood, laminated timber) and fiber panels for thermal insulation apart from their use in decorative laminates. Epoxies and polyurethane foams are also known to find use in buildings. From fire protection point of view two additional classifications of plastics are desirable. They refer to the 'low density' and the 'high density' plastics. Low density plastics refer to foams or cellular polymers.

HAZARD CLASSIFICATION OF POLYMERIC MATERIALS

Of the two types of polymers, the thermoplastics deserve particular attention, for their characteristics and for their actual and potential applications, from fire safety view point. As a matter of fact thermosets do not find difficulty in meeting fire protection requirements. In fact some of them such as melamine are even added to other plastics as flame retardant additives.

The low density foams are of considerable concern to fire protection as they are used extensively throughout the construction industry, primarily for insulation but also used in furniture in the form of upholstery materials. They constitute the most hazardous class of polymeric materials and in large quantities should be used with caution because of their flammability and low melting point. Foam plastics are sold as preformed blocks or panels or in the case of polyurethane, may also be sprayed or formed in-situ. Fire performance of rigid foams of expanded polystyrene. polyurethane and phenolic resins can however be improved by bonding them to non flammable supports. High density polystyrene and acrylonitrile butadiene styrene degrades under fire conditions resulting in monomers i.e. styrene, having a low flash point (900F). Thus exhibiting fire characteristics similar to flammable liquids and have a heat release rate of approximately twice that of ordinary CLASS A combustible materials and constitute the next or the second hazard class of polymers. The third level hazad classification includes Polyethylene. Polypropylene and similar synthetic resins of flammability lesser than Polystyrene. The fourth class includes Poly Vinylchloride (depending upon the nature of additives in the form of fillers and plasticizers etc.) and various thermosetting plastics such as Nylon [1].

POLYMER COMBUSTION PROCESS

The three stages necessary to initiate the combustion process in plastics are: heating, decomposition and ignition of the polymer. The solid plastics tend to soften or melt and start flowing when heated by an external heat source, initiating decomposition of the polymer into volatile organic fragments. Decomposition is an exothermic process requiring sufficient energy to overcome the bond energy between individual atoms and to provide any necessary activation energy. The flammable gases formed during pyrolysis mix with atmospheric oxygen to result in ignition. Heat from these exothermic radiations is radiated back to the polymer surface to increase the temperature of the pyrolysis zone, resulting in an increase in decomposition and production of combustible organic fuel.

The different stages involved in polymer decomposition and combustion are shown [2] in Figure 1. In presence of sufficiently intense heat a polymer will pyrolyse

breaking down to low molecular weight species. These species, in the dispersed phase, comprise smoke in the absence of flame. At high heating rates and with ignition, these low molecular weight species fuel the polymer flame. In the absence of sufficient oxygen, solid smoke constituents are formed at higher temperatures particularly in the form of soot in the flame zone. One of the best known path of soot formation from polymers is as follows [3]:

heat

- a) Polymer → Pyrolysate mixture (fuels) (including liquid smoke components)
- b) aliphatic fuel \rightarrow radicals \rightarrow C₁.C₂ species \rightarrow conjugated polyenes \downarrow aromatic fuel \rightarrow aromatic radicals \rightarrow SOOT (including polybenzoids)

HAZARDS FROM SMOKE

Polymers are inherently combustible, being organic in nature. A Large number of flame retardant compositions reported in the literature [4,5] are known to result in a consequential increase in smoke generation. More than half the deaths attributed to fire are caused by smoke rather than heat or actual burning. Therefore, plastics are rightly blamed in fire accidents both for obscuration and toxicity resulting from the combustion products. More than half the deaths attributed to fire are caused by smoke rather than heat or actual burning. It has been observed that smoke damage often sharply increases the total property damage resulting from fires. Smoke from fires has been found to be hazardous due to the following aspects:

- 1. They are irritating to eyes and respiratory system.
- 2. If dense, smoke impede escape from fire and hinders the efforts of fire fighters and rescue personals.
- 3. Smoke is toxic either directly (by virtue of the products of combustion) or indirectly (because of oxygen depletion).
- 4. Smoke may engender panic in escape.
- 5. Certain constituents of smoke e.g. acid gases can be detrimental to property.

Thus it becomes important to study the intensity and rate of development of visible smoke which is an important factor in assessing fire survivability.

SMOKE MEASUREMENT

Smoke generation from the burning of materials pose danger to human life, particularly in the initial phases of a fire, due to the loss of orientation caused by sight obscuration. This can lead to panic and irrational behaviour which makes the escape as well as fire fighting difficult, often with fatal results. It is therefore essential to assess the smoke generation propensity of material prior to their use in buildings. Detection and control of smoke have attained high priority in view of the phenomenal increase in the use of plastics, leading to the accentuation of the problem of smoke in fires. Methods for the measurement of visible smoke from various materials have been reviewed by many authors [5-7]. These include methods based on mechanical, electrical and optical techniques. The most frequently used tests, however, are based on optical methods, i.e. on the principle of attenuation of light beam by smoke particles.

The degree of attenuation of light due to smoke depends largely upon the number and size of smoke particles and the length of light path. It also depends upon other parameters such as the extent of ventilation in test chamber, refractive index of gases, ignition source, size and conditioning of the samples, temperature etc. In practice this complex phenomenon is simplified by assuming the particles to be of uniform size, using a monochromatic light and combining both absorption and scattering in an empirical extinction coefficient, sigma (σ), based on the Beer-Lambert Law:

$$I = I_0 e^{-\sigma X}$$

where I is the intensity of light attenuated by the smoke layer: I_0 , the intensity of light at source: is the attenuation coefficient, and x is the path length through smoke

or
$$D = log_{10} I_0 / I = \sigma x / 2.303$$

where D is the optical density, a measure of smoke concentration.

Some of the widely used methods for smoke measurement are given in Table 1. Optical methods of smoke measurement can be grouped as the static (accumulative) and the dynamic (flow) methods. Most of the smoke measurement equipments are based on optics and use incandescent lamp as a light source, which gives polychromatic light. Beer- Lambert law being valid only for monochromatic light, the error introduced in smoke measurement could be up to 25%, if a non monochromatic light is used [10]. Studies have been reported where He-Ne laser has been used along with white light in NBS smoke chamber as well as in dynamic systems [11,12].

Table 1 Methods Of Smoke Measurement

Method	Туре	Smoke Measure ment	Energy input		ation of Light source	Reference

NBS Smoke Chamber	S	P	R+F	V/H	V	ASTM E 662
Rohm And Hass Smoke Chamber	S	P	F	Н	Н	BS 5111 Pt 1 ASTM D 2843
Steiner Tunnel	D	P	F	Н	Н	ASTM E 84
Radiant Panel Tes	t -	G	R+F	30 ⁰	•	ASTM E 162
Araphoe Smoke B	Sox -	Ğ	F	+	•	ASTM D 4100
Michigen Test	D	Р	F	V	Н	[2]
British Building N Fire Propagatio)	faterial S [#]	P	R-F	V	Н	[8] and BS 476 pt 6
CURRENT METH	HODS				-	
ISO Single	ş.		•			,
Chamber	S	P	R+F	Н	V	ISO/DIS 5659
ISO Dual Chambe	er S	P	R+F	Н	V	ISO/DIS 5924
OSU-RHR	D	P	R+F	, V .	Н	ASTM E 906
Cone Calorimeter	D	Ļ	R	V/H	Н	ASTM E 1354
Fumenometer	D	P	R	H*	Н	[9]

S = Static, $S^* = Smoke$ collected in a sperate chamber

D = Dynamic

P = Photometric System (Tungsten Filament Lamp)

L = He - Ne Laser

G = Gravimetric

F = Pilot flame

R = Irradiance

H = Horizontal, H* = Specimen in poweder form

V = Vertical

+ = With or without

Several factors are important in assessing smoke propensity of materials. The present trend, therefore is to measure smoke from materials at different stages of its preparation e.g. raw materials, products, components/structural units [13].

SMOKE SUPPRESSION FROM POLYMERIC MATERIALS

It is evident from the literature [14,15] that plastics tend to give more smoke than wood, especially under flaming conditions. Contrary to the thermoplastics, thermosets with the exception of unsaturated polyester resin crosslinked with polystyrene emit minimal amount of smoke due to their tendency to form char. However, the smoke generation tendency of polymers can be effectively reduced by addition of certain smoke retardants when required.

The interest in smoke generation tendencies and the potential for related standards have simulated the industry to seek methods for reducing smoke output from those products which may become involved in fire. The combustion of polymers involve a variety of processes occuring in several phases. Thus, polymers should lend themselves, atleast in principle, to varied smoke suppressant treatments. Much of polymer smoke inhibitor technology has been reviewed [5,16]. For a given smoke suppressant to be effective, simultaneous contribution of any number of processes in both the dispersed phase and condensed phase are possible.

Since selection of an alternate polymer to suit the requirements of flame retardance and smoke suppression is not always desirable, the use of smoke suppressants is a viable solution of achieving this goal. Smoke suppressants can broadly be classified into four groups: Fillers, Additives, Surface treatments and polymer modifications as shown in Table 2.

Fillers are non polymeric compounding ingredients used at concentrations greater than about 20 % of the polymer mass. They serve to reduce the amount of smoke generated from a polymer mass by diluting the amount of combustible substrate and by absorbing heat to reduce the mass burning rate. The fillers which absorb relatively more heat per unit weight through endo thermal processes such as dehydration or calcination are referred to as active fillers. They also release gases such as carbon dioxide, ammonia and water vapours which dilute the fuel mixture and intervene in the flame process. The physical properties of polymers can however, be affected adversely by the large amount of fillers required to achieve the desired properties.

Additives, on the other hand, are generally used below 20 % of polymer mass. Metal compounds are by far the most widely used additives for smoke suppression in polymers, transition metal complexes have been found to reduce smoke generation by 60-86% in plasticized PVC [17,18] when used upto 3 phr (parts per hundred parts of resin).

Carboxylic acids, aldehydes, alcohols and sulfur have been reported effective as flame retardant smoke suppressant (FRSS) when used in polyurethane and polyisocyanurate foams.

Smoke Suppressants	Loading*	Examples
Fillers	> 20 phr	
Inert Fillers		Silica, Asbestos, Clay
Active Fillers		Aluminium trihydrate, Magnesium hydroxide
Additives	< 20 phr	
Metal containing additives		Antimony compounds e.g. Sb ₂ O ₃ Iron Compounds e.g. Ferrocene Molybdenum Compds. e.g. MoO ₃ Zinc Compounds eg ZnO Mixed metal compounds e.g. Zinc molybdate
Carboxylic acids	-	Fumaric acid
Aldehydes	about 10%	Benzaldehyde
Alcohols	about 10%	Furfury lalcohol
Fluoroborates	• .	Ammonium Fluoroborate
Sulfur	3- 20 %	Elemental Sulfur
Surface Treatment	N.A.	Intumescent Paint,
Polymer Modification	N.A.	Electroless plating
Clean Burning Pyrolyzates		Copolymerisation, Crosslinking
Increased Thermal Stability		Use of Polyisocyanurate based foam in polyimides
Increased Char Formation		Post chlorination of PVC

^{*} Quantity added to the polymer per parts per hundred parts of polymer N.A. Not applicable

Only a few examples or claims of surface treatment for reducing smoke are known. A prime example is intumescent paint which chars and expands upon exposure to heat, forming a layer which insulates the polymer surface below. Another example is electroless plating of polyblends with metals such as Ni, Cu or Cr [19]. Use of 'flame barrier' interliner to an otherwise flammable, smoking polymeric article e.g. PU foam cushion is also known. Examples of such materials are: Du Pont's Vonar interliner, Kimbar - a flame retardant nonwoven fabric of Kimberley Clark Co. and Fire blocking Layer- a treated cloth developed by CBRI.

The main purpose of polymer modification is to generate clean burning pyrolyzates, increase thermal stability of the polymer and enhance its char forming capacity, so as to achieve the end result of FRSS polymer.

The most desirable of these apporaches would appear to be those which minimize the generation of combustible species. This not only contributes to the reduction of visible smoke but also tends to reduce flammability and limit the volume of combustion products formed, thereby mitigating the fire hazards from polymers.

CONCLUSION

Polymers offer very attractive and innovative applications in buildings. They are inherently combustible and thus pose hazards when used in buildings. The fire and smoke hazards can however be overcome with suitable treatments without compromising with the advantages offered by polymers.

REFERENCES

- Robert G.Planer, Ed. "Fire Loss Control- A management Guide", Chapter 4, pp 48-99, Marcel Decker Inc., New York, 1979.
- 2 M.M.Hirschler, Soot from Fires: I Mechanisms of Soot Formation, J. Fire and Flammability 3, 380-414, 1985.
- A.M.Calcraft, R.J.S.Green and T.S.Mc Roberts, Burning of Plastics: Part I Smoke Formation, Plast. Polym. 42, 200, 1974.
- 4 C.F.Cullis and M.M.Hirschler, 'The Combustion of Organic Polymers'. The Oxford University Press, Oxford, 1981.
- 5 D.F.Lawson in "Flame Retardant Polymeric Materials", Vol 3, eds by M.Lewin, M.Atlas and E.M.Pearce. pp 39-95, Plenum Press, New York, 1982.
- J. Troitzsch, International Plastics Flammability Handbook, Chapter 9, pp 385-418, Hanser, Munich, 1983.
- 7 U.Flisi, Proceedings of the Third Meeting on Fire Retardant Polymers. Associazione Italiana di Scienza e Technologia Delle Macromolecole, Torino, Italy, 220-237, 21-22 Sept 1988.

- J.Dipietro and H.Stepniczka, A study of Smoke Density and Oxygen Index of Polystyrene, ABS and Polyester Systems, J Fire and Flammability, 2(2), 36-53, 1971.
- A.Jouandean, C.Colas, J.P.Desjardin, Measurement of Smoke Potential with the Furnenometer, Private Publication of Prodemat, France, 1991.
- G.W.Mulholland, How Well are We Measuring Smoke?, Fire and Materials, 6(2), 65-67, 1982.
- B.A.L.Ostman and L.D.Tsantaridis, Smoke Production in The Cone Calorimeter and the Room Fire Test, Fire Safety J 17(1), 27-43, 1991.
- V.Babrauskas, Development of the Cone Calorimeter A Bench Scale Heat
 Release Rate Apparatus Based on Oxygen Consumption (NBSIR 82- 2611)
 {US} Nat. Bur. Stand., 1982.
- Sunil K. Sharma, Measurement of Smoke from Fires: The Present Trend. J. Scientific and Industrial Research, 54(2), 98-107, 1995.
- U.Filisi in Fire in Buildings Ed. R.Mourarean and M.Thomas, pp 326-336, Elsevier Applied Science Publishers, UK, 1985.
- Subodh Kumar Bhatnagar, Sunil K.Sharma and Naurang Lal Yadav, Selection of Plastics for Buildings- A Fire Safety Point of View, in Proceedings of National Workshop on Plastics & Polymers in Buildings and Building Material Technologies and Pollution Abatement, pp 4.4.4-4.2.15, March 1987.
- Sunil K.Sharma and S.K.Srivastava, Smoke Suppression in Poly (vinylchloride), Fire Safety Science, 4(2), 38-51, 1995.
- 17 Sunil K.Sharma, Indian Patent (provisional) 1244/DEL/95. 1995
- Sunil K. Sharma and S.K.Srivastava, Tris (2,4 Pentanediono) Chromiun III A Fire Retardant Smoke Suppressant for Plasticized Poly (vinylchloride), J. Polymer Materials, 10, 145-154, 1993.
- 19 F.J.O'Neill, US Pat. 4005241 (1975) to Monsanto Co.

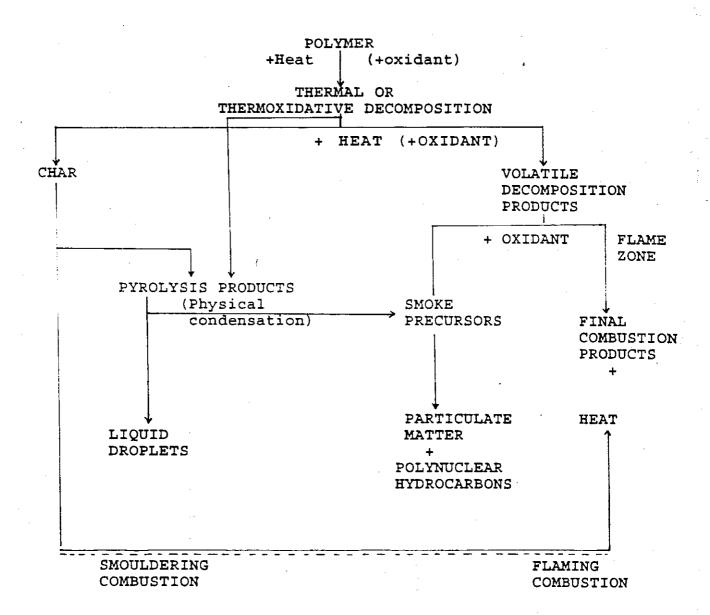


FIGURE 1 . DIFFERENT STAGES INVOLVED IN POLYMER DECOMPOSITION AND COMBUSTION