
NEW TECHNIQUES FOR THE STUDY OF FIRE BEHAVIOUR OF FLAME RETARDANT SMOKE SUPPRESSANT POLYMERIC MATERIALS

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Abstract

Study of fire behaviour of materials is an important aspect in their selection for use in buildings. This becomes all the more significant where polymeric materials are concerned. Since polymers are inherently combustible materials and generation of smoke is their main fire hazard, use of Flame Retardant Smoke Suppressant (FRSS) is the desirable option. However, FRSS modified polymers can not be assessed for their fire behaviour using conventional fire test methods. This is basically because of the fact that the experimental conditions of these methods are not rigorous enough. Two new techniques, which are specifically suited to the study of fire behaviour of FRSS modified polymeric materials are discussed in the present communication.

INTRODUCTION

Plastics, as the synthetic polymers are generally referred to, touch every facet of our life. They have permeated all spheres of human activity. Their unique, versatile and wide ranging properties make plastics the most economically viable material for use in: agriculture, building and construction, communication, defence and aerospace, education, entertainment, consumer durable, medicare and transportation etc.

However, since plastics are organic in nature they are inherently combustible. On burning, plastics produce copious amount of smoke in addition to heat and other combustion gases. This inherent property results in their hesitant acceptance by the common man. Of late the use of flame retardant compositions, to improve the fire performance of these materials, has become a general practice.

Study of fire behaviour of materials is an important aspect in their selection for use in buildings. A large number of National and International standard methods are available for this purpose. New fire test methods are, however,

being developed in order to determine the fire behaviour of materials in more elaborate way than by the present fire test methods. The new tests are both of the small and large scale. While the small scale tests are necessary as practical tools the full scale tests are generally used to validate the results of small scale tests. Two new techniques for the study of fire behaviour of polymeric materials are discussed in the present communication. These are especially suitable for FRSS materials.

POLYMER COMBUSTION

When a polymer encounters external heating or burning conditions, it first melts and then starts flowing, this is followed by decomposition into volatile organic fragments. These are then mixed with air and combustion takes place. For continuity of the pyrolysis it is essential that the heat produced by flames is transferred to the surface of the polymer. The volatile products diffuse into the flame zone introducing a radical chain process. In presence of sufficiently intense heat a polymer will pyrolyse breaking down to low molecular weight species which comprise smoke in the absence of flame. At higher heating rates and with ignition, these species fuel the polymer flame.

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SMOKE

Smoke poses a danger to human life, particularly in the initial phase of a fire, due to reduction in visibility. This can lead to panic and irrational behavior which makes escape difficult leading to increased number of fatal casualties.

Considerable amount of carbon may be formed during the combustion, some of which is deposited in combustion region as char while the rest is released as finely divided particles i.e. soot [1]. In the absence of sufficient oxygen, solid fuel constituents are formed at higher temperatures particularly in the form of soot in the flame zone. Soot forms a significant proportion of smoke. Since soot is derived from the volatile decomposition products of polymers, the chemical structure of polymer is an important parameter in determining the relative amount of soot produced by different polymers under similar conditions of exposure. Aromatic hydrocarbons lead to the formation of greater amount of smoke as compared to the aliphatic hydrocarbons. Polyacetylenes dominate among the combustion products of aliphatics while polycyclics are found in large quantity in case of aromatic compounds.

While smoke poses hazards to life, char is free from these, thus a potential method of decreasing soot formation is generation of additional char.

SMOKE SUPPRESSION

There are essentially two ways in which we may deal with the problem of smoke from polymers. The first is to select materials which generate low quantity of smoke and the second is to modify those that do. The first approach is not suitable in most applications because of the many advantageous properties of the selected polymer. The second approach is possible through use of different chemical compositions.

Polymer combustion involves thermal degradation of the solid matrix to gaseous and liquid components. The gaseous components include combustion gases and smoke. The zone corresponding to the formation of volatile decomposition products from the semi

decomposed substrate is the interphase and it is here where most of the initial reactions take place, particularly the action of additives such as flame retardants and smoke suppressants. Several flame retardant chemicals, when used to modify polymers, are known to increase the amount of smoke and toxic gases generated by them [2-3]. Flame retardance at the cost of increased smoke generation is not desirable. To achieve an overall improvement in the fire performance, use of flame retardant smoke suppressants (FRSS) followed by fire performance evaluation of the modified polymers is an obvious consequence.

STUDIES ON FIRE BEHAVIOR OF FRSS MODIFIED POLYMERS**Flammability**

As is evident from the term 'FRSS' the modified polymers are easily ignitable. However the problem arises when they are subjected to the normal tests for burning behaviour of materials since their fire behaviour can not be differentiated from one another. Therefore flammability of such polymers is normally studied by the Limiting Oxygen Index Method (ASTM D 2863).

Limiting Oxygen Index

(LOI) method, employs a flammability unit to study the flammability behavior of specimens. LOI is defined as the minimum concentration of oxygen expressed as volume percent in a flowing mixture of oxygen and nitrogen that will just support the flaming combustion. The equilibrium is established by the relation between the heat generated from combustion of the specimen and the heat lost to the surroundings as measured by one or the other of the two arbitrary criteria, namely three minutes of sustained burning or 100 mm length of specimen burnt. In order to establish the LOI (or Oxygen Index) this value is approached from both sides of the critical oxygen concentration. The oxygen index 'n' is defined as

$$n = \frac{100 \times O_2}{N_2 + O_2} \quad [1]$$

Where N_2 = Volume concentration of nitrogen,
and

O_2 = Volume concentration of oxygen.

Though in real situations oxygen levels higher than the atmospheric (21%) are not achievable, the significance of higher LOI values lies in the fact that it indicates the extent of flame retardance acquired by the treated polymer. Materials with LOI greater than 30 are considered flame retardant.

DYNAMIC METHOD FOR SMOKE MEASUREMENT - A NEW TECHNIQUE

Methods for measurement of visible smoke from different materials are based on mechanical, electrical and optical techniques. Optical methods are the one most frequently used. In these the smoke measurements are based on Beer-Lambert Law which has 'Attenuation Of Light Beam By Smoke Particles' as the underlying principle. Measurement of smoke generated by a material may be carried out either by Static Method i.e. accumulation of smoke in a closed chamber, or by allowing it to flow through a duct i.e. Dynamic Method.

Dynamic Method

Conventionally an accumulative type of method is used (ASTM E 662, NFPA 258-T-34, BS 6401 and ISO DIS 5924) for study of smoke generation from a material. However, since the smoke generated in a small interval of time is added to the smoke already accumulated in the chamber, the method has an inherent problem of lower sensitivity to variation in smoke evolution rate. Also, since the Beers Lambert law is only valid for monochromatic light, a 'dynamic' method using He-Ne Laser as the light source was specifically developed for measurement of smoke generated from FRSS modified polymers [4]. Since the FRSS modified polymers can not be ignited under the conditions of exposure specified in the conventional methods, the apparatus employed an enriched oxygen atmosphere.

Specimen Ignition Specimens are ignited and burnt in an Oxygen enriched atmosphere

using the flammability unit FTA/HFTA of Stanton Redcroft UK. The system is versatile in the sense that flow rate, oxygen concentration as well as the temperature of the environment surrounding the specimen can be varied over wide ranges - Oxygen concentration from 0 to 100% , temperature from ambient to 400°C and flow rate from 0 to 25 l min⁻¹ . At the top of the glass chimney of flammability unit a 100 mm diameter duct is mounted with a 300 mm hood at the inlet side so that no smoke issuing out from the specimen is lost. The other end of the duct has an exhaust fan attached to it which is used to maintain the desired flow rate (Figure 1).

Light Source A 2 mW randomly polarised He-Ne laser (Aerotech) is used in the apparatus. The light beam is passed through the duct at about 300 mm from the top of the hood. Laser beam intensity is monitored by the matching Radiometer (Silicon diode photo-detector) - Aerotech Model 71 and laser power displayed on a digital panel meter. The radiometer also has an analogue output for recording. On the two sides of the vertical section of the duct, i.e. at the entry and the exit ports for laser beam, windows with glass plate are provided which can be removed for cleaning any soot deposition (Figure 2).

Experimental Procedure Samples are clamped in the sample holder and mounted inside the glass chimney. The atmosphere inside the chimney is controlled for a desired Oxygen : Nitrogen ratio. The entire top of the sample is ignited with the ignition flame so that the specimen is well lighted. Resulting smoke is allowed to flow through the duct where a suction velocity of 0.5 m s⁻¹ is created. Smoke will attenuate the laser beam and density is indicated by a decrease in radiometer output. Optical density (OD) profiles are recorded in terms of percentage light transmission (T%) Vs. time.

Estimation of Smoke Yield For an optical density (OD) profile , the time integral of $D(t)dt$

gives an index or measure of the total particulate production ie smoke index from the sample. But estimate of total smoke will also depend on the volumetric flow rate (V) of purging air/gas and must be accounted for in the time integral. Therefore smoke yield or smoke index (S) is given by :

$$S = \int_0^T V D(t)dt \quad [2]$$

where T is the time for which the sample burns.

As V is constant, comparison of smoke index obtained from two OD profiles can readily be done by equation:

$$\frac{S_1}{S_2} = \frac{\int_0^{T_1} D_1(t)dt}{\int_0^{T_2} D_2(t)dt} \quad [3]$$

Where S_1 and S_2 are the amount of smoke generated, D_1 and D_2 are OD profile and T_1 and T_2 are the time of burning of samples 1 and 2 respectively. Integrals on the right hand side can be evaluated by measuring the area under the OD profile with the help of a planimeter or by using a recorder with an integrator.

Since the high frequency fluctuations present in OD profile cause the main difficulty in evaluation of the integrals of OD, an integrator formed by resistor and capacitor was connected to analogue output of the photodetector to suppress these high frequency variations [4].

Determination of Smoke Suppression Index (SSI)

Keeping the volumetric flow constant, a comparison of the amount of smoke generated from the two samples can be made by equation 3. Hence the whole problem of comparing the two

smoke suppressing formulations or comparing treated and untreated samples is reduced to evaluation and comparison of time integrals of their optical density (i.e. area under their OD profiles) generated under similar flow conditions. This approach is followed in the experiments on evaluation of effectiveness of smoke suppressant.

When smoke suppressant systems are used, their efficacy - the Smoke Suppression Index (SSI) - can thus be calculated by equation 4

$$SSI = \frac{S - S_1}{S} \times 100 \quad [4]$$

Where S = area under the OD profile of untreated sample, and

S_1 = area under the OD profile of treated sample.

In case where the initial weight and/or the weight loss for each sample may not be identical, A and A_1 may be used in place of S and S_1 . The equation 4 now becomes

$$SSI = \frac{A - A_1}{A} \times 100 \quad [5]$$

Where A = Area under OD profile of untreated sample/ weight loss of the sample, and

A_1 = Area under OD profile of treated sample / weight loss of the sample.

Positive values of SSI (i.e. $S > S_1$) indicate reduction in amount of smoke generated whereas a negative value represents an increment.

STUDY OF FRSS BEHAVIOUR USING CHAR MORPHOLOGY - A NEW TECHNIQUE

Though the effect of FRSS complexes on fire behaviour of polymeric materials is normally studied by different standard fire test methods, indirect methods such as thermal analysis are also used as supporting tool to understand the behaviour of FRSS modified polymers. We have made a pioneering attempt of using a scanning electron microscope as a supporting tool to this effect [5].

Electron microscopic techniques have earlier been used for studies on dispersion of additives in the polymer matrix [6] as well as their effect on soot formation from polymers [7]. However little work has been reported on correlation of char morphology with FRSS characteristics of polymers. In the present communication an attempt made to correlate the FRSS characteristic of plasticized PVC with the morphology of its char has been described.

The final residue left after degradation of a polymer is very rich in carbon having the character of metallurgical coke in some cases e.g. PVC. However when compared to coke, the char residue has a higher bulk density often being very cohesive and rigid. Char from rigid PVCs has been reported to be swollen, rigid and brittle with numerous pores having a honeycombed appearance while that from the plasticized PVCs is vitreous, when observed through an optical microscope [8]. The motivation for undertaking such type of investigation was the nature of the char obtained during the combustion studies of FRSS modified polymers, which differed with the type of complexes (additives) added.

Technique and Sample Preparation The solid phase residue (char) left after the combustion of the samples was studied with the help of a Scanning Electron Microscope (SEM). In SEM studies an electron beam is made to impinge upon a specimen surface and the reflected 'electron signals' are amplified and analyzed mainly to ascertain surface topographical details. It is possible to do so mainly due to the large depth of focus inherent to this technique. A 'Phillips 501' scanning electron microscope was used for the original studies which were carried out at an operating voltage of 15 KV [5].

Initially the specimens of PVC are burnt and the 'solid residue' i.e. the char collected for SEM studies. The samples are dried for 24 hrs at 100±5°C and sealed in 'labeled' air tight specimen bottles. The sample holders of SEM are first coated with an adhesive tape on which

small amount of the char sample is spread. These are then coated (shadowed) with gold dust to make them conducting and thus suitable for the study.

Burning Process in context of Char Morphology

Promotion of carbonisation i.e. char formation which preserves the structural integration (matrix retention) of the polymer, is one of the most efficient method of reducing the flammability of a polymer. In order to understand the SEM micrographs it would be necessary to understand the process(es) responsible for polymer degradation when subjected to fire conditions. The net process(es) of burning may be summed up as comprising the following steps:

melting resulting in matrix retention

inhibited burning resulting in matrix retention along with formation of char, soot, smoke and other combustion products

burning resulting in little char and ash formation.

It will also not be out of place to recapitulate that carbon can be formed in essentially two ways from an organic polymer: (a) by the stripping off, in the condensed phase, of most or all non carbonaceous material from the polymer leaving solid char residue, or (b) by chain scission reaction in the condensed phase, leading to the formation of volatile low molecular weight compounds which can then undergo dehydrochlorination reaction via polyacetylenes or polynuclear aromatic hydrocarbons in gas phase to produce soot. Promotion of carbonisation i.e. char formation which preserves the structural integrity (matrix retention) of the polymer, is one of the most efficient method of reducing the flammability of a polymer. The enhancement of char formation from polymer may also be associated with a decrease in smoke production; as is observed when the polymer is modified by additives. In other words, metal based organic (MBOs) complexes produce carbon by promoting chain stripping. If smoke production increases from the

polymeric system (PVC) containing a metal based organic compound, its action is to enhance chain scission reaction at the expense of chain stripping. Some of the representative results are reported in the form of SEM micrographs. On the basis of the extent of burning or smoke formation these may broadly be classified in to four types of micrographs namely: Matrix retention, Char formation, Honeycombing and Ash (Figure 3). These four types can be defined as:

Matrix retention represents melting or inhibited burning i.e. flame retardance.

Char formation without ash patches represents flame retardance of second level i.e. not as efficient as in case of matrix retention.

Honeycombing represents smoldering condition which may represent combustion of char leading to the evolution of CO, CO₂ and than ash formation.

Ash Formation represents total burning or no flame retardance. It may also represent smoke suppression by MBOs via incandescence if other supporting observations are there.

Excellent correlations between char morphology and the FRSS behaviour of the additives could be arrived at. Some of the general conclusions for an additive to act as a flame retardant and the preferred SEM observations on the char are:

MR > MR + C (D) > MR + C (P) > ONLY C

Where MR = matrix retention

C = Char formation

D = dense (char)

P = Porous (char)

A = Ash

and H = Honeycomb formation,

The sole residue as carbon (only C) has little significance as it represents total loss of material.

For an additive to act as a smoke suppressant the preferred SEM observations on char are

MR > MR + C (D) > MR + A > A

The last option namely, ash formation represents the worst case. However if 'Honeycombing' is observed then the preferred observations should be

MR > MR + C (D) > MR H > MR + A > A

The results are not conclusive so far. Further work is in progress. However, one thing is clear that char morphology can be used as a supporting tool to study the mechanism of FRSS complexes.

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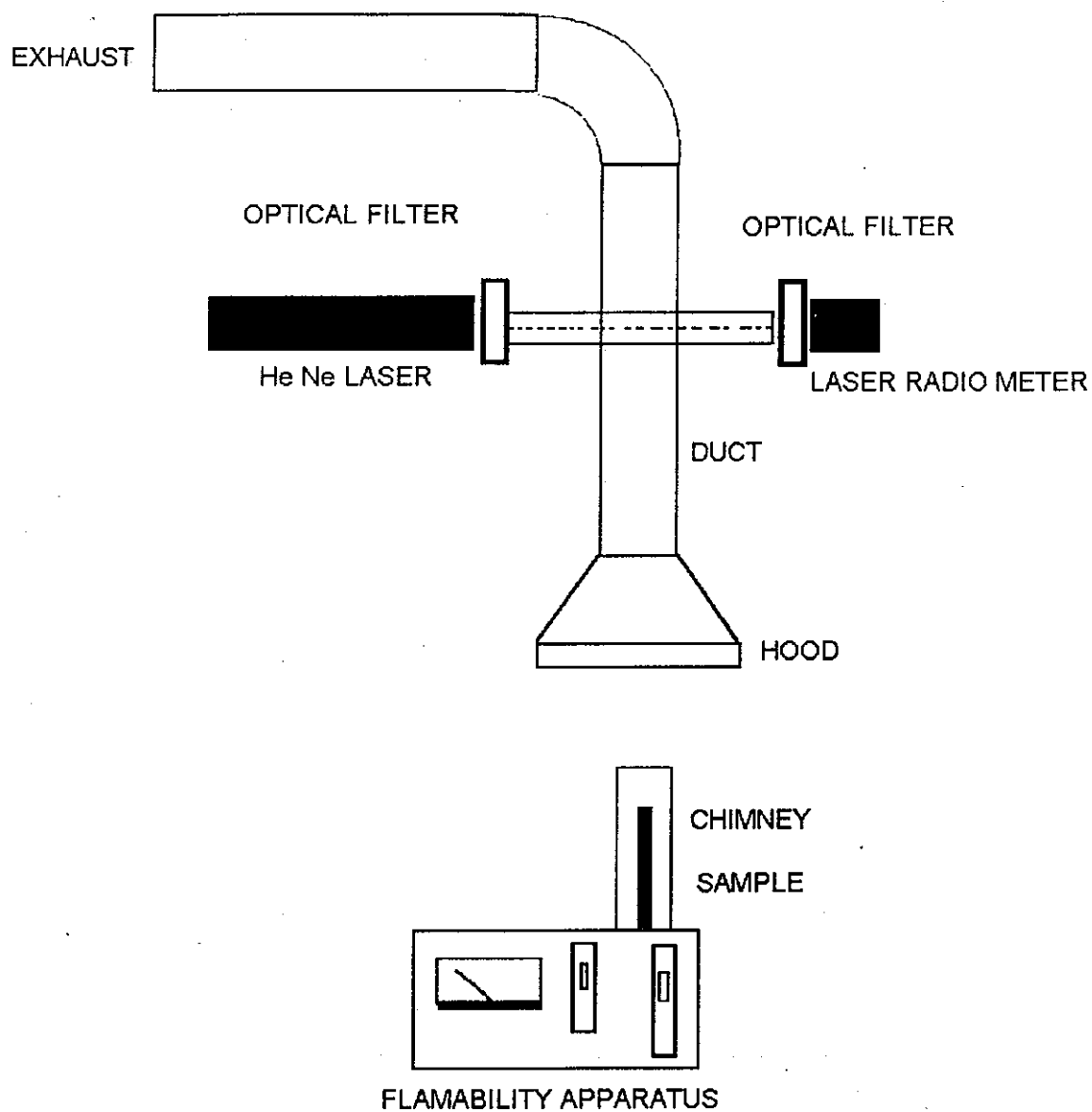


FIGURE 1 SCHEMATIC DIAGRAM OF APPARATUS FOR SMOKE MEASUREMENT

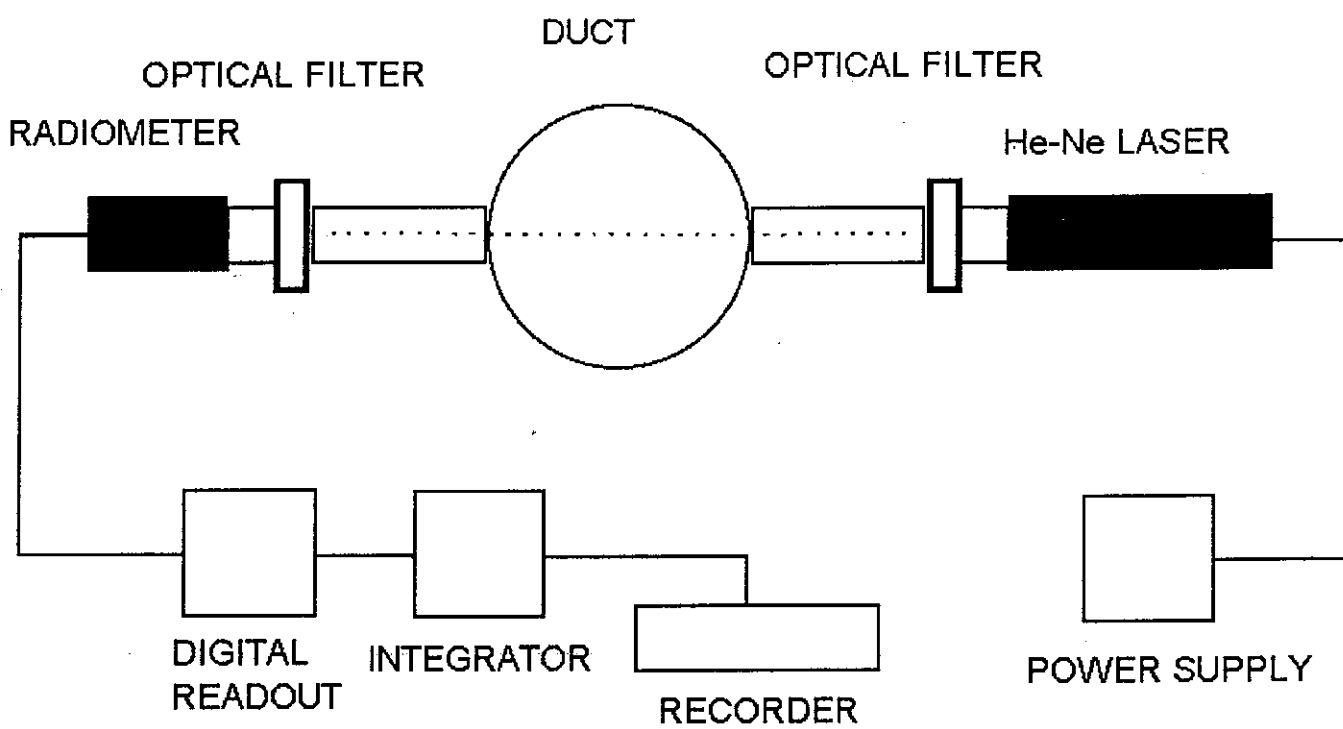
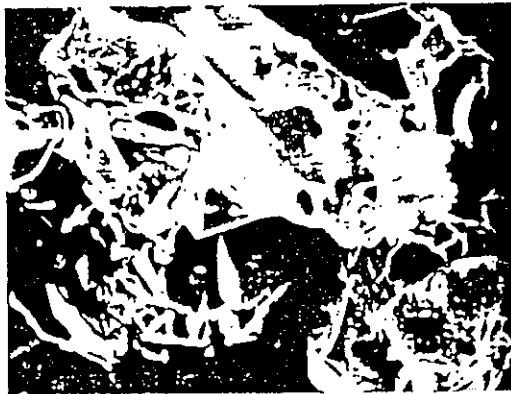


FIGURE 2 SMOKE MONITORING USING LASER

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MATRIX RETENTION



HONEYCOMB FORMATION



CHAR



ASH

FIG. 3 TYPICAL SEM MICROGRAPHS