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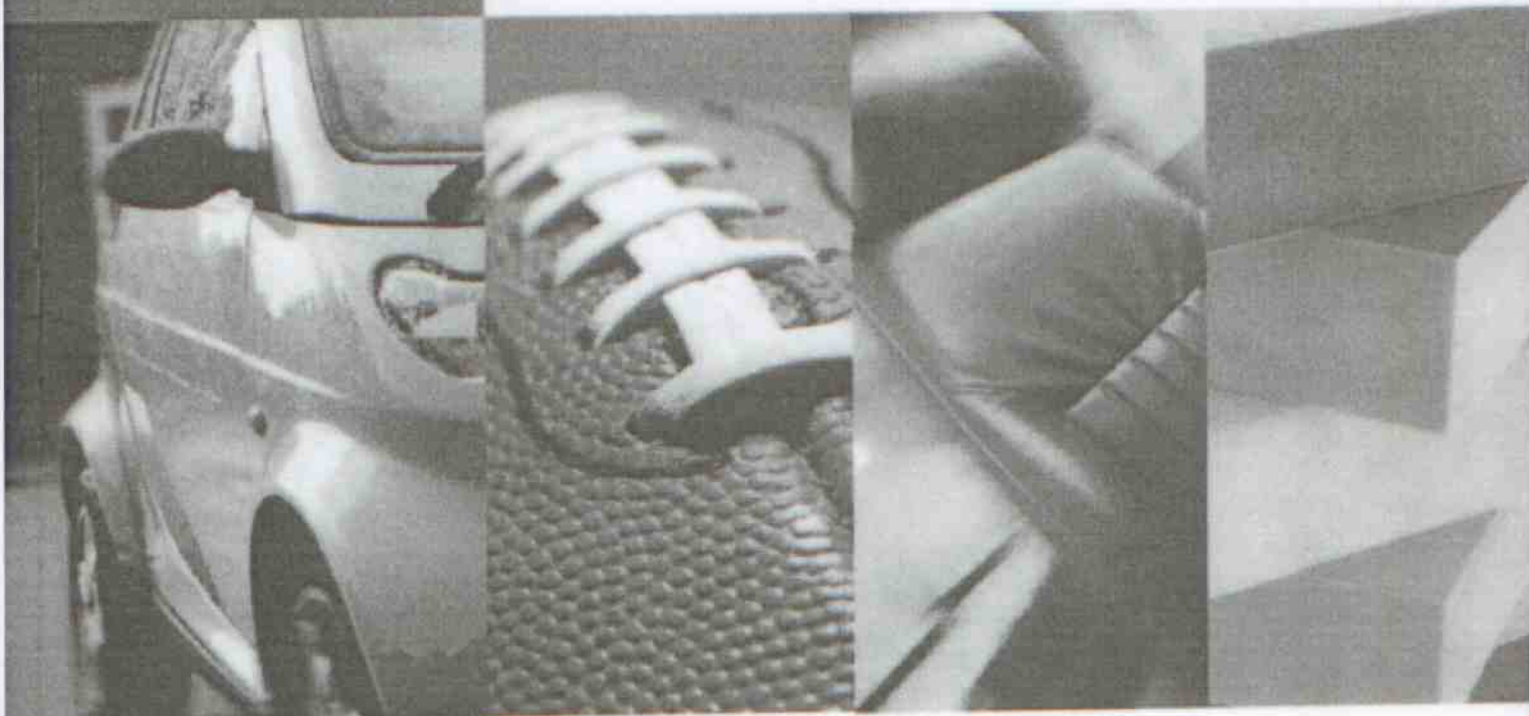
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Morphological, Elemental, Thermal and Burning Behaviour Properties of Flame Retardant Additives Incorporated Rigid Polyurethane Foams

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ABSTRACT

Rigid polyurethane foam (RPUF) samples were prepared from crude 4, 4'-diphenylmethane diisocyanate (CMDI), polyether polyol, triethylene diamine (TED), 1, 4 butane diol, polysiloxane ether, methylene chloride and water. The density of RPUF samples blown by water, methylene chloride and mixture of water and methylene chloride was ranged from 240.1 to 33.4 kg/m³ with an increase of blowing agent contents when measured as per ASTM D1622. The structure and properties of the conventional and flame retardant additives incorporated RPUF samples were investigated with scanning electron microscopy (SEM), energy dispersive x-rays (EDX), thermogravimetric analysis (TGA), derivative thermogravimetry (DTG) and differential thermal analysis (DTA). Fire performance of conventional and flame retardant additive incorporated rigid polyurethane foam is evaluated as per BS: 4735 and ASTM E 662. SEM results exhibit the average increase in the cell size of the RPUF samples from 162 to 278 mm with the increased water content. The SEM also shows the deposition and distribution of flame retardant additives on cell walls and changes in the cell structure after addition of flame retardant additives. EDX study shows the presence of maximum number of elements in the RPUF structure which are present in the raw materials used in the RPUF formulation. EDX study also shows the attachment and presence of flame retardant element quantitatively into the foam structure. TGA, DTG and DTA results on the conventional and flame retardant additives incorporated RPUF samples indicate weight changes in three steps through exothermically under an air atmosphere. BS: 4735 and ASTM E662 show that phosphorus, chlorine and phosphorus-chlorine flame retardant additives added into the rigid polyurethane foam formulation is quite effective in enhancing the fire performance with low smoke density of the samples.

Key words: Rigid polyurethane foams; morphology; density; methylene chloride; NCO index; flame retardant; thermal behaviour: flame retardant; phosphorus-chlorine

INTRODUCTION

Rigid polyurethane foam is extremely large and complex thermoset polymer produced by the reaction of isocyanate (R-N=C=O) and polyol (R-OH-) in the presence of other ingredients. The chemistry of rigid polyurethane foam makes use of the reactions of organic isocyanates with compounds containing at least two active hydrogen atoms. When polyfunctional isocyanates and intermediates containing at least two active hydrogen atoms per mole reacted at proper ratios and under certain conditions of temperatures, catalysts etc., a polymer results that can produce rigid foam. An isocyanate group reacts with the hydroxyl groups of a polyol to form the repeating urethane linkages. The isocyanate and polyol reaction is catalysed by organotin catalyst. The isocyanates also react with water to form carbamic acid, which is unstable intermediates and decomposes readily to evolve carbon dioxide and an amine. This carbon dioxide acts as blowing agent during the formation of polyurethane foams. The maximum expansion of polyurethane foam i.e. 80% is controlled by the carbon dioxide itself and remaining 20% expansion is controlled by the addition of external foaming agents. This important isocyanate-water reaction is catalysed by tertiary amine compound. The amine formed during the isocyanate-water reaction, reacts with additional isocyanate to form disubstituted urea. In addition, a number of cross-linking side reactions may also take place, depending upon the reaction conditions such as temperature, the presence of catalysts, the structure of the isocyanate, polyols and amines involved. These reactions form linkages of biuret (reaction between substituted urea and isocyanate), allophanate (reaction between urethane-isocyanate). Isocyanate also undergoes self-addition reaction to form isocyanurate (trimerisation of isocyanate groups), uretidinedione and carbodiimide (dimerisation of isocyanate groups). Isocyanurate and carbodiimide linkages provide improved thermal stability and flammability performance to polyurethane foams to a certain extent. A typical rigid polyurethane foam structure may contain in addition to the urethane linkages, aliphatic and aromatic hydrocarbons, esters, amides, disubstituted urea, biuret, allophanate, isocyanurate, uretidione and carbodiimide groups.[1]

The insulating efficiency of rigid foam is unsurpassed. A mere 50 mm of rigid polyurethane foam is equivalent in its insulating capacity at ambient temperature to 75 mm of polystyrene foam, 90mm of mineral wool, 100mm of cork, 150mm of glass fibre mat, 275mm of wood or 7500mm of cemented concrete blocks. Due to great insulation and structural capacity this foam find many applications. Rigid polyurethane foam is universal material with an unsurpassed

high insulation value and potentially finds greater use in the Building Construction/Industry in the form of insulation boards (flat roofs, ventilated roofs, pitched roofs, ventilated facades, ventilated double wall masonry construction single wall masonry system, interior walls, floors and ceilings), sandwich elements (metal sandwich elements for walls and facades), specialty elements (sanitary walls, bathrooms and window sills), PU light weight concrete, wall blocks with integrated insulation, curtain wall construction, preformed rigid panels and spray-applied wall construction and rigid PU foam igloos. The market for these include residential homes, commercial and industrial buildings such as large refrigerated warehouses. The other important uses of polyurethane rigid foam are technical insulation (pipe insulation and insulation of tanks), automotive industry (interior liners and cavity foaming), transportation (refrigerated vehicles, insulation for transportation of special products and caravans and mobile homes), shipbuilding (foaming of cavities, insulation of cold storage holds in fishing boats, boat building), Packaging (direct encapsulation, transportation protection in vehicles and sandwich-card board boxes), horticulture , sporting goods, furniture, solar technology and radomes. The other important uses of rigid polyurethane foam is in Refrigeration Technology and Appliances such as refrigerators and freezers, commercial display cases, refrigerated trucks (milk trucks, ice-cream trucks and trailers) and container, refrigerated warehouses and walk-in-coolers and water heaters.[2]

Because rigid polyurethane foam, like most organic materials, tend to be combustible unless care is taken to render it flame retardant. The flammability and evolution of deadly poisonous thermal decomposition products of rigid polyurethane foam, makes them undesirable for use in many applications. Rigid polyurethane foams are cellular plastics which are easily ignitable and highly flammable, flame spread very fast on these materials and results engulfing the entire area in a few minutes. On burning, rigid polyurethane foam undergo thermal decomposition resulting in volatile/combustible vapours, particulate matter and highly toxic and deadly poisonous combustion products. These combustion products in the form of solid, liquid and gas are the main threat to life in a building fire. The solids and liquids suspended in gas phase form smoke. Due to its particulate nature smoke obscures vision and hence reduces the ability of a person to escape from a fire zone. The delayed escape may result in panic and rapid breathing causing a person to inhale more of the toxic gases generated during fire. In short, more people die as a result of smoke and toxic gases than because of fire injuries. One of the surest ways of minimizing smoke and toxic combustion products is to render rigid polyurethane foams flame retardant.

The present study deals with the composition, preparation and incorporation of flame retardant additives into the foam formulation. The effects of chemical blowing agent, physical blowing agent, mixture of chemical and physical blowing agents on physical and morphological properties of RPUF samples were investigated. Elemental analysis and thermal behaviour of prepared RPUFs were also studied. RPUFs were prepared from crude 4, 4'-diphenylmethane diisocyanate (CMDI) with a functionality of 2.2 and polyether polyol with a functionality of 4.3 and hydroxyl value 440. CMDI and polyether polyol have a major impact on the properties of the RPUF. Triethylene diamine (TED), 1, 4 butane diol and polysiloxane ether were used as amine catalyst, chain extender and surfactant respectively during RPUFs preparation. Water as chemical blowing agent and methylene chloride as physical blowing agent were used. By varying the compositions and amount of water, methylene chloride and mixture of water and methylene chloride, RPUF sample of various densities were obtained. Phosphorus and chlorine based flame retardant additives were incorporated into the foam formulation prior to the addition of CMDI. Physical properties such as cream time, gel time, tack-free time and density, morphological properties, elemental structure, thermal behaviour in an air atmosphere and burning behaviour characteristics of RPUF samples were studied with scanning electron microscopy (SEM), energy dispersive x-rays (EDX), thermogravimetric analysis (TGA), derivative thermogravimetry (DTG) differential thermal analysis (DTA) and BS: 4735, ASTM E662, respectively.

ERERIMENTATION

RPUF Formulation

Formulation of rigid polyurethane foam (RPUF) is basically based on polyether polyol, CMDI, triethylene diamine (TED), polysiloxane ether, 1, 4 butane diol, water and methylene chloride. The amount of polyether polyol was set to 100 parts by weight. The amount of CMDI required for the reaction with polyether polyol, 1, 4 butane diol and water was calculated from their equivalent weights. About 5 % weight excess CMDI was used for the completion of the reaction. This 5 % weight excess CMDI is calculated from isocyanate index (NCO/OH = 1.05) which is based on used number of equivalents of diisocyanate, polyether polyol and water.[3] The amount of amine catalyst and water were varied to obtain desired cream time, gel time and tack-free time. The amounts of water and methylene chloride were varied and calculated in order to obtain desired foam densities. The amounts of triethylene diamine, polysiloxane ether, 1, 4 butane diol, water and methylene chloride per 100 parts polyether polyol by weight (php) were selected as optimal after carried out a series of foam preparation experiments.[3] The amount of phosphorus and chlorine based flame retardant additives was selected optimal after conducting a series of experiments on compatibility with foam ingredients and fire performance of RPUF samples. The basic formulation used for the flame retardant rigid polyurethane foam (RPUF) preparation is presented in Table I.

RPUF Sample Preparation

RPUF samples with different amount (php) of ingredients were prepared through one-shot method.[1-2] Except CMDI, all the raw chemicals such as TED, polysiloxane ether, 1, 4 butane diol, water, methylene chloride and phosphorus and chlorine based flame retardant additives were first manually well blended with polyether polyol for 30 seconds in a stainless steel beaker. Then CMDI was added into the blended polyol and mixed for 20 seconds under overhead electric stirrer. The stirrer speed was set at 3000 rprn throughout the mixing. After mixing, the reactants were discharged into an open mould (200 ´ 200 ´ 250 mm) lined with paper to produce free-rise foam. As the reactants mixture was poured into the mould, formation of many very small bubbles was observed which were dispersed into the reaction mixture. These tiny gas bubbles formed the nuclei into which the blowing gas diffused as the reaction proceeded. Number, size and distribution of the nuclei determine the final foam structure.[4] The foam cake was then cured for 48 hours at room temperature. Although foam can also be cured at elevated temperatures, however we preferred to perform the curing at room temperature to observe the foam properties at ambient processing conditions. Two replications for all the RPUFs were prepared. The charging and mixing of all the foam ingredients inside the stirrer is illustrated in Figure 1.

The effect on RPUF properties blown by chemical, physical and mixture of both blowing agents was investigated by varying the amounts of water and methylene chloride respectively. The amount of water was varied from 0 to 3.0 php with an increment of 0.5 php. Similarly the amount of methylene chloride varied from 0 to 30 php with an increment of 5 php. The mixture of water and methylene chloride was also used by varying the amount of one blowing agent, while the amount of other blowing agent was constant and vice-versa. The amounts of polyether polyol, TED, polysiloxane ether and 1, 4 butane diol were fixed at 100, 0.6, 1.0 and 20 php respectively. The amount of CMDI required for the reaction with polyether polyol, 1, 4 butane diol and various amounts of water was calculated from their equivalent weights. 5 % excess (NCO/OH = 1.05) CMDI was used to assure the complete reaction of the polyol. When water is used as blowing agent, it reacts with CMDI to produce disubstituted urea and carbon dioxide. The carbon dioxide inflates the reactants which resulted into a cellular structure. Similarly methylene chloride when used as blowing agent, it boils and evaporates by the heat generated through exothermic reaction of CMDI and polyether polyol and inflates the reactants.

The effect of phosphorus, chlorine and combination of phosphorus-chlorine based flame retardant additives was investigated by varying their concentrations during the foam preparation. The concentrations of phosphorus and chlorine were varied from 0.5 - 6.0 % with an increment of 0.5%. To investigate the effect of phosphorus-chlorine combination additives, the phosphorus additive concentration was fixed at 2% while chlorine additive concentration was varied from 0.5 to 3.0 % with an increment of 0.5%. Three specimens of each conventional and flame-retardant additives incorporated rigid polyurethane foams of dimensions 150´50´13.nm were prepared by inserting the rigid foam cake in the specially designed box. The foam cutter moves vertically in the slits provided for its movement in the walls of the box. The vertical slits provided in the box in such a way that the final thickness of the rigid polyurethane foam specimen should not be more than 13mm. A gauge mark was provided on each specimen by marking a line across its width 25 mm from one end.

To investigate the effect of phosphorus, chlorine and phosphorus-chlorine combination based additives incorporated rigid polyurethane foam and conventional foam samples under flaming and non-flaming modes, six specimens of each foam of size 75 ´ 75 ´ 25 mm were prepared. These rigid polyurethane foam samples were containing the different concentrations of phosphorus, chlorine and phosphorus combination flame retardant additives.

Measurements

The densities of conventional and flame retardant additives incorporated rigid polyurethane foam samples were measured according to ASTM D1622. The size (length ´ width ´ thickness) of the specimen was 30 ´ 30 ´ 30 mm respectively. RPUF specimens were conditioned at 25ºC and 55 % relative humidity for 48 hours prior to their density measurement. The densities of five specimens per sample were measured and averaged.

The morphology of conventional and flame retardant additives incorporated rigid polyurethane foam samples was observed with LEO (438 VP, UK) scanning electron microscopy (SEM). The samples were cryogenically fractured and gold coated prior putting under scanning. During scanning 15 KV accelerating voltage was used. The SEM was used to observe the shape and size of the cells and deposition and dispersion of flame retardant additives on the cell wall of RPUF samples. To define the cell size, measured cell sizes were averaged except the sizes for the largest and smallest cells.

Elemental analysis study of conventional and flame retardant additive incorporated RPUF samples was carried out with energy dispersive x-rays (EDX). The same RPUF samples which were used for morphological scanning, were also used for the elemental analysis. RPUF samples under EDX were elementally analyzed for both qualitatively and quantitatively.

Thermal properties of conventional and flame retardant additives incorporated rigid polyurethane foam samples were measured under an air atmosphere on a Pyris Diamond Perkin-Elmer (USA). The RPUF samples were crushed into power. Platinum pan was used to place 4.167 and 1.981 mg of powder sample inside the heating chamber. The RPUF samples were heated up to 980°C for 98 min. at a rate of 10°C/min. under an air atmosphere. After complete heating of the samples TGA, DTG and DTA curves obtained were taken for analysis.

To evaluate the fire performance of flame-retardant additives incorporated rigid polyurethane foam and its comparison with foam without flame retardant additives, both conventional and flame retardant additives incorporated foam specimens were subjected to fire test as per BS: 4735 (horizontal burning characteristics of cellular plastics). To assess the fire performance of conventional and flame retardant additives incorporated foams, the burn length, burning rate and weight loss of each three specimens were measured and averaged.

The measurement of the smoke concentration evolved from conventional and flame retardant additives incorporated rigid polyurethane foams during both flaming and non-flaming modes was evaluated as per ASTM E 662 (specific optical density of smoke generated by solid materials). Specific optical density (smoke concentration) measurement is made of the attenuation of a light beam (transmittance) by smoke accumulating with in a closed chamber due to non-flaming pyrolytic decomposition and flaming combustion of conventional and flame retardant additives incorporated rigid polyurethane foams. To assess the smoke concentrations evolved from conventional and flame retardant additives incorporated foams, the percent tansmittance and specific optical density of each six specimens were measured and averaged.

RESULTS AND DISCUSSION

Density Measurement

The densities of RPUF samples blown with and without blowing agent and mixture of blowing agents were measured. The density of RPUF samples in the absence of blowing agent was 240.1 kg/m³. The density of RPUF samples (RPUF-W) blown by water was decreased from 240.1 to 56.5 kg/m³, as the water content increased from 0 to 3.0 php respectively. The densities of the RPUF samples (RPUF-W) blown by water are shown in Figure 3. The densities of the RPUF samples blown by methylene chloride (RPUF-MC) and by the mixture of water and methylene chloride (RPUF-W-MC) are shown in Figure 4 . As shown in Figure 4, the density of the RPUF samples blown by methylene chloride was decreased from 240.1 to 49.3 kg/m³ as the content of methylene chloride increased from 0 to 30 php respectively. When mixture of water and methylene chloride was used as blowing agent, the density of the RPUF samples (RPUF-W-MC) ranged from 240.1 to 33.4 kg/m³.

Further, the density of rigid polyurethane foams incorporated with flame retardant additives also increases with the increase content of flame retardant additives. When phosphorus additive concentration was increased from 0.5 to 6.0 %, the densities of RPUF samples also increased from 1.7 to 17.2 kg/m³. When chlorine additive concentration was increased from 0.5 to 6.0 %, the densities of RPUF samples also increased from 0.6 to 11.02 kg/m³. Similarly when the combination of phosphorus-chlorine additive concentration was increased from 2.0 – 0.5 to 2.0 – 3.0 %, the densities of rigid polyurethane foam samples also increased from 7.3 to 13.3 kg/m³. The increased densities of rigid polyurethane foam samples incorporated with phosphorus, chlorine and phosphorus-chlorine combinations are shown in Figure 4, 6 and 7 respectively.

Morphology

The cross-sectional surfaces of the RPUF samples individually blown by 0.5 (RPUF-0.5-0) and 3.0 (RPUF-3.0-0) php water content, and by 5 (RPUF-0-5) and 30 (RPUF-0-30) php methylene chloride content were observed under SEM. All the four RPUF samples were scanned at the similar magnification in the free-rising direction. The micrographs of the RPUF samples blown by water content are shown in Figures 8 (a,b). Figure 8 (a,b) shows the micrographs of RPUF-0.5-0 (density 164.2 kg/m³) and RPUF-3.0-0 (density 56.5 kg/m³) blown by water respectively. These figures show that RPUF cells formed the spherical and polyhedral shapes, and the cell size increased with decrease in the density of the RPUF samples. Foaming and formation of cell size and shape processes of RPUF samples can be explained by nucleation and growth mechanism.[6] Blowing gas is formed by the reaction of isocyanate and water as well as by the evaporation of physical blowing agent such as methylene chloride utilizing the reaction heat of polyol and isocyanate. Exothermic reaction of polyol and isocyanate causes the supersaturation of the reactive mixture resulting in the blowing gas being expelled from the reactive mixture and diffused into the nuclei. The diffusion of blowing gas into the nuclei begins the nucleation process. As a result nuclei changes to bubble and bubble growth ends with unification of different sizes of bubbles. The unification of these bubbles forms the spherical shape. Spherical bubbles form the cells which are separated by the cell membranes and change their shape to polyhedral. During the foam formulation the reaction heat steadily raises the viscosity of the mixture until the foam has been cured and stabilized.[7] The whole foam preparation process passes through the various physical and chemical phases. Some of the physical phases are illustrated in Figure 2. Niyogi et al. reported that during the foaming process the rate of nucleation was smaller with physical blowing agent and larger with chemical blowing agent at a higher initial blowing agent concentration. As a

result, the average bubble diameter was changed with the initial blowing agent concentrations.[6] However, the cell size and shape did not significantly change with the type of blowing agent. The cell size of the RPUF sample blown by either water or methylene chloride increased with the increase in the blowing agent concentration. The increase in the size of the RPUF cells may be due to the coalescence of the RPUF cells. Thus cell size of the RPUF samples blown by water increased from 162 mm to 278 mm with an increase in water content from 0.5 to 3.0 php respectively. This is due to the fact that the increase of water content generates more bubbles, and increased bubbles combine with each other. Therefore, the cell size of the RPUF sample increases with the increase of the water content. Similarly the cross-sectional surface of flame-retardant additive incorporated rigid polyurethane foam sample observed by SEM is shown in Figure 9. The cellular structures of the rigid foam sample was observed in the free-rising direction. In Figure 9, the micrograph of rigid polyurethane foam shows the deposition and dispersion of incorporated flame retardant additive on the cell wall. The deposition of flame retardant additive on the cell wall is further confirmed by the increase in the cell wall thickness as compare to the cell wall thickness of conventional foam.

The shape and size of rigid polyurethane foam cell are important to the mechanical properties and thermal conductivity.[6] [6,11] The foaming process can be explained by nucleation and growth mechanism. When polyol and diisocyanate reacts, the temperature of the mixture rises because of the exothermic reaction heat. The added physical blowing agent vaporizes utilizing the reaction heat. A chemical blowing agent generates carbon dioxide through the reaction with diisocyanate accompanying exothermic reaction heat. Because of the increase of temperature of he reactant mixture, the concentration of blowing gas in the mixture exceeds its solubility limit, and bubble nucleation begins. During the rise time, the already formed bubbles grow, and new bubbles nucleate. [6,11] Thus the cell size of the rigid polyurethane foam increases with the increase of the chemical-blowing agent. Therefore it is quite clear that the increased cell wall thickness is only due to the deposition of flame retardant additive.

Elemental Analysis

The elemental analysis of the conventional RPUF sample observed with EDX is shown in Figure 10. The spectra obtained after analysed the RPUF sample under EDX shows the presence of carbon (64.31%), oxygen (32.63%), chlorine (2.64%), silicone (0.12%), magnesium (0.12%) and bromine (0.09%) in the form of elements. The higher elemental presence of carbon and oxygen are due to their maximum presence in the raw materials used for RPUF sample preparation. Chlorine and silicone are present due to the inclusion of methylene chloride and polysiloxane ether as physical blowing agent and surfactant respectively in the RPUF formulation. Minute quantities of bromine and magnesium were also found to be present, may be due to the impurities in the raw materials or in the sampling preparation of RPUF for EDX. EDX study shows the presence of maximum number of elements in the RPUF structure which are present in the raw materials used in the RPUF formulation. Similarly the sample of flame-retardant additive incorporated rigid polyurethane foam was also put under the observation of elemental analysis through energy dispersive x-rays (EDX). The presence of phosphorus element into the rigid foam structure is due to the incorporation of flame retardant additive in the foam formulation. This phosphorus element is responsible for the flame-retardant activity of rigid polyurethane foam.

Thermal Analysis

The weight changes, the rate of weight changes and state of thermal energy changes of conventional and flame retardant additive incorporated RPUF samples under an air atmosphere at elevated temperature measured through TGA, DTG and DTA profiles is shown in Figure 11 (a,b). Figure 11 (a) shows the thermal changes in the conventional RPUF sample in oxygen atmosphere, while Figure 11 (b) shows the thermal changes in the flame retardant additive incorporated RPUF sample in oxygen atmosphere. As shown in Figure 12 (a), the combustion of RPUF sample was occurred in three stages. During the heating of RPUF sample under an air atmosphere, three overlapping steps in the temperature region (1) at 175 – 476°C, (2) at 476 – 580°C and, (3) 580 – 730°C were observed. Three weight loss steps corresponding to these temperature regions observed in TGA/DTG profiles are (1) 1 - 47 % weight loss at the rate of 0.191 mg/min., (2) 48 – 81 % weight loss at a rapid rate of 0.230 mg/min. and (3) 82 – 91 % weight loss at a very slow rate of 0.054 mg/min. In the first region (175 – 476°C), the RPUF sample was ignited at 175°C and 1 % weight loss after 16 min. of heating. Ignition after 16 min. and slow rate of weight loss may be due to the moisture absorption by the RPUF sample. The second region (478 – 580°C) shows the rapid rate of weight loss which due to the thermal decomposition and combustion of RPUF sample. In the third region (580 – 730°C) the rate of weight loss is very slow due to the combustion of RPUF sample. After third region and till the end of heating, no further weight loss is observed. This may be due to the maximum charring of the sample at 730°C and some impurities in the sample. Three exotherm peaks obtained in DTA profile also support the sample weight loss in three steps. DTA shouldering peaks are obtained when sample under heat decomposed exothermically by releasing the energy. [12] All these results show that RPUF sample was ignited at 1 % weight loss and extinguished at 91 % weight loss. Weight data confirms that RPUF sample contains 91 % volatile components and 9 % non-volatile components which was left in the form of black char residue. This black residue may contains carbon, and condensed aromatic components, because biuret , allophanate, urea, urethane and disubstituted urea are the thermally weakest links in the polyurethane network.[13,16] RPUF sample under an air atmosphere does not melt because melting is an endothermic process while it was decomposed exothermically. As shown in Figure 12 (b), the flame retardant additive incorporated rigid polyurethane foam sample under similar

condition also shows the weight changes in three stages. In the first phase the 5% weight loss commences at about 190°C and continues up to 300°C at a rate of 0.279 mg/min. Second weight loss phase starts at 325°C with 31% weight loss and continue up to 520°C with a weight loss of 68 % at a rate of 0.242 mg/min. The third phase starts at 600°C with 71 % weight loss and continues up to 730°C with 82 % weight loss at a rate of 0.074 mg/min. Thus flame retardant additive incorporate rigid polyurethane foam was ignited at 5 % weight loss and extinguished at 82 % weight loss. Therefore, it contains 82 % volatile and 18 % non-volatile components which were left in the form of black char residue.

The TGA, DTG, DTA and DSC studies carried out on conventional and flame retardant additive incorporated rigid foams show that the ignition of both the foams occur in three stages. TGA and DTG curves confirm that weight losses and weight loss rates are higher in conventional foam and lower in flame retardant rigid foam. But weight loss temperature ranges are higher in flame-retardant foam than conventional foam. Flame retardant foam ignites at190°C on 5% weight loss while conventional foam ignites at 175°C on 1% weight loss at a similar heating rate of 10°C/min. The maximum weight loss in flame-retardant foam is 82% while it is 91% in conventional foam under similar heating conditions. Thus flame retardant and conventional rigid polyurethane foams contain 18% and 9% non-volatile components respectively, which are left in the form of black char residue. DTA exotherms of flame retardant and conventional rigid polyurethane foams show that on exposure to heat both foams get decomposed exothermically by releasing the heat or energy. DSC indicates that conventional foam release more heat than flame retardant foam and thus weight loss in conventional foam is more than flame retardant foam. It is quite clear from the TGA, DTG, DTA and DSC curves that the presence of the flame retardant additive reduces the thermal stability of the polyurethane, which indicates that a reaction occurs between the flame retardant additive and the polyurethane.

FIRE PERFORMANCE

Conventional rigid polyurethane foam during fire exposure burns entire length with 2.22 mm/sec. burning rate, which resulted in 100 % weight loss. Under similar fire exposure conditions the data obtained from extent burnt (31mm), weight loss (11.60 %) and burning rate (0.81 mm/sec.) indicate that 2 % phosphorus additive concentration was enough to render rigid polyurethane foam flame retardant. More than 2 % concentration is not able to enhance further flame-retardant properties. This is due to the fact that on 2 % concentration, the extent burnt and weight loss are 31 mm and 11.60 % respectively but when concentration increases up to 6 % the values of extent burnt and weight loss almost remain constant. Although the burning rate value mainly depends upon extent burnt and flame extinction time but flame extinction time plays an important part in the determination of the burning rate. The burning rate value on 2 % concentration is 0.81 mm/sec. (36 seconds flame extinction time) which almost remains constant when concentration reaches up to 6 %. Thus 2 % phosphorus additive concentration was enough to render rigid polyurethane foam flame retardant. The extent burnt and burning rate, percent weight retained and extinction time are shown in Figure 12 (a,b) respectively.

Chlorine additive 5.5 % concentration was enough to render rigid polyurethane foam flame retardant because rigid polyurethane foam specimens incorporated with this concentration show minimum extent burnt (33mm), weight loss (11.75 %) and burning rate (0.91 mm/sec.) with flame extinction time of 33 seconds. As the overall fire behaviour of rigid polyurethane foam incorporated with different concentrations of chlorine additive is concerned, the extent burnt is equal to conventional foam at the initial chlorine additive concentration. But extent burnt reduces drastically at the 2 % chlorine additive concentration, which further reduces to all time low (33 mm) at the 5.5 % chlorine additive concentration. Weight loss data shows that up to 1.5 % chlorine additive concentration is ineffective because at these concentrations the weight losses are equal to conventional foam i.e. 100 %. But as the concentration rises to 2 % the weight loss immediately reduces to 20.19 %. Further weight loss almost remains constant at chlorine additive concentrations 2.5 – 5 %. As concentration rises to 5.5 % weight loss goes down to all time low i.e. 11.75 %. Burning rate also shows the similar pattern which is maximum at chlorine additive concentrations 0.5 – 1.5 % and minimum at 5.5 % concentration. Thus from the above data and results it is quite clear that 5.5 % chlorine additive concentration was enough to render rigid polyurethane foam flame retardant. The extent burnt and burning rate, percent weight retained and extinction time are shown in Figure 13 (a,b) respectively.

Rigid polyurethane foam specimens incorporated with 3–2 % phosphorus – chlorine additive concentration show minimum extent burnt 28 mm, weight loss 10.40 % and burning rate 0.60 mm/sec. with flame extinction time 44 seconds. Thus rigid polyurethane foam incorporated with 3 – 2 % phosphorus – chlorine additive concentration was enough to render such foam flame retardant because under fire exposure they exhibit all time low extent burnt (28 mm), weight loss (10.40 %) and burning rate (0.60 mm/sec.). Extent burnt (charred length), weight loss and burning rate mainly depend upon the chemical retention in the foam. The burning behaviour data show that as chemical retention increases, the extent burnt, weight loss and burning rate are decreased. Flame extinction time data show that there is no direct relationship between flame extinction times, extent burnt and weight loss. According to flame extinction time data it is not necessary that extent burnt and weight loss will be less when flame extinguished in a short period of time and vice-versa. But burning rate will be low when flame takes more time to extinguish and vice-versa. Similarly chemical retention does not have direct relationship with flame extinction time. When some foam specimens have high degree of chemical retention it does not mean that flame extinction time will be less and vice-versa. Therefore, it is concluded that rigid polyurethane foam samples exhibit more flame retardancy with phosphorus-chlorine additive combination than when they are used individually. This due to the synergistic effect between phosphorus and chlorine

additives. The extent burnt and burning rate, percent weight retained and extinction time are shown in Figure 14 (a,b) respectively.

SMOKE DENSITY

During flaming combustion of conventional rigid polyurethane foam the starting maximum transmittance percent value 287 reduces to its lowest value 157 after 8 minutes exposure. After complete 20 minutes exposure the lowest transmittance percent value 157 increases to 212. Specific optical density (Ds) was 0 at the starting maximum transmittance percent value 287 but Ds value increases to its maximum 34.82 (Dm) at the lowest transmittance percent value 157 after just 8 minutes exposure. After 20 minutes exposure the Ds value decreases to 17.34 at light transmittance percent value 212. Under the similar flaming combustion flame-retardant rigid polyurethane foam exhibits different smoke behaviour pattern. During flaming combustion the starting maximum transmittance percent value 274 reduces to its lowest value 170 after total 20 minutes exposure. Specific optical density Ds was 0 at the starting maximum transmittance percent value 274 and Ds value increases to its maximum 28.28 (Dm) at the lowest light transmittance percent value 170 after complete 20 minutes exposure.

Thus it is quite clear from Fig. 10 that under smouldering (non-flaming decomposition) conventional rigid polyurethane foam generates rapid and more smoke in the beginning which reaches to maximum after 7 minutes smouldering and this smoke quantity remains constant for 5 minutes (from 7 to 12 minutes). After 12 minutes smouldering this smoke level reduces slowly-slowly till the total 20 minutes smouldering time. This due to the fact that when light transmittance percent value minimum and Ds value is maximum (Dm) then smoke generation is maximum and vice-versa. Corrected maximum specific optical density Dm (corr) value 5.06 is very close to Dm value, which again confirms the quantity of smoke evolved. Dm (corr) is the average value of Dm of samples (maximum 4 samples) smouldered under similar conditions. Similarly flame retardant rigid polyurethane foam under non-flaming decomposition generates less smoke in the beginning, which increases slowly up to 11 minutes smouldering. Smoke evolution level remains constant up to 17 minutes smouldering. After 17 minutes the smoke level increases slightly and reaches to maximum at 18 minutes and continues up to total 20 minutes smouldering. The smoke generation from conventional and flame retardant rigid polyurethane foams is shown in Figure 15 (a).

During the non-flaming decomposition of conventional rigid polyurethane foam the starting maximum light transmittance (T) percent value 266 reduces to its lowest value 240 after 7 minutes smouldering. This lowest value 240 remains constant up to 12 minutes smouldering. After 12 minutes smouldering the lowest transmittance percent value 240 increases slowly to 243 after total 20 minutes smouldering. Specific optical density (Ds) was 0 at starting light transmittance percent value 266 but Ds maximum value 5.98 was obtained at lowest transmittance percent value 240. This maximum value 5.98 is known as maximum specific optical density (Dm). This Dm value remains constant from 7 – 12 minutes. After 12 minutes smouldering when transmittance percent slowly increases to 243 then Ds value reduces to 5.56. Flame retardant rigid polyurethane foam was also put under the similar non-flaming decomposition condition. The starting maximum light transmittance percent value 283 reduces to its lowest value 257 after total 20 minutes smouldering. But before this lowest value, its next higher value 258 was obtained at eleven minutes smouldering and this value (258) remains constant up to 17 minutes. Specific optical density (Ds) was 0 at starting light transmittance percent value 283 but Ds maximum value i.e. Dm 5.42 was obtained at lowest transmittance percent value 257 after complete 20 minutes smouldering. Slightly lower Ds value 5.19 was obtained at 11 minutes smouldering and this value remains constant up to 17 minutes. Corrected maximum specific optical density Dm (corr) value 4.29 is almost equal to Dm value. The smoke generation from conventional and flame retardant rigid polyurethane foams is shown in Figure 15 (b).

It is evident from Figure 15 (a,b) that under flaming combustion conventional rigid polyurethane foam generates more and rapid smoke in the beginning which reaches to maximum after 8 minutes exposure and after that the smoke level reduces slowly till the complete 20 minutes exposure. Corrected maximum specific optical density Dm (corr) value 32.31 is very close to Dm value that again confirms the quantity of the smoke evolved. On the other hand flame retardant rigid polyurethane foam under flaming combustion generates less and slow smoke, which increases slowly and reaches to maximum after complete 20 minutes exposure. Corrected maximum specific optical density Dm (corr) value 27.44 is almost equal to Dm value, which again confirms the concentration of smoke evolved.

CONCLUSIONS

The density of RPUF samples blown by water was decreased from 240.1 to 56.5 kg/m³ with an increase in water content from 0 to 3.0 php respectively. Similarly the density of the RPUF samples was also decreased from 240.1 to 49.3 kg/m³ with the methylene chloride content from 0 to 30 php respectively. The mixture of water and methylene chloride reduces the RPUF samples density in the range of 240.1 to 33.4 kg/m³. Hence it is concluded that the density of RPUF samples decreases with water, methylene chloride and mixture of water and methylene chloride content. The results of morphology by SEM demonstrate that the cell size of the RPUF samples increased from 162 mm to 278 mm with an increase in water content from 0.5 to 3.0 php respectively. The cell size of RPUF samples blown by methylene chloride and mixture of water and methylene chloride exhibits behaviour almost similar to the behaviour of the RPUF

samples blown by water. It is also quite clear from the SEM micrograph that the increased cell wall thickness is only due to the deposition of flame retardant additive.

Elemental analysis of the RPUF samples observed with EDX shows the qualitative and quantitative presence of elements present in the raw materials structure used for the preparation of RPUF. Little quantities of some other elements may be due to the impurities in the raw materials or in the sampling of RPUF for EDX. EDX study also confirms the presence of phosphorus element into the rigid foam structure which is due to the incorporation of flame retardant additive in the foam formulation. This phosphorus element is responsible for the flame-retardant activity of rigid polyurethane foam. Thermal behaviour of conventional and flame retardant additive incorporated RPUF samples observed was based on TGA, DTG and DTA profiles. It shows that both RPUF samples decompose exothermically under an air atmosphere. The weight of RPUF samples changes in three stages under an air atmosphere. The maximum weight loss of conventional RPUF sample under an air atmosphere was 91 % while it was 82 % in flame retardant additive incorporated RPUF sample. Therefore, it can be concluded that conventional and flame retardant additives incorporated RPUF samples are affected exothermically under an air atmosphere by change in their weights. It is quite clear from the TGA, DTG, DTA and DSC studies that the presence of phosphorus-chlorine additive reduces the thermal stability of the polyurethane, which indicates that a reaction occurs between the flame retardant additive and the polyurethane.

Conventional rigid polyurethane foams available in the markets are easily ignitable, highly flammable and on decomposition produce large quantity of black dense smoke containing deadly poisonous toxic gases. Fire retardant additive incorporated rigid polyurethane foam formulation is quite effective in enhancing the fire performance of rigid polyurethane foam. Fire retardant rigid polyurethane foam generates less smoke than conventional foam under both flaming and non-flaming modes. Once the fire performance of polyurethane foam is improved, the smoke and toxicity are reduced accordingly because during fire exposure the foam charred up to certain length and remain self-extinguished. The color and texture of fire retardant foam remains unchanged. Thus by the use of flame retardant rigid polyurethane foams in the construction of industrial and residential buildings, life and property losses could be minimised and sufficient energy saving could be achieved.

REFERENCES

1. Szycher, M. Handbook of Polyurethanes; CRC Press, Washington DC, 1999
2. Oertel, G. Polyurethane Handbook; Hanser Publisher, New York, 1985
3. Singh, H.; Sharma, T.P.; Jain, A. K. J Appl Polym Sci (To be published, 2005)
4. Kumar, B.; Decker, T. G. J Cell Plast 1969
5. Niyogi, D.; Kumar, R.; Gandhi, K. S. Polym Eng Sci 1999, 39, 199
6. Niyogi, D.; Kumar, R.; Gandhi, K. S. AichE J 1992, 38, 1170
7. Rompala, T. A.; Sulzbach, M.; Wirth, J. Polyurethanes Division Bayer Corporation, Pittsburg, PA 15205, 2001
8. Wood G, The ICI Polyurethane Handbook; Wiley New York, (1990)
9. Oertel G, Polyurethane Handbook; Hanser: New York, (1993)
10. Klempner D, Frisch KC, Handbook of Polymeric foams and foam Technology; Oxford University Press, New York, (1991)
11. Gibson LJ, Ashby MF, Cellular Solids; Cambridge University Press, New York, (1997)
    Dodd, J. W.; Tonge, K. H. Thermal Methods; John Wiley & Sons, London, 1987

Table I Chemical Formulation of Rigid Polyurethane Foam (RPUF)

Ingredients	Parts per 100 polyether polyol by weight (php)
Polyether polyol	100.00
Triethylene diamine (TED)	$0 - 0.9^a$
Water	$0 - 3.0^b$
Polysiloxane ether	$0 - 2.0^c$
1, 4 butane diol	$0 - 30^d$
Methylene chloride	$0 - 30^e$
Crude 4, 4' -Diphenylmethane diisocyanate (CMDI)	Stoichiometric + 5 %
Flame retardant additives	$0.5 - 6.0 \%$

a 0 – 0.9 parts of triethylene diamine with an increment of 0.1 parts

b 0 – 3.0 parts water with an increment of 0.5 parts

c 0 – 2.0 parts polysiloxane ether with an increment of 0.25 parts

d 0 – 30 parts 1, 4 butane diol with an increment of 2.5 and 5.0 parts

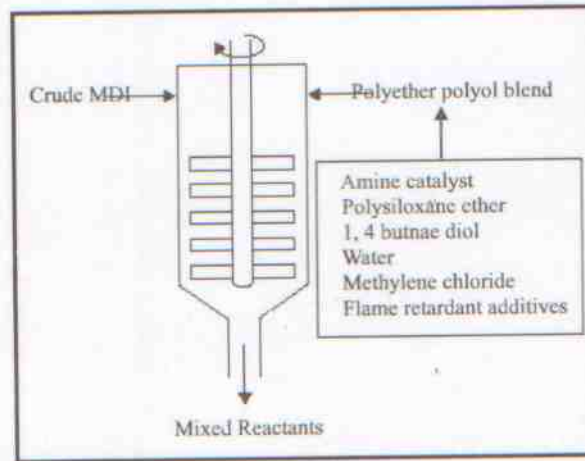e 0– 30 parts methylene chloride with an increment of 5.0 parts

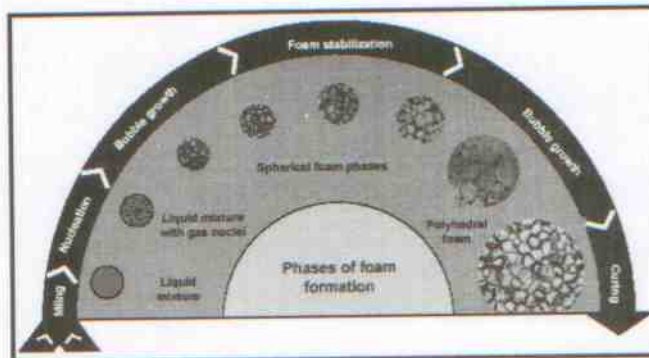Figure 1. **Blending and mixing process of RPUF ingredients**
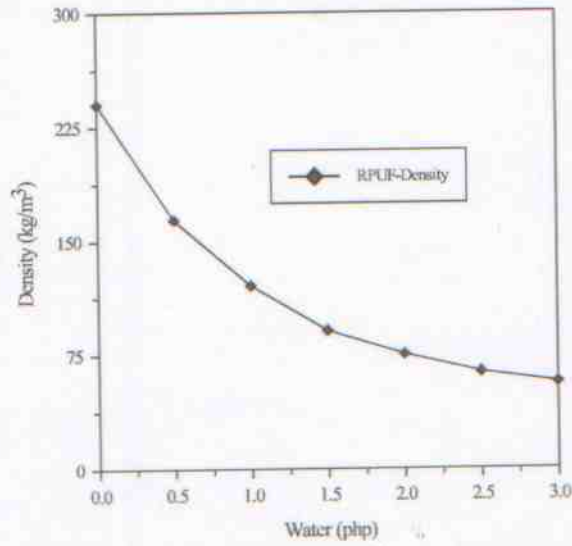

Figure 2. **Different physical phases during RPUF formation**

Figure 3. Density of the RPUF samples blown by water (RPUF-W
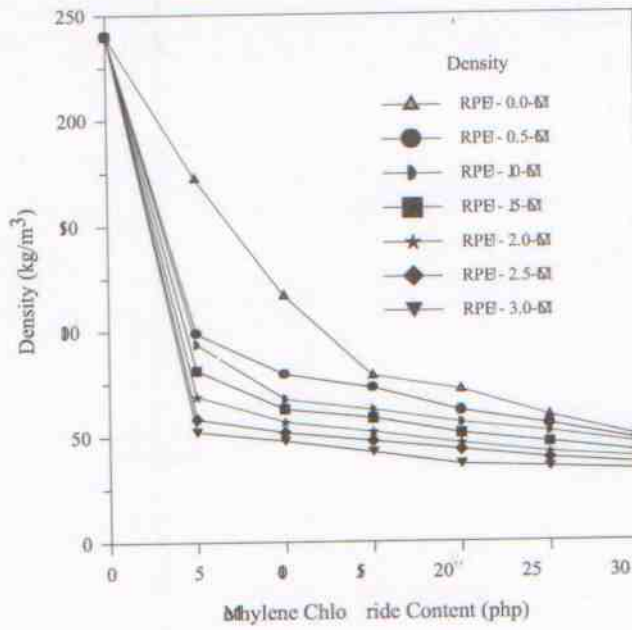
Figure 4. Density of the RPUF samples blown by mixture of water and methylene chloride (RPUF-WMC)
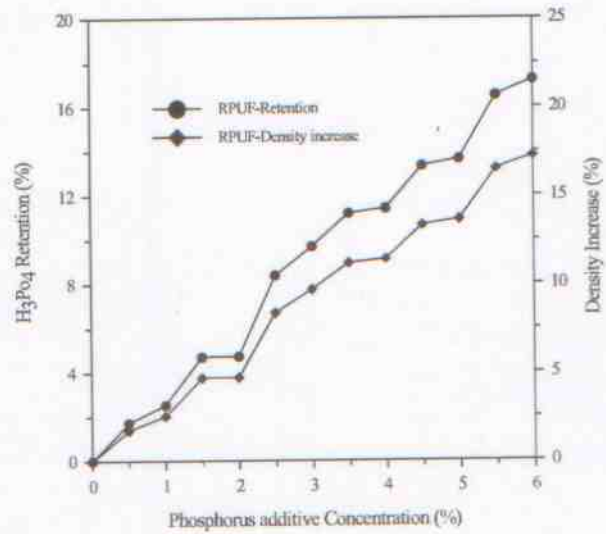
Figure 5Effect of phosphorus additive on the density of RPUF samples
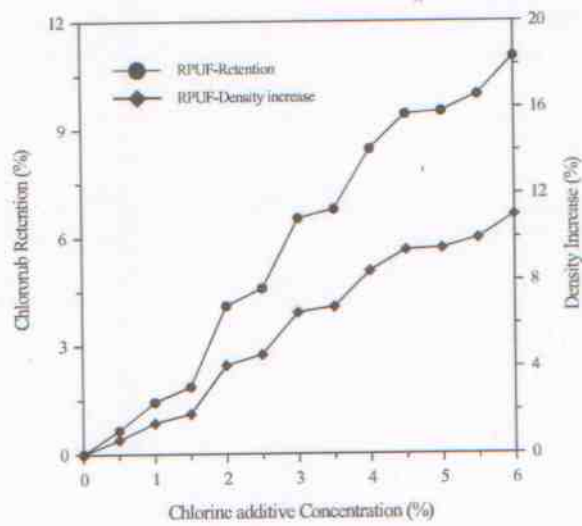
Figure 6. Effect of chlorine additive on the density of RPUF samples
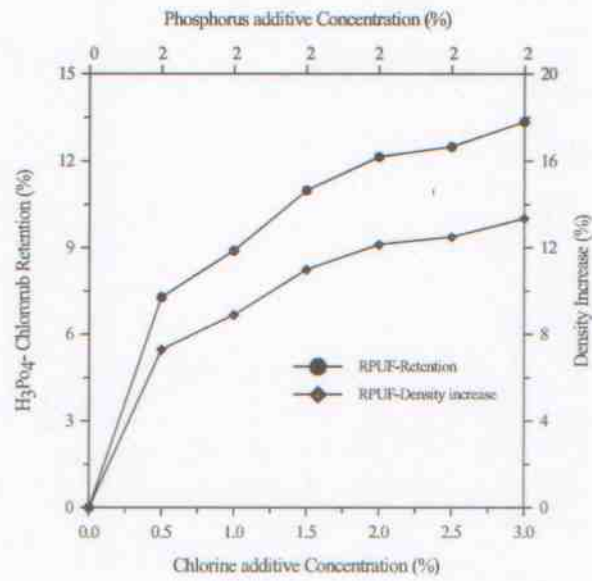
Figure 7. Effect of phosphorus - chlorine additives on the density of RPUF samples
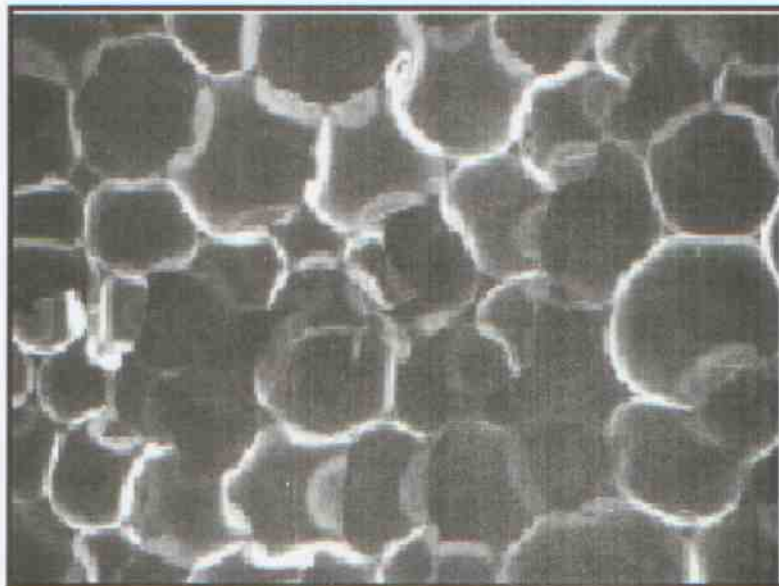
(a)
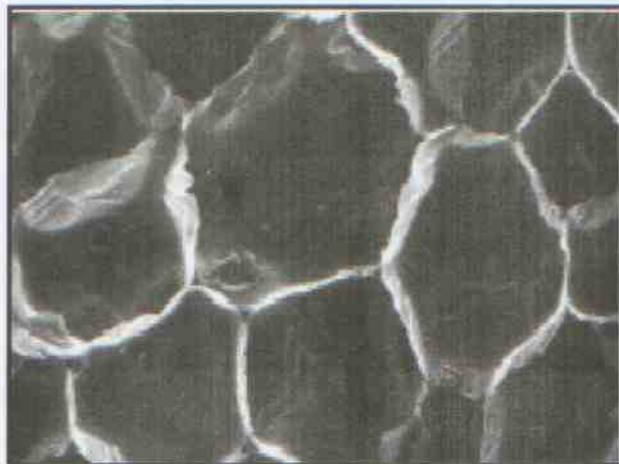
(b)

Figure 8 Scanning electron micrographs of RPUF samples blown with water: (a) RPUF- 0(6.5 kg/m³) and (b) RPUF-30(164.2 kg/m ³)

Figure 9. Scanning electron micrograph of flame retardant additive incorporated RPUF samples
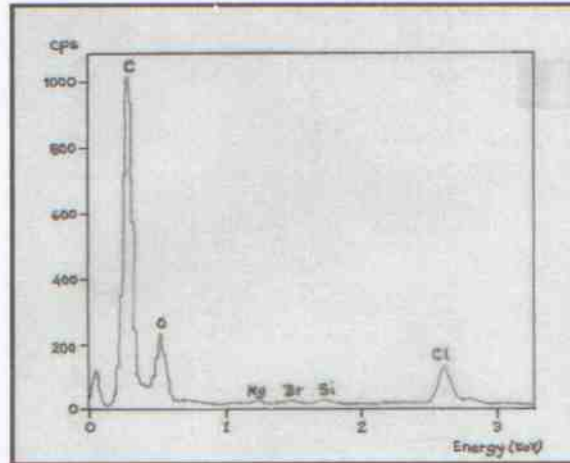
Figure 10 Energy dispersive xrays spectra of conventional RPUF samples
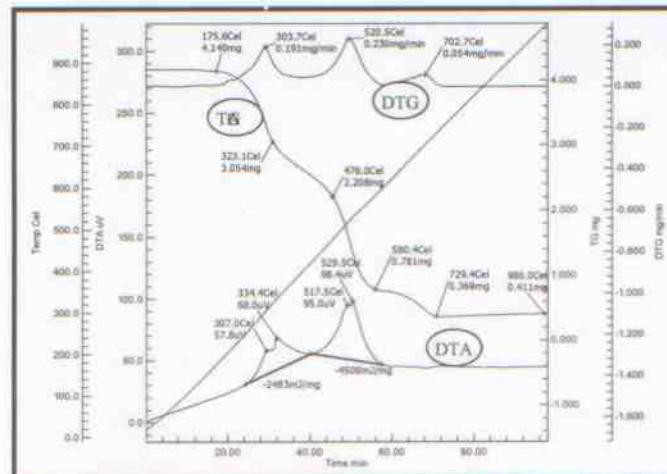
Figure 11 (a). Thermograms of conventional RPUF sample under an air atmosphere
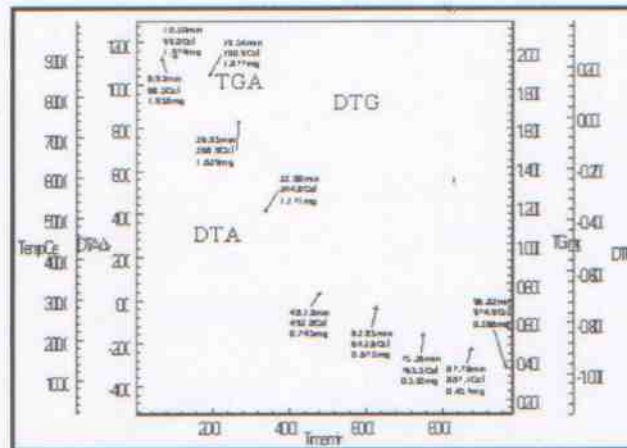
Figure 11 (b). Thermograms of flame retardant RPUF sample under an air atmosphere
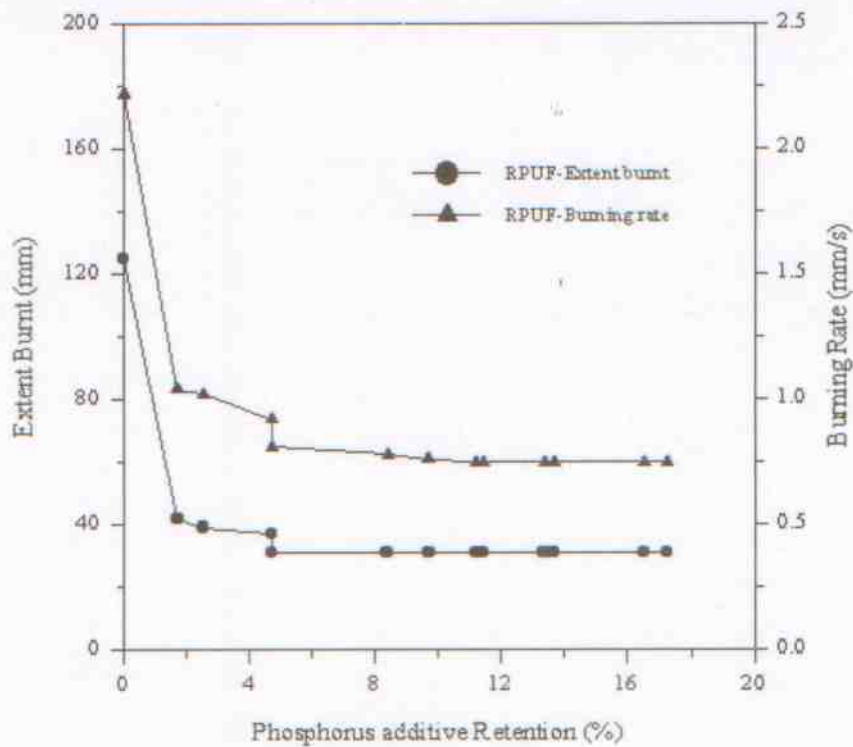
(a)
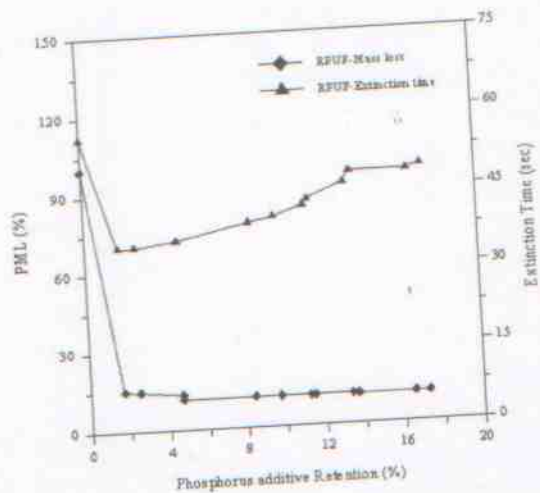
(b)

Figure 12. Effect of phosphorus additive on RPUF samples: (a) etent burnt and burning rate, (b) percent weight retained and etinction time
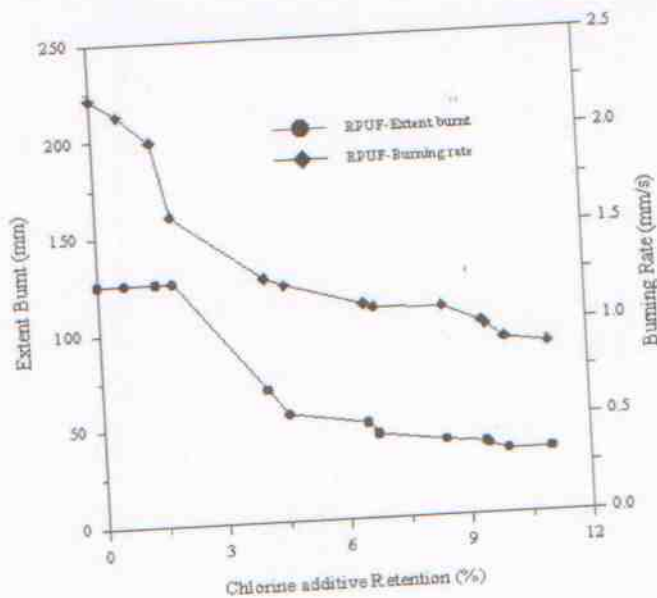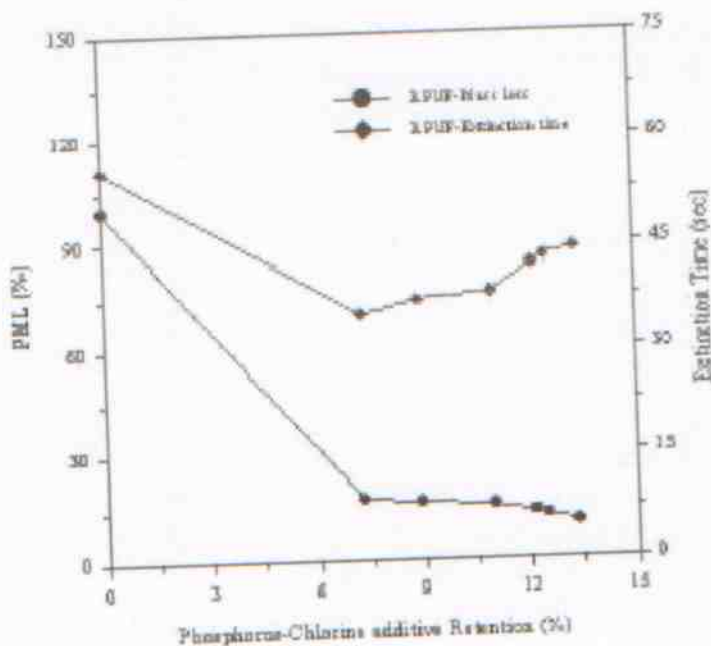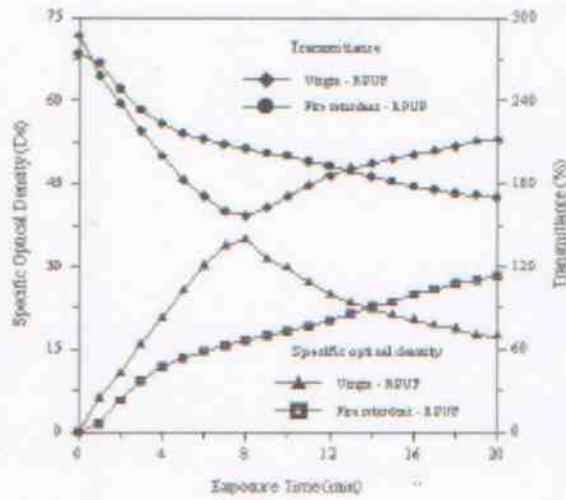

(a)
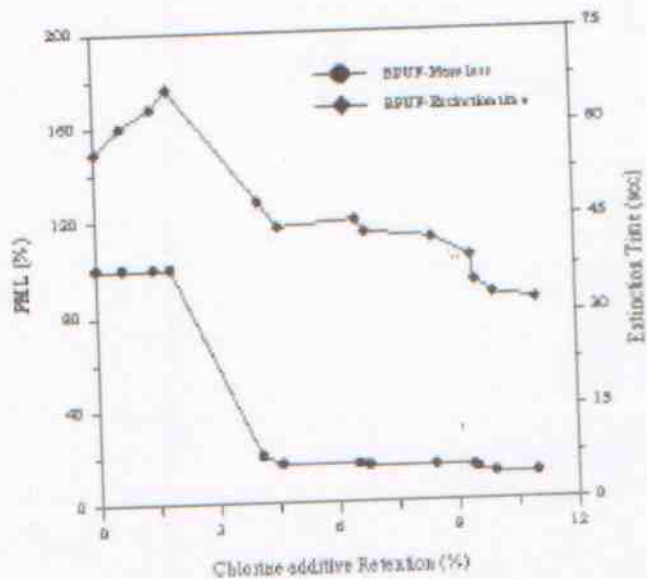
(b)

Figure 13   Effect of chlorine additive on RPUF samples: (a) etent burnt and burning rate, (b) percent weight retained and etinction time
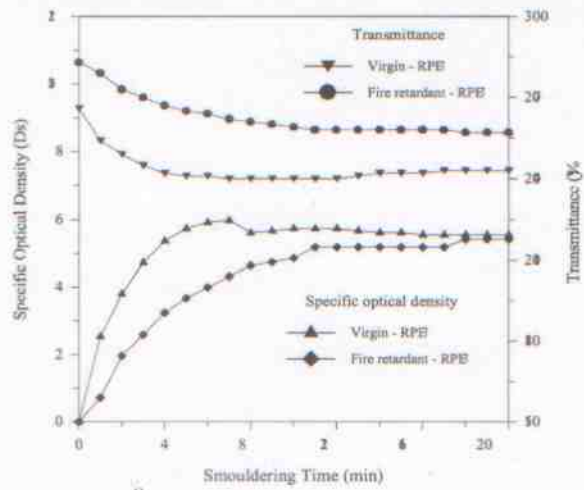

(a)

(b)

Figure 14. Effect of phosphorus - chlorine additive on RPUF samples: (a) etent burnt and burning rate, (b) percent weight retained and etinction time

(b)

Figure 15 Smoke generation of conventional and flame retardant RPUF samples: (a) flaming combustion mode, (b) non -flaming smouldering mode